Biogeochemical and Hydrological Processes Controlling the Transport and Fate of 1,2-Dibromoethane (EDB) in Soil and Ground Water, Central Florida

By BRIAN G. KATZ

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CONTENTS

FIGURES

TABLES

CONVERSION FACTORS

Multiply	By	To obtain
	Length	
millimeter (mm)	0.0394	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
	Area	
square centimeter (cm^2)	0.1550	square inch
square meter (m^2)	1.196	square yard
hectare (ha)	2.471	acre
	Volume	
cubic centimeter (cm^3)	0.06102	cubic inch
liter (L)	1.057	quart
	Mass	
kilogram (kg)	2.205	pound avoirdupois

Temperature in degrees Celsius (^{o}C) may be converted to degrees Fahrenheit (^{o}F) as follows:

$$^{o}F = 1.8\ ^{o}C + 32$$

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

ACRONYMS

ADL = above the detection limit
DBCP = 1,2-dibromo-3-chloropropane
EDB = 1,2-dibromoethane or ethylene dibromide
FDER = Florida Department of Environmental Regulation
FHRS = Florida Department of Health and Rehabilitative Services
MCL = maximum contaminant level
PCMS = Pesticide Contaminant Monitoring System
VOC’s = volatile organic compounds

ADDITIONAL ABBREVIATIONS

grams per cubic centimeter=g/cm^3
grams per mole=g/mol
liter per hectare=L/ha
meters per day=m/d
meters per second=m/s
micrograms per gram=μg/g
micrograms per kilogram=μg/kg
micrograms per liter=μg/L
milliequivalents per 100 grams=meq/100 g
milligrams per gram=mg/g
milligrams per liter=mg/L
milliliter=mL
milliliter per gram=mL/g
millimolar=m*M*
molarity=*M*
parts per billion=ppb
square centimeters per day=cm^2/d
square meters per day=m^2/d

Biogeochemical and Hydrological Processes Controlling the Transport and Fate of 1,2-Dibromoethane (EDB) in Soil and Ground Water, Central Florida

By Brian G. Katz

Abstract

Widespread contamination of ground water in central Florida by 1,2-dibromoethane (EDB) has resulted because of its heavy usage as a soil fumigant during a 20-year period, its relatively high aqueous solubility, and the low sorption capacity of the highly permeable sandy soils lacking organic matter. Two models were used to improve understanding of biogeochemical and hydrological processes that control the transport and fate of EDB in soil and ground water. First, a mass-balance model was developed to estimate the maximum concentration of EDB in ground water resulting from known application rates of EDB. Key processes that were quantified in the model included volatilization, diffusion of EDB vapor in soils, partitioning between aqueous and gaseous phases, sorption of EDB vapor on organic carbon and soil particles, chemical and biological degradation reactions, and nonreversible binding of EDB to soils. Model calculations using an EDB half-life of 0.65 year closely reproduced the maximum observed concentrations in ground water, 37 and 0.22 micrograms per liter, at downgradient sites in two study areas in central Florida.

Maximum concentrations of EDB in ground water also were estimated in a second model that incorporated an analytical solution to the three-dimensional advection-dispersion equation for instantaneous point sources of EDB entering the flow systems in the two study areas. The model used an EDB half-life of 0.65 year (obtained from the mass-balance calculations), mean ground-water flow velocities of 0.6 to 1 meter per day, coefficients of longitudinal hydrodynamic dispersion of 0.6 to 1.0 square meter per day, and coefficients of transverse hydrodynamic dispersion of 0.1 square meter per day. Peak concentrations of EDB in ground water calculated from the analytical model agreed closely with observed peak concentrations measured from 1983 through 1987.

INTRODUCTION

The organic chemical 1,2-dibromoethane, commonly known as EDB or ethylene dibromide, has been found in ground water used for public supply in Florida and in many other States in the United States. EDB has also been found in ground water in other parts of the world, such as Japan, Israel, and Australia, mostly as a result of its widespread use as a soil fumigant beginning in the early 1950's (Pignatello and Cohen, 1989). In 1983, all registered agricultural uses of EDB in the United States were canceled by the U.S. Environmental Protection Agency on the basis of studies showing that EDB is a potent carcinogen and mutagen (U.S. Environmental Protection Agency, 1987). EDB was also used as an antiknock compound in leaded gasoline, and leaking underground gasoline storage tanks might have contributed to EDB contamination of ground water in some areas.

In Florida, where more than 90 percent of the population receives drinking water from ground-water resources, water from more than 11,000 wells has been tested for EDB. Water samples from more than 1,200 wells in 22 of the 67 counties tested contained EDB in concentrations that exceeded the maximum contaminant level (MCL) set by Florida for this compound, which is 0.02 microgram per liter (μg/L) (Dykes, 1987). This MCL represents the analytical detection limit for the method used to measure EDB concentrations in water (Glaze and Lin, 1984).

In 1987, a study was begun by the U.S. Geological Survey, as part of the National Water Quality Assessment Program, to evaluate the areal and vertical distribution of EDB in the surficial, intermediate, and Floridan aquifer systems in central Florida. The main objectives of this study were (1) to determine the key factors affecting the occurrence of EDB in ground water and (2) to study the biogeochemical and hydrological processes that control the transport and fate of EDB in the soil and ground water.

In central Florida, where most ground-water samples for EDB analysis have been collected, a unique opportunity exists to improve understanding of the processes and rates of EDB transport and transformation in the subsurface. Detailed information is available on the rate of application of EDB from the mid-1960's until its statewide ban in 1983. The hydrogeology of the aquifer systems has been defined in most areas, and soil characteristics have been described in detail. Laboratory studies have been conducted on ground water and soils from central Florida to investigate biological and chemical degradation rates of EDB and mechanisms of binding to soils.

The transport and fate of EDB in soil and ground water are controlled by chemical, microbiological, and physical processes. By integrating the information on these processes with knowledge of the hydrogeology, the persistence of EDB in ground water can be evaluated with a reasonably high level of confidence. Furthermore, recognition of the processes that control the transport and fate of EDB in soil and ground water can be used to aid the design of networks that characterize contamination of ground water by organic chemicals from agricultural activities.

Purpose and Scope

The purpose of this report is twofold: (1) to present an overview of the major biogeochemical and hydro-logical processes that exert the most control on the transport and fate of EDB in soil and ground water and (2) to quantify these processes and calculate the maximum concentration of EDB in ground water at selected downgradient sites in two study areas. The report presents a review of the information on key chemical, biological, and physical processes that affect the movement and transformation of EDB in soil and ground water, with emphasis on hydrological and soil characteristics in central Florida. A conceptual model is described that incorporates the major biogeochemical processes controlling the transport and fate of EDB in soil and ground water. Each component of the conceptual model is quantified, and a resulting mass-balance model is used to calculate the maximum concentration of EDB in ground-water flow systems in the two study areas.

An extensive data base (described below) that contains information on the concentration of EDB in ground water in central Florida for the period 1983–87 was used for the study. Results from previous studies on rate constants for selected chemical and biological reactions were incorporated into the mass-balance model, along with information on EDB application methods, soil characteristics, rainfall distribution, and hydrogeology.

Previous Studies

After the detection of EDB in Florida ground water in 1983, the Florida Department of Environmental Regulation (FDER) contracted with several private firms to acquire additional background information on the characteristics of EDB in soil and ground water. These studies were conducted in the citrus-farming areas of Polk and Highlands Counties in central Florida and in a peanut- and soybean-farming area in Jackson County in northwestern Florida. These three counties had the most ground-water samples with detectable concentrations of EDB. In Polk and Highlands Counties, it was evident that EDB had migrated downward from the surficial, unconfined aquifer system to the underlying intermediate and Floridan aquifer systems (CH2M-Hill, Inc., 1986; Geraghty and Miller, Inc., 1986). The Floridan aquifer system (the source of potable water) is particularly vulnerable to contamination from EDB in areas where it is in direct contact with the surficial aquifer through sinkhole lakes or where the intermediate confining unit is absent or has been breached. The mechanisms and rates of chemical and bacterial degradation of EDB in selected soils and ground water from these three counties have been studied extensively. More detailed information on the mechanisms of transformation reactions involving EDB is presented in a later section of this report.

Several investigators have reported on EDB contamination in ground water in areas other than Polk and Highlands Counties. Roaza and others (1989) reported that in Jackson County, Fla., where EDB was frequently detected in the Upper Floridan aquifer, many areas of ground-water contamination had soils with high hydraulic conductivities. In many areas of Jackson County, confining units that separate the surficial soils from the Floridan aquifer system have been breached by sinkholes. Without detailed information on EDB application rates, the authors could not determine the relation between the occurrence of EDB and the amount of EDB applied to the soils. McConnell (1987, 1988) reported that, in central Seminole County in southwestern Georgia, EDB was still present in water in the Upper Floridan aquifer 4 years after it was last applied. The persistence of EDB in the Upper Floridan aquifer was not fully explained.

Cohen and others (1984) reported that low concentrations of EDB were also detected in ground water in California, South Carolina, New York, and Hawaii. The persistence of EDB in soil and ground water has been the topic of considerable research. Laboratory experiments have indicated that the half-life of EDB in ground water can range from less than 1 year (Moye and others, 1987) to 8 years (Jungclaus and Cohen, 1986) at temperatures of 20 to 25 ^{o}C and pH values near 7. The persistence of EDB might be much greater than the half-life extrapolated from laboratory experiments would indicate; for instance, EDB was detected in ground water in Connecticut in 1984, more than 20 years after its last known application (Pignatello, 1986).

Description of the Data Base

The source of data used in the investigation described in this report is the FDER's Pesticide Contaminant Monitoring System (PCMS) data base. This data base contains information on EDB concentrations in water sampled from privately owned residential wells and public supply wells during 1983 through 1987. The intent of the sampling program was to locate as many contaminated wells as possible for potential remediation. After a preliminary, broad areal sampling of sites where contamination was suspected, subsequent sampling by personnel of the Florida Department of Health and Rehabilitative Services (FHRS) in each county was concentrated in regions where EDB was detected. Many of the wells sampled in Polk and Highlands Counties were installed before permits were required. Thus, hydrogeologic and well-construction information, such as the screen location in soil and ground water and total depth of the well, could not be incorporated into the design of the sampling program.

Most of the residential water-supply systems that were sampled have a water-storage (holding) tank and distribution piping. Because of the different configuration of these systems, some water samples were not collected at or near the wellhead. Most domestic water tanks are pressurized with small volumes of air to maintain pressure in the distribution system. The air in the tank is periodically released to prevent overpressurization, resulting in a possible loss of volatile organic compounds such as EDB. Roaza and others (1989) reported that, in Jackson County, samples collected farthest from the wellhead generally contained the lowest median and mean concentrations of EDB. They concluded that EDB most likely volatilizes into the air within the holding tank and is lost from the water. A resulting problem is that the concentrations of EDB stored in the PCMS data base might not accurately reflect concentrations in ground water if the sample was collected from the distribution system. Unfortunately, no information was stored in the data base that would describe the location of sample collection at each site, and it was not possible to evaluate the effect of the location of sample collection on EDB concentration for the study areas in Polk and Highlands Counties. When the water samples were collected for the analysis of EDB, no measurements were made of water levels in the sampled wells nor of any other physical or chemical characteristics of the water.

1,2-Dibromoethane Application Methods

Two methods of applying soil fumigants were used under the direct supervision of the Florida Department of Agriculture and Consumer Services, Division of Plant Industry (Poucher and others, 1967), to control the spread of the burrowing nematode in commercial citrus groves. A push-and-treat procedure was used in severely infested areas. Infested trees were bulldozed toward the center of the affected area. The trees were then burned, and the following amounts of soil fumigants were injected at a depth of 25 to 30 cm in narrow troughs approximately 46 cm apart: EDB, 240 L/ha (1971–83); a mixture of 1,2-dichloropropane and dichloropropene, 940 L/ha (1962–71). The soil was tamped with a soil packer immediately following fumigation. In the second method, soil fumigants were applied in a buffer zone. This is an area that is established, treated, and maintained for the purpose of preventing the spread of the burrowing nematode from one grove to another. The width of a buffer zone generally ranged from 5 to 10 m. Buffer zones were fumigated with EDB at the rate of 470 L/ha during the initial application and 240 L/ha every 6 months thereafter.

Field and Laboratory Methods

Triplicate samples of ground water were collected by State and county agencies between the well and the pressure tank or treatment system at each sampling site. After at least three volumes of water were evacuated from the well casing, 40-mL vials were filled without headspace and then capped with a silicone septum faced with polytetrafluoroethylene (Teflon). At least two vials were collected at each sampling site so that positive results for samples with concentrations above the analytical detection limit of 0.02 µg/L (which is also the MCL) could be confirmed. Duplicate field blanks were prepared in an identical manner and were included in each sample set. The samples were cooled to 4 ^{o}C in the field at the time of collection, then iced and mailed to the laboratory. Samples received at ambient temperature were rejected.

EDB was analyzed by using a modification of a method developed by Bush (1983), which is similar to the U.S. Environmental Protection Agency method 504 used for analysis of other soil fumigants (Glaze and Lin, 1984). The 40-mL water sample was extracted once with 3 mL of n-pentane; 3 µL of extract was then injected into a gas chromatograph with a linearized electron capture detector for detection and quantification. Aqueous calibration standards were treated in an identical manner to compensate for extraction losses. Samples that had detectable concentrations of fumigants were submitted for gas chromatograph and mass spectrometry confirmation or were confirmed by analysis on a second gas chromatograph column, depending on the concentration of the analytes. This method yields a reported detection limit for EDB of 0.02 μg/L. Reagent water blanks were analyzed daily, and duplicate laboratory spikes were analyzed every 10 samples to monitor the accuracy and precision of the instrument. Recoveries determined from the calibration standard were within the range of 75 to 135 percent and generally averaged 95 percent for all analytes (G.W. Coppenger, Florida Department of Health and Rehabilitative Services, written commun., 1989; M.M. Malogodi, University of Florida, written commun., 1989).

Acknowledgments

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DESCRIPTION OF STUDY AREAS AND AVAILABLE 1,2-DIBROMOETHANE DATA

The two areas selected for study of the major chemical, biological, hydrological, and other physical processes that control the transport and fate of EDB in soil and ground water were the Lake Francis study area in Highlands County and the Lake Pierce study area in Polk County. These areas were selected because they have (1) a well-defined ground-water flow system, (2) a continuous record of EDB application information, and (3) a substantial number of wells that had been sampled more than three times during the period of sampling (1983–87). Further-more, the hydrological characteristics of the ground-water flow systems in these study areas were similar to those of other local flow systems in Highlands and Polk Counties. These study areas are described in the following sections in terms of pertinent information on observed EDB concentrations in ground water, land use, hydrological characteristics of the ground-water flow system, the amount and rate of EDB applied over time, and soil characteristics at the application sites.

Lake Francis Study Area

The Lake Francis study area is in southern Highlands County (fig. 1) and lies in the Intraridge Valley of the Lake Wales Ridge (White, 1970); the Intraridge Valley ranges in altitude from approximately 3.7 to 15 m above sea level. The area is predominantly agricultural; large citrus groves have been in commercial operation for about 40 years on the east side of Lake Francis.

A total of 258 water samples were collected from 64 wells in the study area during the period from 1983 through 1987. Water from 25 wells (189 samples) had EDB concentrations above the detection limit (ADL) of 0.02 μg/L. The summary statistics for EDB concentrations (ADL) in these samples, in micrograms per liter, are as follows: range, 0.02 to 37; median, 1.18; mean, 2.08; and standard deviation, 3.57. The maximum EDB concentration, 37 μg/L, was detected in a water sample collected from well 911 (fig. 1), which has a depth of 47 m and is about 610 m downgradient from the EDB application sites. Ten water samples were collected between 1984 and 1986 from well 911; EDB concentrations in the samples ranged from 2.19 to 37 μg/L. Ten wells were sampled 10 or more times during 1983 through 1987. EDB concentrations in water from 9 of the 10 wells decreased significantly (90 percent confidence level) over time (A.F. Choquette and others, U.S. Geological Survey, written commun., 1991).

The wells sampled in the Lake Francis study area were used for domestic supply and were generally constructed with a metal casing having a diameter of 5 cm and a 3-m-long metal screen at the bottom of the well. Many residential wells were probably installed using the cable-tool drilling method, and the annular space in some of these wells might not have been reliably sealed with cement grout or other nonpermeable material (Geraghty and Miller, Inc., 1986). As a result, contaminants from the surface could have moved downward along the exterior of the casing into the deeper intermediate and Floridan aquifer systems, especially in areas where there is a net downward gradient from the surficial aquifer to the underlying aquifer systems. This process might have resulted in higher EDB concentrations in the ground water than those expected from the movement of EDB through soils and the unsaturated zone. It was not possible to identify wells in the data base that could have been improperly constructed.

All sampled wells in the study area tap the surficial aquifer. The principal source of recharge to this aquifer is rainfall, which averaged 132 cm annually for the period from 1951 through 1980 at a station approximately 17.5 km south of the study area (National Oceanic and Atmospheric Administration, 1982). More than half of the annual rainfall occurs from June through September. The only other source of recharge is from irrigation water not taken up by the citrus crops. Most of the irrigation water is pumped from the Floridan aquifer system or from lakes that intersect

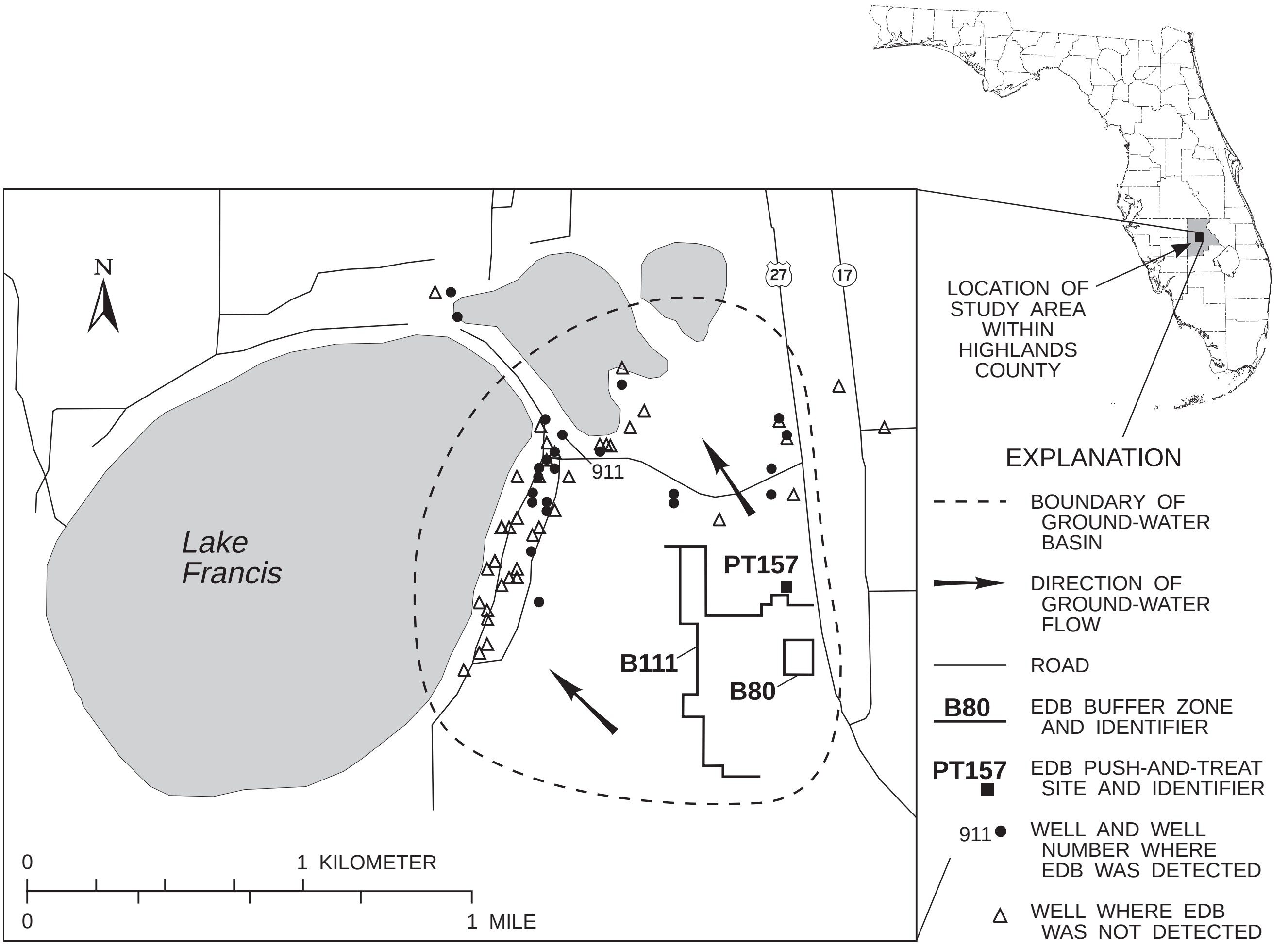


Figure 1. Location of Lake Francis study area, buffer zones, a push-and-treat site, and selected sampling sites (wells) where 1,2-dibromoethane (EDB) was detected and not detected in ground water. Well 911 is discussed in text.

the water table in the surficial aquifer (R. Marella, U.S. Geological Survey, written commun., 1990). The amount of irrigation water that is not taken up and is, thus, available for recharge is unknown.

A comparison of monthly irrigation amounts and monthly water-level data for a well in a citrus grove near the study area indicates that irrigation probably exerts little effect on recharge of water to the aquifer. Although ground-water levels do not respond rapidly to increased irrigation, water levels do respond rapidly to rainfall. Soil moisture conditions can affect recharge rates, but water falling on the study area as precipitation generally reaches the water table in 30 to 60 days, as indicated by an analysis of monthly water-level and monthly rainfall data from 1984 through 1987. Adams and Stoker (1985) reported that recharge originating as precipitation generally reached the water table in about 30 days in a study area about 5 km south of the Lake Francis study area.

The water table in the study area generally reflects the topography of the land surface, and horizontal water movement generally is restricted to the individual lake basin (Sinclair and Reichenbaugh, 1981). However, gradient reversals have been noted for similar systems in Highlands County in response to high recharge from rainfall (Adams and Stoker, 1985). Water discharges from the surficial aquifer by downward leakage to the Floridan aquifer system, particularly in areas where surficial material has subsided into solution cavities in the Floridan aquifer system. Other losses of water from the aquifer occur through evapotranspiration from wetland areas and vegetation and by lateral flow to lakes. Depth to the water table in the area ranges from zero where the lakes intersect the water table to approximately 12 m beneath EDB application sites in the eastern ridge area (fig. 1).

Total annual quantities of EDB applied in the Lake Francis study area (corrected to reflect 85 percent active ingredient) for the period in which applications were documented (1962–83) are shown in figure 2. The total quantity of EDB (active ingredient) applied in the study area during this period was 18,500 kg.

The soil underlying the buffer zone and push-and-treat application sites is a Typic Quartzipsamment and is referred

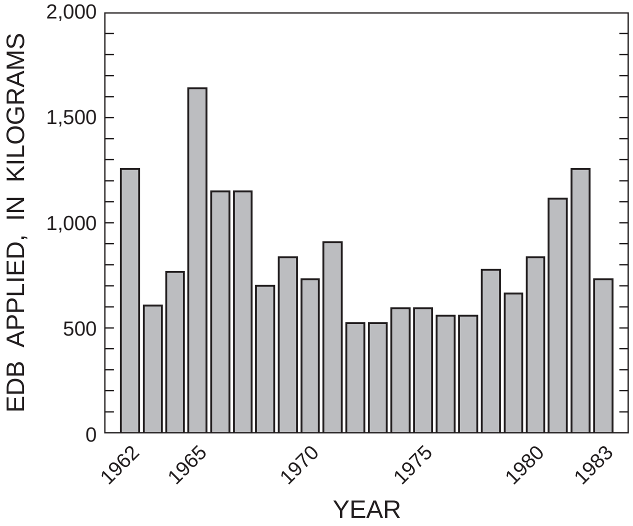


Figure 2. Total annual quantity of 1,2-dibromoethane (EDB) applied to soil at buffer zone and push-and-treat application sites in the Lake Francis study area, 1962–83. Application data for EDB were extrapolated from records on file at the Florida Department of Agriculture and Consumer Services, Division of Plant Industry, Winter Haven, Fla.

to as the Astatula sand in table 1 (U.S. Soil Conservation Service, written commun., 1989). Two distinct horizons were identified (table 1): an Ap (0–20 cm depth) and a C (20–203 cm depth). Both horizons contain almost 98 percent medium and fine sand and have a mean bulk density of about 1.6 g/cm^3. The pH values (1:1 water slurry) for the Ap and the C horizons are similar, 4.9 and about 5.0, respectively. Organic carbon and clay-sized contents for both horizons are low: 0.29 and 1.4 percent, respectively, for the Ap horizon; and about 0.08 and 1.5 percent, respectively, for the C horizon. Saturated hydraulic conductivity is 18.6 m/d for the Ap horizon, and averages 24.0 m/d for the C horizon. Cation-exchange capacity is 2.47 meq/100 g for the Ap horizon, and averages 1.28 meq/100 g for the C horizon.

Lake Pierce Study Area

The Lake Pierce study area is in northeastern Polk County (fig. 3) and lies on the Lake Wales Ridge (White, 1970), an undulating upland that ranges in altitude from approximately 24 to 61 m above sea level. The area is predominantly agricultural; large citrus groves on the west side of Lake Pierce have been in commercial operation for at least 45 years.

A total of 762 water samples were collected from 290 wells in the Lake Pierce study area during 1983 through 1987. Of these, 508 samples of water from 103 wells had median EDB concentrations above the analytical detection limit of 0.02 μg/L. The summary statistics for EDB concentrations (ADL) in these samples, in micrograms per liter, are as follows: range, 0.02 to 73; median, 0.09; mean, 2.74; and standard deviation, 10. The maximum EDB concentration, 73 μg/L, was determined in a sample collected from well 17991, which is approximately 30 m deep and is approximately 100 m downgradient from the EDB buffer application site B109 (fig. 3). Seven wells in the study area were sampled 10 or more times during 1983 through 1987. In contrast to the decreasing trends of EDB concentrations with time observed for water from wells in the Lake Francis study area, water from all seven of these wells showed increasing EDB concentrations with time (A.F. Choquette and others, U.S. Geological Survey, written commun., 1991).

Wells that were sampled in the Lake Pierce study area tap the surficial, intermediate, and Floridan aquifer systems. These wells are predominantly used for domestic supply and were constructed using the cable-tool drilling method (Geraghty and Miller, Inc., 1986). The wells commonly have a metal casing, having a diameter of 5 cm, installed to a depth where the first limestone unit is encountered. Depth to the water table ranges from less than 1 m (near Lake Pierce) to approximately 18 m below land surface beneath EDB application sites on the ridge (fig. 3). As mentioned above for the Lake Francis study area, it was not possible to identify wells in the data base that may have been improperly constructed in the Lake Pierce study area; however, contamination of the aquifer systems through such wells is possible.

The surficial aquifer system ranges in thickness from about 24 to 30 m in the study area. This range is based on lithologic logs for wells that are just west of Lake Pierce and that were installed as part of a State program to replace wells that produced water having EDB concentrations greater than 0.02 μg/L (Geraghty and Miller, Inc., 1986). In the ridge area, to the west of the study area, the thickness of the surficial aquifer system can approach 60 m (Stewart, 1966). The principal source of recharge to the surficial aquifer system is rainfall, which averaged 127 cm per year from 1951 through 1980, as measured at a station about 18 km northwest of the Lake Pierce study area (National Oceanic and Atmospheric Administration, 1982). More than half of the annual rainfall occurs from June through September.

There are no reported values for hydraulic conductivity in the Lake Pierce study area; however, horizontal hydraulic conductivities of the surficial aquifer range from less than 0.3 to 2.5 m/d in a study area approximately 18 km to the northwest (Lee and others, 1991). These values were obtained from slug tests of observation wells. The higher values for horizontal hydraulic conductivity generally were measured in wells finished in the uppermost part of the surficial aquifer along the ridges in the lake basin. The lower hydraulic conductivities (less than 0.3 m/d) were measured in wells finished in the middle and lower parts of the surficial aquifer, where the clay content increases with depth (Lee and others, 1991). Values of hydraulic conductivity reported for another nearby study area are 1.6 and 2.0 m/d (Pride and others, 1966).

Table 1. Characteristics of soils beneath 1,2-dibromoethane (EDB) application sites in the Lake Francis and Lake Pierce study areas

[Source of data: U.S. Soil Conservation Service, written commun., 1989. cm, centimeters; %, percent by weight; mm, millimeter; meq, milliequivalent; g, grams; m/d, meters per day; g/cm^3, grams per cubic centimeter; <, less than; nd, not determined; pH values listed are for 1:1 soil/water mixture]

Depth below land surface (cm)	Soil horizon	Particle size distribution (%)			pH	Organic carbon (%)	Cation-exchange capacity (meq/100 g)	Saturated hydraulic conductivity (m/d)	Bulk density (g/cm^3)	Clay mineralogy (%)			
		2–0.05 mm sand	0.05–0.002 mm silt	<0.002 mm clay						Illite	Kaolinite	Quartz	Smectite
Astatula sand (Lake Francis study area)													
0–20	Ap	98.3	0.3	1.4	4.9	0.29	2.47	18.6	1.58	nd	nd	nd	nd
20–84	C	98.4	.0	1.6	5.1	.08	1.24	21.3	1.61	nd	nd	nd	nd
84–147	C	97.8	.7	1.5	5.0	.07	1.19	28.1	1.61	nd	nd	nd	nd
147–203	C	97.4	1.1	1.5	4.8	.08	1.42	22.9	1.60	nd	nd	nd	nd
Candler sand (Lake Pierce study area)													
0–15	Ap	96.7	0.8	2.5	5.7	0.80	8.18	30.5	1.46	20	72	8	0
15–107	E1	97.5	1.3	1.2	5.6	.07	1.53	19.7	1.53	26	64	10	0
107–160	E2	97.9	1.1	1.0	5.6	.05	1.40	21.5	1.49	0	0	0	0
160–203	E1BT	97.4	.8	1.8	5.4	.02	1.40	19.1	1.50	27	68	5	0
Tavares fine sand (Lake Pierce study area, push-and-treat site PT267)													
0–20	Ap	97.3	1.2	1.5	4.7	0.48	9.67	3.89	1.65	47	20	15	18
20–43	Cl	97.0	1.1	1.9	4.8	.13	5.93	4.97	1.57	0	0	0	0
43–76	C2	96.6	1.4	2.0	4.5	.20	7.24	7.58	1.47	50	32	9	9
76–132	C3	96.4	1.5	2.1	4.3	.27	8.44	8.52	1.51	0	0	0	0
132–203	C4	97.8	.9	1.3	4.7	.05	5.43	9.31	1.55	45	28	14	13

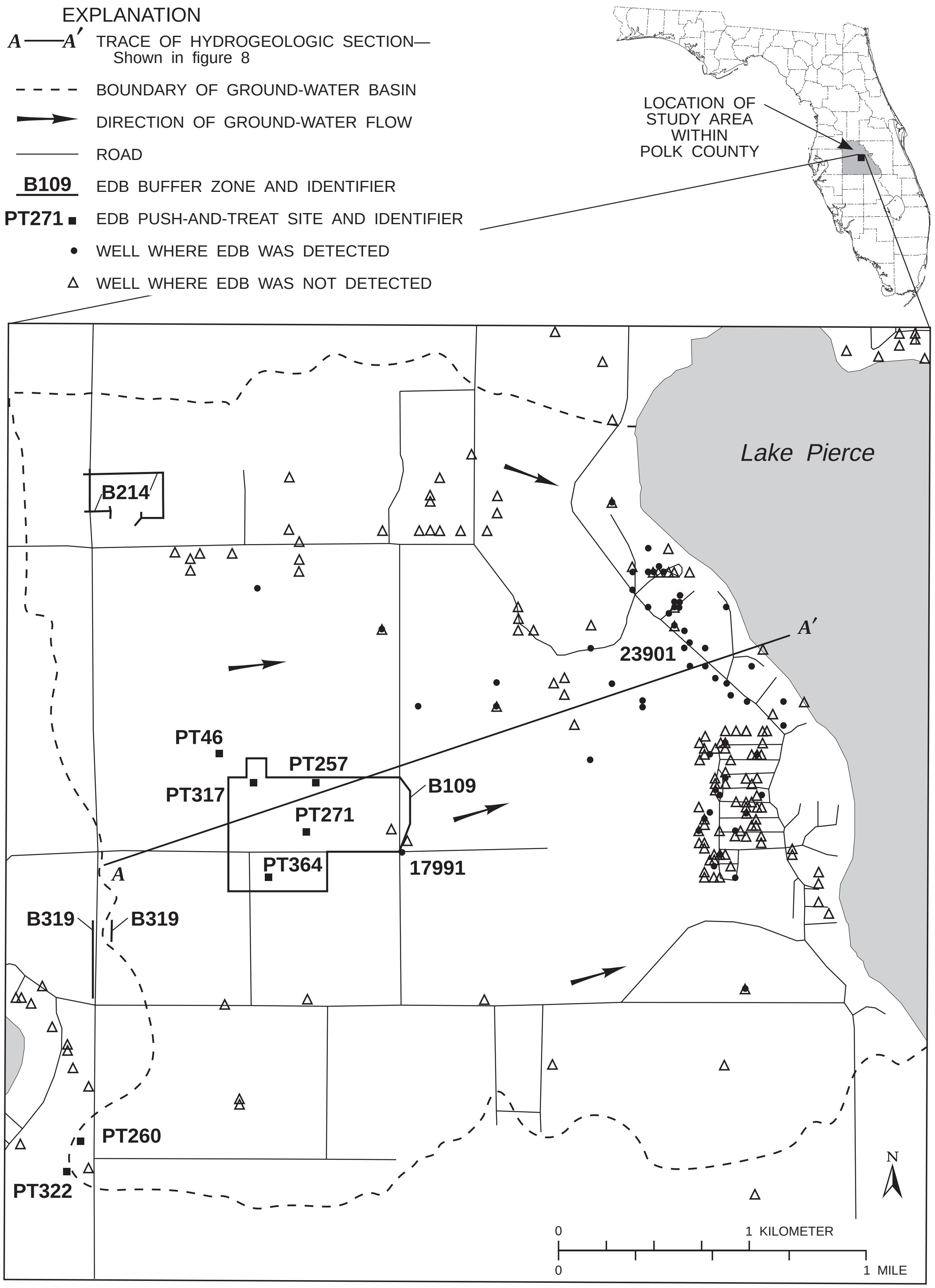


Figure 3. Location of Lake Pierce study area, buffer zones, push-and-treat sites, and selected sampling sites (wells) where 1,2-dibromoethane (EDB) was detected and not detected in ground water. Wells located close together plot as one symbol at this scale. Wells 17991 and 23901 are discussed in text.

The surficial aquifer system throughout most of the Lake Pierce study area is underlain by a dense, relatively impermeable clay of the Hawthorn Group, which is commonly phosphatic, sandy, and dolomitic (Sinclair and Reichenbaugh, 1981). The thickness of this clay in the study area is highly variable and ranges from zero, where it is absent, to about 30 m. Where present, the Hawthorn Group composes the intermediate aquifer and confining unit, which affect movement of water from the surficial aquifer to the limestone of the Floridan aquifer system. Typically, vertical hydraulic conductivities for the clays of the Hawthorn Group range from 4.5×10^{-3} to 2.4×10^{-7} m/d (Miller, 1986). In places where the confining unit is thin, it can be breached by sinkholes and other types of erosional features. Thus, the deeper Floridan aquifer system is directly connected to the surficial aquifer system in some areas.

The Floridan aquifer system consists of limestones and dolomites (Miller, 1986). The part of the Floridan aquifer system of interest in this study is the uppermost part known as the Upper Floridan aquifer. The reader is referred to Miller (1986) for a thorough discussion of the stratigraphy and lithology of the Floridan aquifer system. Hydraulic properties of the upper part of the aquifer system are of interest to this study. Transmissivity values for the Upper Floridan aquifer in nearby study areas are 1,370 m^2/d (Pride and others, 1966) and 2,480 m^2/d (Geraghty and Miller, Inc., 1980). Sinclair and others (1985) estimated that recharge to the Upper Floridan aquifer in this area ranges from 13 to 38 cm per year.

Lateral movement of water through the surficial aquifer system in the study area is eastward toward Lake Pierce and is confined to this individual lake basin. In a nearby area, Sinclair and Reichenbaugh (1981) noted that the water table reflects the topography of the land surface. Lake Pierce probably represents the area of greatest leakage from the surficial aquifer to the underlying Floridan aquifer system, because most lakes in this area occupy basins that have been formed by subsidence of surficial material into solution cavities of the Floridan aquifer (Sinclair and Reichenbaugh, 1981; Lee and others, 1991). In addition to leakage to the Floridan aquifer system, losses of water from the surficial aquifer system include evapotranspiration from wetland areas and vegetation and discharge to lakes.

Rainfall is probably the greatest source of recharge to the surficial aquifer, and irrigation water applied to citrus crops can also recharge the aquifer. However, total annual pumpage for citrus irrigation varies considerably from year to year, depending on the amount and distribution of rainfall. The amount of applied water that percolates past the root zone is unknown. Estimates of pumpage for irrigation in the study area are not available.

Total annual quantities of EDB applied in the Lake Pierce study area (corrected to reflect 85 percent active ingredient) are shown in figure 4 for 1963 through mid-1983. The total amount of EDB (active ingredient) applied in the study area during this period was 47,500 kg, almost three times the amount applied in the Lake Francis study area. (Note: Of the 17,000 kg applied during 1978, 7,000 kg of EDB were applied in March 1978 (fig. 4).)

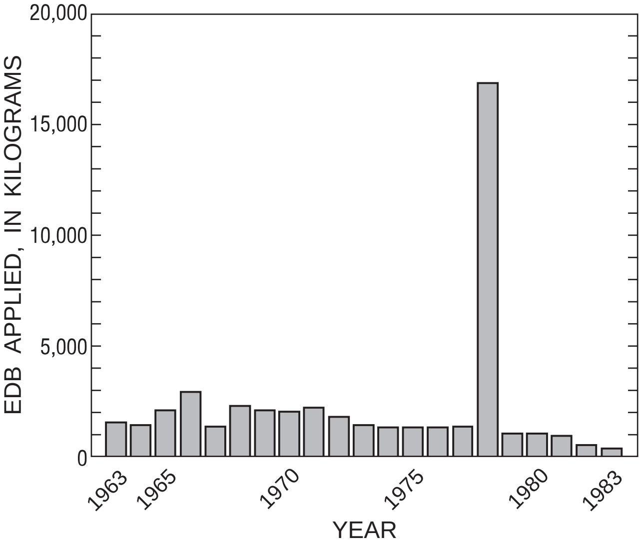


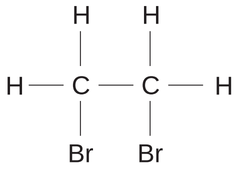
Figure 4. Total annual quantity of 1,2-dibromoethane (EDB) applied to soil at buffer zone and push-and-treat application sites in the Lake Pierce study area, 1963–83. Application data for EDB were extrapolated from records on file at the Florida Department of Agriculture and Consumer Services, Division of Plant Industry, Winter Haven, Fla.

The soil underlying the buffer zone and push-and-treat application sites is a Typic Quartzipsamment (U.S. Soil Conservation Service, written commun., 1989). Two different soil types have been delineated (table 1). The first, referred to as the Candler sand, is the predominant soil type underlying almost all application sites. It consists of two distinct horizons: an Ap (0 to 15 cm depth) and an E horizon divided into E1, E2, and E1BT subregions (15 to 203 cm depth). Both horizons contain about 97 percent medium and fine sand and have a mean bulk density of about 1.5 g/cm^3. The pH values (1:1 water slurry) for the Ap and E horizons are similar, 5.7 and about 5.6, respectively. Organic carbon and clay-sized contents for both horizons are low: 0.80 and 2.5 percent, respectively, for the Ap horizon; and 0.05 and about 1.2 percent, respectively, for the E horizon. Saturated hydraulic conductivities are about 31 m/d and 20 m/d for the Ap and E horizons, and cation-exchange capacities are about 8.2 and about 1.4 meq/100 g for the Ap and E horizons, respectively.

The second soil type, Tavares fine sand, underlies push-and-treat site PT267 (fig. 3). Two distinct horizons were identified at this site: an Ap (0 to 20 cm depth) and a C (20 to 203 cm depth). Both horizons contain almost 97 percent fine and medium sand and have a mean bulk density of about 1.6 g/cm^3. The pH values (1:1 water slurry) for the Ap and C horizons are in the range of 4.3 to 4.8. The contents of organic carbon and clay-sized particles for both horizons are low: 0.48 and 1.5 percent, respectively, for the Ap horizon; and 0.05 to 0.27 and 1.3 to 2.1 percent, respectively, for the C horizons (C1–C4). Saturated hydraulic conductivities are much lower than those of the Candler sand and average 3.89 and 7.92 m/d for the Ap and C horizons, respectively. Cation-exchange capacities are 9.67 and 5.43 to 8.44 meq/100 g for the Ap and C horizons (C1–C4), respectively.

CHEMICAL AND PHYSICAL PROPERTIES OF 1,2-DIBROMOETHANE

The observed persistence of EDB in ground water is related, in part, to its chemical and physical properties. EDB is a low-molecular-weight (187.88 g/mol) halogenated hydrocarbon whose chemical formula is $C_2H_4Br_2$. Its chemical structure can be represented as



The boiling and melting points of EDB are 131.6 ^{o}C and 9.97 ^{o}C, respectively (Verschueren, 1983). In liquid form (the form in which EDB is applied to soils), EDB is more dense than water and has a specific gravity of 2.172 at 25 ^{o}C (Windholz, 1983). During the soil fumigation process, relatively small amounts of EDB were injected into the soil along a shallow trench or furrow. Immediately following application, EDB migrated downward because of its high specific gravity. It could also dissolve in any available soil moisture, diffuse into air-filled pore spaces, volatilize into the atmosphere, or sorb onto soil particles. The water solubility, vapor pressure, and Henry's law constant for EDB at 20 and 25 ^{o}C are presented in table 2. As a result of its high solubility in water, relatively low vapor pressure (table 2), and low sorption affinity for soils (Call, 1957a; Chiou and others, 1979; Steinberg and others, 1987), EDB can be easily leached to the water table by the percolation of rainfall or irrigation water through the soil.

Table 2. Water solubility, vapor pressure, and Henry's law constant (*H*) for 1,2-dibromoethane (EDB) at 20 and 25 ^{o}C

[°C, degrees Celsius; mg/L, milligrams per liter; mm Hg, millimeters of mercury]

Temperature (°C)	Water solubility (mg/L)	Vapor pressure (mm Hg)	*H*
20	3,370[a]	7.69[a]	0.024[d]
25	4,250[b]	13.8[c]	.033[d]

[a] Goring (1962).

[b] Stephen and Stephen (1963).

[c] Stull (1947).

[d] Henry's law constant values (unitless) were calculated from the given solubility and vapor-pressure data.

BIOGEOCHEMICAL AND HYDROLOGICAL PROCESSES CONTROLLING THE TRANSPORT AND FATE OF 1,2-DIBROMOETHANE IN SOIL AND GROUND WATER

Laboratory experiments have shown that EDB is readily biodegradable and relatively volatile (Sawhney, 1989). However, when EDB and other neutral, nonpolar organic compounds have been used as soil fumigants, they have persisted for as many as 20 years in fumigated soils and in the underlying ground water in areas where they had been applied (Steinberg and others, 1987). This unexpected characteristic of these compounds is controlled by a series of interrelated chemical, physical, and biological processes.

Volatilization

Given its vapor pressure of 7.69 mm Hg at 20 ^{o}C, EDB can be transported from soil and ground water to the atmosphere through volatilization, either immediately after its initial application or subsequently over time. This process is controlled by the vapor pressure, which is the pressure of EDB vapor in equilibrium with EDB liquid at a particular temperature. Immediately after application (prior to any sorption on soil particles or organic matter and prior to dissolution in soil water), the partial pressure of EDB in the soil atmosphere in equilibrium with EDB in the liquid phase (assuming ideal solvent behavior) can be described by using Raoult's law:

$$P_i = x_i P_i^o, \qquad (1)$$

where

P_i is the partial pressure of the EDB vapor in the gas phase,

x_i is the mole fraction of EDB in the liquid phase, and

P_i^o is the vapor pressure of the pure EDB liquid.

On the basis of theoretical considerations of soil fumigation, Hemwall (1959) calculated that about 20 percent of a soil fumigant would be lost through the surface to the atmosphere 2 days after the application at a depth of 15 cm. A number of factors affect the volatilization rate over an extended period of time. Those that limit volatilization loss include sorption on organic matter and soil minerals and dissolution in soil water. A more rigorous mathematical description of the volatilization process was presented by Mackay (1981).

Diffusion of 1,2-Dibromoethane Vapor in Soils

The diffusion of EDB vapor through wet and dry soils under steady-state and unsteady-state conditions has been addressed theoretically and experimentally. Hemwall (1959) developed a two-dimensional equation, based on Fick's second law of diffusion, that considered the dissolution of a fumigant in soil water, adsorption of a fumigant onto soil solids, and chemical reaction of a fumigant in the soil. All three processes were accounted for through the use of a modified diffusion coefficient. During the initial stages of diffusion, Hemwall (1959) determined that the rate of fumigant loss through the surface rapidly increases when radial diffusion dominates fumigant movement. As additional fumigant is lost from the surface of the profile, the maximum concentration plane is displaced downward from the original injection depth. Eventually, the maximum concentration or injection plane evolves to a concentration gradient that decreases from the bottom of the profile to the surface. Hemwall's results, which were based strictly on theoretical cal-culations, are in agreement with experimental results by Goring and Youngson (1957) and Call (1957c). For steady-state conditions, Call (1957c) indicated that EDB diffusion coefficients measured in soils (D) were directly related to the diffusion coefficient of EDB in air (D_o) by the following expression:

$$D = 0.66\,D_o(n - 0.1), \tag{2}$$

where n is the porosity of the soil. For unsteady-state transport, Call (1957c) reported that the number of blocked pores and sorption of EDB are extremely important in controlling the value of D for EDB.

Partitioning Between Aqueous and Gaseous Phases

The partitioning of EDB between the aqueous and gaseous phases is a function of the ratio of saturated vapor density to aqueous solubility at equilibrium, which is described by Henry's law constant (H). H is calculated to be 0.033 at 25 °C for EDB (table 2). This low H indicates that most of the EDB is likely to reside in the aqueous phase (97 percent), rather than in the vapor phase (3 percent). Yurteri and others (1987) observed unpredictable deviations from the pure-water values of H in natural waters. They attributed these deviations to complex molecular phenomena such as association, solvation, and ionic-strength effects. These discrepancies were also likely to have been caused in part by the presence of dissolved humic substances and by the surface-active properties of natural organic matter.

Sorption of 1,2-Dibromoethane Vapor on Organic Carbon and Soil Particles

Chiou and others (1988) reported that the sorption capacity for EDB vapor by humic acid was 37 mg/g (mass of EDB/mass of humic acid). Sorption capacities for EDB and other nonpolar organic compounds are approximately an order of magnitude smaller than sorption capacities for polar organic compounds. Chiou and others (1988) reported that organic matter as a whole is about twice as effective as the humic acid isolated from soil organic matter in the uptake of relatively nonpolar organic compounds. On dry soils, adsorption of EDB on mineral surfaces can be substantial (Goring, 1962). However, water effectively suppresses the vapor sorption of organic compounds on soil organic matter.

Sorption of EDB vapor on soil particles can prevent EDB from migrating to ground water. Call (1957a) reported that the sorption of EDB vapor on soils at field capacity could be described by a Freundlich isotherm:

$$S = KC^n, \tag{3}$$

where

S is the mass sorbed per unit mass of sorbent,
K is the sorption coefficient,
C is the equilibrium vapor concentration, and
n is exponential term and is equal to 1.0.

For the special case of a linear isotherm,

$$S = K_d\,C\,, \tag{4}$$

where K_d is the distribution (sorption) coefficient. Call (1957a) reported a K_d of 5 µg/g at 15 °C for EDB in a soil similar to the Candler sand present in the Lake Pierce study area. The soil used by Call (1957a) had an organic carbon content of 0.23 percent and the following particle sizes, in weight percent: coarse sand, 13.4; fine sand, 69.8; silt, 7.6; and clay, 8.6. The sorption coefficient was related to temperature (T in degrees Celsius) by the following expression (Call, 1957a):

$$K_{d,T} = K_{d,15\,^{\circ}\mathrm{C}}[1 - 0.0485(T\,^{\circ}\mathrm{C} - 15)]. \tag{5}$$

Therefore, at 20 and 25 °C, the sorption coefficients for EDB by this soil are calculated to be 3.8 and 2.6 µg/g, respectively.

Call (1957c) reported that, at low moisture content, EDB penetrated freely into calcium-smectite crystal lattices, but when water molecules were present between the crystal sheets, the penetration of EDB was hindered. This exclusion effect was attributed to a high degree of orientation of the water molecules as a result of hydrogen bonding between the water molecules and the oxygen atoms of the smectite crystal sheets (Call, 1957c).

Chemical and Biological Transformation Reactions

There are two major processes by which EDB is transformed to other compounds in soil and ground water: chemical hydrolysis and microbial degradation. Other reactions by which EDB is transformed include nucleophilic substitution (Schwarzenbach and others, 1985) and reductive dehalogenation (Castro and Belser, 1968).

Chemical Hydrolysis

Four studies involving the chemical hydrolysis of EDB report half-lives that range from 1.5 to 15 years. These studies were performed under laboratory conditions that were designed to represent field conditions. In the first study, Weintraub and others (1986) determined rate constants for shallow ground waters from Polk, Highlands, and Jackson Counties in Florida at their ambient pH values (7.60 to 8.20) at temperatures of 40, 50, 60, 70, and 80 ^{o}C. These waters and a deionized water blank were either autoclaved or filtered to eliminate microbial activity. On the basis of Arrhenius plots, Weintraub and others (1986) reported half-lives of 1.5 to 2 years and 2.2 years at 22 ^{o}C and 15 ^{o}C, respectively. For solutions containing 100 ppb of EDB at 63 ^{o}C and tested in buffered systems, the reaction was independent of pH between pH values of 4 and 9. The chemical hydrolysis of EDB followed pseudo-first-order kinetics between 40 and 70 ^{o}C (Weintraub and others, 1986). Ethylene glycol and bromide ion were the major products of the hydrolysis reactions.

In the second study, Vogel and Reinhard (1986) used experimental procedures that were similar to those used by Weintraub and others (1986) and obtained a half-life of 2.5±0.3 years at pH 7.5 and 25 ^{o}C. Vinyl bromide was presumed to be the major hydrolysis product, although the product identification methods of Vogel and Reinhard (1986) could not detect ethylene glycol. This presumption was probably not correct, as subsequent studies have demonstrated that vinyl bromide is not the major product of EDB transformation in aqueous solution. Haag and Mill (1988a) measured a 12±3 percent yield of vinyl bromide in unbuffered, distilled water at 60 ^{o}C, and Barbash and Reinhard (1992b) observed negligible yields of vinyl bromide (less than 0.7 percent) in deionized water and sodium nitrate solutions up to 0.5 *M* at 62.5 and 37.5 ^{o}C. The latter study concluded that vinyl bromide yields increased with increasing concentrations of pH buffers for all buffers examined—phosphate, borax, and an organic buffer (4-[2-hydroxyethyl]piperazine-1-propanesulfonic acid).

In the third study, Jungclaus and Cohen (1986) investigated the hydrolysis of EDB in buffered distilled water at pH values of 5, 7, and 9 and at temperatures of 30, 45, and 60 ^{o}C. They reported hydrolysis half-lives of 8 and 15 years at 20 and 15 ^{o}C, respectively, with no estimates of the errors associated with these values. As in the study by Weintraub and others (1986), the reaction was independent of pH between 5 and 9 after corrections were made for catalysis by buffers. It is important to note that pH buffers have been shown to cause dramatic increases in EDB hydrolysis rates, sometimes by as much as a factor of four (Barbash and Reinhard, 1989a, 1992b). Jungclaus and Cohen (1986) speculated that ethylene glycol was the major product of the reaction; that speculation was based on the production of bromide in a 2:1 stoichiometric ratio relative to the removal of EDB from solution.

A fourth EDB hydrolysis study, reported to be in progress (Weaver and others, 1988), is following the hydrolysis of EDB longer than any of the aforementioned investigations. After 379 days, the increase in bromide ion concentration corresponded to a 6.6 percent decline in EDB concentration when the researchers assumed a stoichiometric ratio of two bromide ions formed for every molecule of EDB removed. A half-life of 10 years at 25 ^{o}C was extrapolated from these data (Weaver and others, 1988).

Microbial Degradation

EDB undergoes aerobic and anaerobic microbial transformations that can be described using first-order kinetic expressions. Pignatello (1986, 1987) reported that EDB was degraded in all nonsterile samples of aquifer materials under both anaerobic and aerobic conditions and that half-lives ranged from 35 to 350 days. The aquifer material was incubated in suspension with ground water using conditions that were representative of the saturated zone in Pignatello's study area, EDB concentrations of 0.5 to 5 μg/L, and 9 ^{o}C. At higher concentrations of EDB (15 to 18 mg/L), degradation was much slower, possibly indicating that microbial adaptation to higher EDB concentrations was not achieved during the 3.5 months of incubation (Pignatello, 1986). Under aerobic conditions, EDB at microgram-per-liter concentrations was transformed within 2 days in soil suspensions (Pignatello, 1986). The products of the degradation reaction included two equivalents of bromide ion, carbon dioxide, cell biomass, and some carbon compound that was nonvolatile and water soluble. However, neither highly volatile organic products, such as ethylene, nor products extractable by organic solvents were detected.

Wilson and others (1986) added EDB at 140–194 µg/L to suspensions of soil obtained from an anaerobic, organic-matter-rich, saturated zone at a site adjacent to a landfill. In their experiments, EDB degraded within 16 weeks at 17 °C, but no products were identified.

Weintraub and others (1986) reported that microorganisms in soils collected from Polk and Highlands Counties were only weakly capable of degrading EDB under anaerobic conditions. These soils were collected at sites that are approximately 5 km north of the Lake Francis study area in Highlands County and 7 km southeast of the Lake Pierce study area in Polk County. One soil collected at 1 m depth in Polk County and treated with EDB showed a 40 percent decrease in EDB after 7 months. Carbon dioxide was not produced; however, degradation products, which included ethylene, were volatile. Moye and others (1987) concluded that either appropriate microorganisms were not present or that these soils lacked sufficient secondary carbon sources for maintaining cometabolism. Weintraub and others (1986) also reported that EDB at concentrations of 1–2 mg/L was degraded in anaerobic seeded culture incubations using facultative and methanogenic sludges at 25 °C. These sludge incubations produced ethylene, which is consistent with the results from previous studies (Castro and Belser, 1968; Bouwer and McCarty, 1985).

Nucleophilic Substitution

Several studies have reported that the rate of EDB transformation in aqueous solution is substantially enhanced in the presence of H_2S and HS^- (bisulfide ion) compared to neutral hydrolysis. Weintraub and Moye (1987) reported that the degradation kinetics involving HS^- are first order with respect to EDB; half-lives for the reaction ranged from 19 to 134 days at 25 °C and pH 6.7 to 9.0. The rate of EDB removal or transformation was inversely related to the HS^-concentration. The reaction products that were identified included cyclic alkyl sulfides and cyclic alkyl disulfides (Moye and others, 1987). More recent studies (Haag and Mill, 1987, 1988b; Barbash and Reinhard, 1989a, 1992a) have shown that the principal product of the reaction between EDB and HS^- is actually the substitution product, 1,2-dithioethane. The partially oxidized products detected by Moye and others (1987) were likely to have resulted from the reaction of the 1,2-dithioethane with oxygen contamination in their reaction vessels (Haag and Mill, 1987, 1988b).

In samples of Florida ground water collected at sites where EDB contamination was expected but not detected, Watts and Brown (1985) reported compounds (ethyl mercaptan, diethyl disulfide, triethyl disulfide) that could have been produced by the reaction of EDB with sulfur nucleophiles. Barbash and Reinhard (1987) reported that the pseudo-first-order rate constant at 25 °C in the presence of 1 m*M* sulfide was 3.6 times higher than the rate constant for the hydrolysis reaction at neutral pH. Haag and Mill (1987) estimated that the EDB reaction with 0.5 m*M* thiosulfate ion would be approximately six times as fast as the reaction with H_2O at 25 °C. In ground water, thiosulfate can be formed as an intermediate compound in the microbially mediated reduction of sulfate. Swain and Scott (1953) reported that HS^- is at least eight times as reactive as hydroxide and 100,000 times as reactive as H_2O.

Depending on ambient sulfide concentrations in the surficial, intermediate, or Floridan aquifer systems, nucleophilic substitution reactions involving HS^- can be an important mode of EDB transformation. Unfortunately, no samples were collected or analyzed for reduced sulfur species. Sulfate concentrations of 58 mg/L have been reported (Belles and Martin, 1985) in ground water beneath groves near Lake June in Winter, which is in Highlands County approximately 3 km south of the Lake Francis study area. These sulfate concentrations indicate that there is a potential for production of H_2S (aq) as a result of reduction by indigenous microbiota or by slower abiotic processes (Moye and others, 1987).

Nonreversible Binding of 1,2-Dibromoethane to Soils

The quantity of EDB that is bound chemically or physically to soil particles and that subsequently is nonreactive both chemically and biologically is currently (1992) a topic of active research. Steinberg and others (1987) reported that 27 µg/kg of EDB were bound to topsoil in fields that had not been fumigated for almost 19 years. The persistence of EDB in these soils was attributed to entrapment of EDB in soil micropores where it was unavailable for further chemical or microbiological reactions (Steinberg and others, 1987; Sawhney and others, 1988). When these soil samples were treated with EDB, the added EDB could be readily degraded microbially; however, the bound EDB required hot methanol extraction for release from the soil.

Soil samples of Spodosols and Entisols from a site in Highlands County (which had characteristics similar to those of the soils in the two study areas) were used by Moye and others (1991) to perform laboratory experiments to determine if a radiolabeled EDB-soil mixture that had been incubated for 1 and 3 months would release EDB under conditions designed to simulate solar heating and rainfall. They reported that the 3-month incubation always resulted in a higher retention of the radiolabeled EDB in the soil. After 3 months of allowing EDB radiolabeled with C-14 to incubate in their soil samples, hot methanol extractions (75 °C) still left considerable amounts of residual fumigant (measured as radioactivity) in the soil. H.A. Moye and J.K. Tolson (University of Florida, written commun., 1991) concluded from this that the amount of EDB in soils may be underestimated by as much as 500 percent by using this technique; however, they could not tell whether the residual soil-bound radioactivity was due to EDB or to products of degradation processes. Heating soils for various periods of time prior to aqueous extraction had little effect on the release or recovery of EDB in their experiments. The Highlands County soil retained approximately 10 percent of the added radiolabeled EDB, 50 percent of which was not released by aqueous extraction.

On the basis of many sorption experiments with EDB and 1,2-dibromo-3-chloropropane (DBCP), Moye and others (1991) concluded that soil molecules have a limited number of sites where EDB can be tightly bound. They hypothesized that the most likely type of site or "domain" for sorption is within an apolar cavity of a cyclodextrin. A cyclodextrin molecule could contain cavities in which a hydrophobic compound such as EDB could displace water, but microbes would be excluded from the cavity because of their larger size. Moye and others (1991) believed that an entrapped EDB molecule could, therefore, be immune to both hydrolysis and microbial degradation reactions. They noted that these molecular-sized cyclodextrin cavities in soils have not yet been identified but could be present in some humic materials in soils.

Conceptual Model for the Transport and Fate of 1,2-Dibromoethane in Soil and Ground Water

Conceptually, the processes controlling the movement and fate of EDB in soil and ground water can be grouped into three major types: transport, transformation, and storage (fig. 5). In the following sections of the report, the various components of the conceptual model will be quantified using the aforementioned information from laboratory and field experiments performed under carefully controlled conditions. The concentration of EDB in ground water will then be calculated in each study area using a mass-balance modeling approach. The model incorporates EDB application rates and information on hydrogeologic and soil characteristics for each study area. The EDB concentrations in ground water calculated by using the mass-balance model are compared with observed concentrations of EDB in ground water to determine the predictive capability of the model, given information on hydrogeologic characteristics, EDB application rates, and rates of key chemical and biological reactions.

MASS-BALANCE MODELING APPROACH

In aqueous geochemistry studies, a mass-balance calculation typically involves a budget that delineates the sources from which the dissolved constituents in a water are derived (Drever, 1982). A general equation for the overall reaction can be represented by:

$$\begin{aligned}&\text{rock minerals} + \text{atmospheric input}\\&\quad = \text{altered rock minerals} + \text{solution.}\end{aligned} \tag{6}$$

Plummer and others (1983) presented a related mass-balance modeling approach that uses chemical and mineralogical data along ground-water flow paths to determine which chemical reactions have occurred (for example, mineral dissolution, precipitation, and ion exchange). Other information that can be obtained from this modeling approach includes the mass transfer through each reaction, the conditions under which the reactions occur (constant or variable temperature, open or closed systems), and how natural processes and perturbations affect the water chemistry and mineralogy. The primary mechanism of transport is considered to be advection. Neither sorption nor chemical or microbial transformations are considered in the budget. In this modeling approach, biological processes are typically considered to be in a steady state, and it is assumed that there is no net supply or uptake of any constituent by microbes.

To make an analogy with previous geochemical mass-balance modeling efforts, the mass-balance approach presented in this study considers the applied EDB to be the reactant "rock mineral" phase in equation 6. The measured concentration in ground water is the product "solution," and any EDB that is removed from further reaction can be thought of as the "altered rock" (equation 6). The mass-balance model that is developed for describing the transport, transformation, and storage processes includes reactions that account for the chemical and microbial transformation of EDB in soil and ground water. The relative importance of these reactions varies depending on the elapsed time of reaction and the initial concentration. The following sections describe the principal biogeo-chemical reactions that have been incorporated into the mass-balance model to calculate the concentration of EDB in ground water at a particular time.

Transport Processes in the Unsaturated Zone

The principal mechanisms that prevented EDB from leaching to ground water were volatilization and diffusion. The method of application of EDB attempted to minimize volatilization losses (Poucher and others, 1967). On the basis of estimates of loss of DBCP from soil (Green and others, 1986), approximately 10 percent of the EDB applied is assumed to have been lost to direct volatilization. DBCP and EDB have similar chemical properties (Chiou and others, 1979), and application methods were nearly identical.

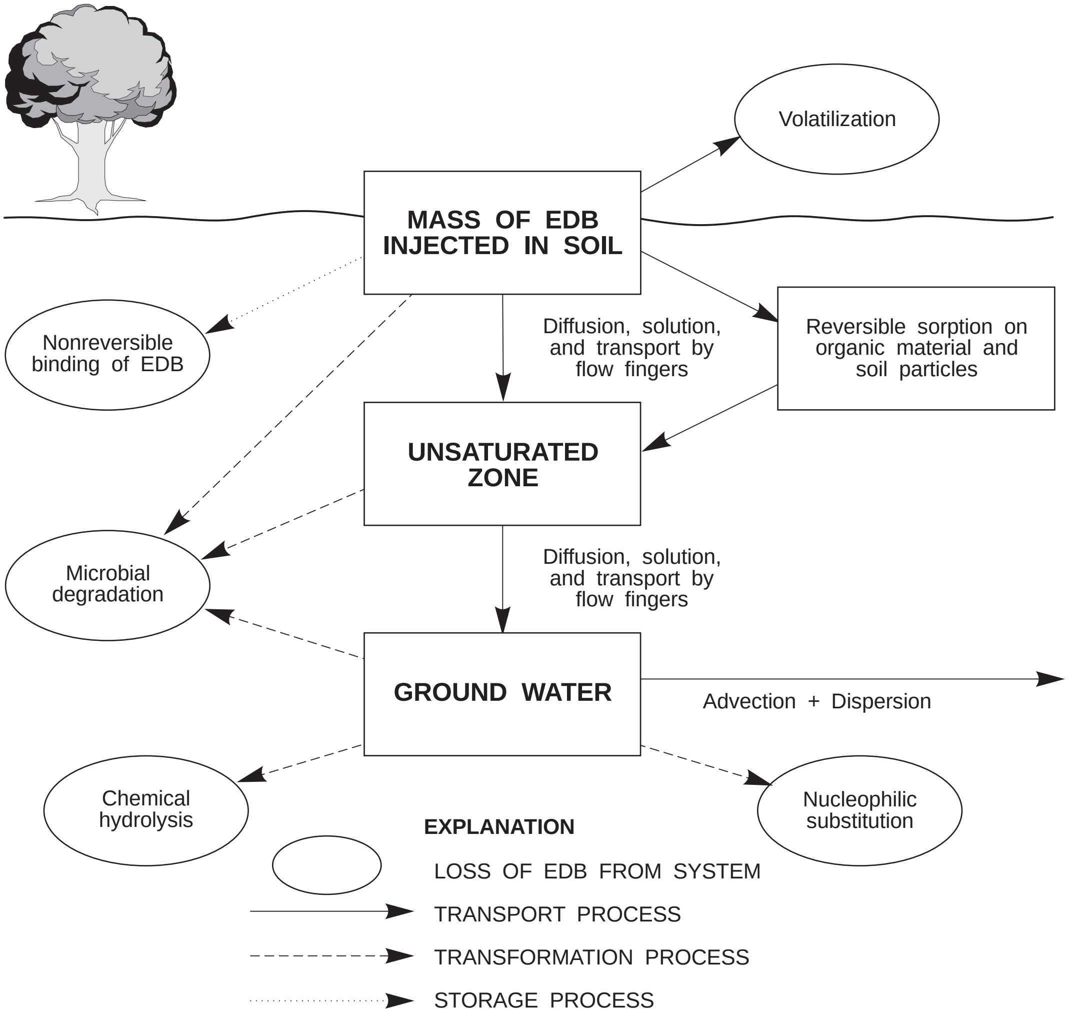


Figure 5. Conceptual model of biogeochemical processes controlling the transport, transformation, and storage of 1,2-dibromoethane (EDB) in the subsurface.

The radial diffusion of EDB vapor through air-filled soil pores was an important mechanism of transport immediately following fumigation. However, between applications of fumigants to soils at the buffer zones, the amount of rainfall entering the soil was sufficient to solubilize the EDB remaining from the last application after volatilization and sorption of EDB vapor. Therefore, to simplify the model of the transport of EDB in the unsaturated zone, it is assumed that approximately 90 percent of the EDB that diffused radially from the injection site was ultimately incorporated into solution when it encountered water that was present either as soil moisture or as rainfall or irrigation water moving through the soil toward the water table. Furthermore, measured vapor diffusion coefficients for EDB are low, approximately 1.7×10^{-12} cm^2/d (Steinberg and others, 1987). This value for diffusion was obtained in a study area where EDB was applied approximately 10 years prior to the study. Steinberg and others (1987) proposed that a finite amount of EDB could diffuse into micropores or blocked pores through which water would not move. The processes influencing the fate of the bound or nonreversibly sorbed EDB are discussed below.

The organic carbon content of the soils in the study areas was used to estimate the amount of EDB vapor that could be removed from further transport to ground water because of sorption reactions. All EDB application sites in the Lake Francis study area are underlain by the Astatula sand (table 1). In the Lake Pierce study area, the Candler sand underlies all application sites (both buffer zones and push-and-treat sites) with the exception of push-and-treat site PT267 (fig. 3), which is underlain by the Tavares fine sand (table 1). Only the Ap horizons of the Astatula and Candler sands contain sufficient organic carbon (0.29 and 0.8 percent, respectively) to sorb a significant proportion of the applied EDB. For the Tavares fine sand, the Ap horizon (0 –20 cm) and the C1, C2, and C3 horizons (20 –132 cm) contain sufficient organic carbon to sorb significant quantities of EDB vapor (table 1). The mass of EDB that could be sorbed on the organic carbon in the soil was calculated for each buffer zone and push-and-treat site in the two study areas. Table 3 shows data for buffer zone B109 in the Lake Pierce study area (fig. 3); the volume of soil is obtained by multiplying the average linear distance of EDB application (1,410 m) by the width of application (4.9 m), the thickness of the Ap horizon (table 1), and the fraction of solid material (1.0 minus the porosity).

Table 3. Date, amount applied, and distance of 1,2-dibromoethane (EDB) application for buffer zone B109 in the Lake Pierce study area (fig. 3)

[Application data for EDB were extrapolated from records on file at the Florida Department of Agriculture and Consumer Services, Division of Plant Industry, Winter Haven, Fla.]

Date of application		Amount of EDB applied (kilograms)	Distance of application (meters)
Month	Year		
7	1963	1,540	2,820
2	1964	748	3,252
8	1964	678	2,940
2	1965	678	2,760
5	1965	678	2,610
11	1965	678	2,610
5	1966	678	1,670
11	1966	678	1,670
5	1967	678	1,670
11	1967	678	1,670
5	1968	678	1,670
11	1968	678	1,670
5	1969	678	1,670
11	1969	678	1,670
5	1970	678	1,670
11	1970	678	1,670
5	1971	678	1,670
11	1971	678	1,670
5	1972	279	945
11	1972	279	945
5	1973	279	945
11	1973	279	945
5	1974	279	945
11	1974	279	945
5	1975	279	945
11	1975	279	945
5	1976	279	945
11	1976	279	945
5	1977	279	945
11	1977	279	945
6	1978	140	530
11	1978	140	530
5	1979	140	530
11	1979	140	530
5	1980	140	530
11	1980	140	530
5	1981	140	530

The porosity of the soil and unsaturated zone material (n) was estimated by using the expression,

$$n = 1 - (\rho_b/\rho_d), \tag{7}$$

where

ρ_b is the bulk density of the soil and
ρ_d is the particle density, both in grams per cubic centimeter (Fetter, 1988).

For most soil and rock, the particle density is approximately 2.65 g/cm^3 (Fetter, 1988). Average values of bulk density for the Ap horizon of the Candler sand, the Astatula sand, and the Tavares fine sand (table 1) were used to calculate porosity for the organic-matter-rich Ap horizon in these three soils as 0.45, 0.41, and 0.38, respectively.

The mass of organic carbon beneath the application site B109 was calculated by multiplying the soil volume (solid fraction) by its bulk density (1.46 g/cm^3) and multiplying that product by the organic carbon content (0.8 percent). The mass of humic acid in the soil was estimated by multiplying the mass of organic carbon by 0.3 (W.C. Cooper, Florida State University, written commun., 1989). The maximum amount of EDB vapor that could sorb onto the mass of humic acid was calculated by multiplying the mass of humic acid by the limiting sorption capacity of 37 mg/g (Chiou and others, 1988). According to this calculation, a maximum of 76.1 kg of EDB could be sorbed by the humic acid present in the Ap horizon of the soil beneath the application site. During the period in which EDB was injected at this buffer zone (1963–81), 17,464 kg of EDB was applied: if 10 percent was lost by volatilization, then 15,718 kg was left in the soil. Thus, the fraction of EDB in the soil that could have been sorbed by humic acid in the soil was very small, only about 0.48 percent.

Chiou and others (1988) reported that soil humic acid is about 50 percent less effective than soil organic matter in the sorption of nonpolar organic compounds, such as EDB. When the calculations used a limiting sorption capacity of 74 mg/g and a soil organic matter content of 0.8 percent, the fraction of EDB applied that could be sorbed on the soil organic matter was approximately 3.2 percent. However, on the basis of experimental studies involving binding of EDB to, and leaching of EDB from, a Highlands County soil having characteristics similar to those of soils in the study areas, H.A. Moye and J.K. Tolson (University of Florida, written commun., 1991) reported that approximately 50 percent of the bound EDB was released with subsequent aqueous extractions that were designed to simulate rainfall at different soil temperatures. Therefore, in the mass-balance model calculations, it was assumed that 1.6 percent of the EDB remaining after volatilization was nonreversibly sorbed onto organic carbon in soils beneath buffer-zone application sites.

Mass-balance calculations for the sorption of EDB vapor on soil organic matter at push-and-treat sites result in considerably different quantities of EDB that would be available for transport to ground water at the different locations. Soil characteristics (table 1) for push-and-treat site PT267, located in the Lake Pierce study area (fig. 3), can be used to calculate the mass of organic matter as was done for soils in the buffer zones. The maximum amount of EDB that could potentially be sorbed by the total amount of organic matter present in the Ap horizon is 2,664 kg. At this site, the largest single application of EDB was 1,590 kg (table 4), and 1,430 kg may have been left after volatilization. Because of the large surface area over which EDB was applied (36,800 m^2), the entire mass of EDB applied could have been removed by sorption on the organic matter present and may not have been available for transport to ground water. At push-and-treat site PT271, 11,600 kg of EDB could be sorbed by organic matter present; the application of 13,970 kg of EDB in 1978 (table 4) may have resulted in the immediate release of 2,370 kg of EDB for transport to ground water. The mass of EDB available for transport to ground water beneath each push-and-treat site was calculated individually by subtracting 50 percent of the amount potentially sorbed on organic matter in the soil (using the aforementioned method and taking volatilization losses into account) from the amount of EDB applied.

The amount of EDB vapor that will sorb on soil particles such as clay minerals and coatings on grains is assumed to be extremely small because Call (1957a) reported that the limiting sorption capacity is 3.8 µg EDB per gram of soil. This value, however, was determined for a soil that contained 2 percent organic carbon. The soils collected for the present study contain less than 1 percent organic carbon.

Table 4. Date, amount applied, and area of 1,2-dibromoethane (EDB) application for push-and-treat sites PT267 and PT271 in the Lake Pierce study area (fig. 3)

[Application data for EDB were extrapolated from records on file at the Florida Department of Agriculture and Consumer Services, Division of Plant Industry, Winter Haven, Fla.]

Date of application		Amount of EDB applied (kilograms)	Area of application (square meters)
Month	Year		
Push-and-treat application site PT267			
6	1965	76.9	1,800
6	1966	1,590	36,800
10	1972	27.9	607
10	1972	55.9	1,300
Push-and-treat application site PT271			
3	1978	13,970	324,000

As a first approximation in the mass-balance model, it is assumed that any EDB removed by the soil has been sorbed onto organic matter.

The rate of transport of dissolved EDB through the unsaturated zone and into the surficial aquifer is enhanced by the development of wetting-front instabilities and preferred pathways of flow, commonly referred to as flow fingers (Glass and others, 1988, 1989). The size and spacing of these flow fingers that develop along a wetting front as it percolates downward through a porous medium are related to spatial heterogeneities in the physical properties (porosity and grain size) and hydraulic properties (unsaturated conductivity and moisture content) of the sediment. Pendexter and Furbish (1991) found that small-scale heterogeneities are involved in development of flow fingers in sands composing the Highlands Ridge in Polk and Highlands Counties, central Florida. Localized retardation of flow by capillary action occurred at one site as compared to the relatively enhanced downward flow at neighboring sites (Pendexter and Furbish, 1991). In places, the rate of transport of water to the saturated zone through flow fingers may be a factor of two or three times the rate expected from the vertical movement of a stable, uniform wetting front. The spatially variable percolation rates may introduce an almost infinite degree of complexity in attempting to describe the mass loading rate to ground water because EDB is introduced to the water table at variable rates and at many different times following an application.

Transport Processes in Ground Water

Once EDB enters the ground water, the primary mass transport processes are advection and hydrodynamic dispersion. Other processes, such as hydrolysis and biodegradation reactions, tend to retard or restrict the movement of EDB. Together, these processes control the maximum extent of spread of a plume of contamination and the resulting geometric character of the concentration distribution. The shape of the plumes formed beneath EDB application sites would also be controlled by sorption and the mass loading rate. Sorption processes are often the most difficult and uncertain to quantify in aquifer systems (Domenico and Schwartz, 1990); however, it is assumed that EDB will tend to remain in the aqueous phase and be transported by advection with the moving ground water because the amounts of organic carbon and clay minerals in soils are extremely low (less than 1.0 and 2.5 percent, respectively). The mass loading rate of EDB to ground water is related to the amount and rate of EDB applied, the amount and rate of rainfall and infiltration following application, and the development of flow fingers that would expedite the transport of EDB to the water table. Domenico and Schwartz (1990) noted that adding the same quantity of mass to a flow system over increasingly longer times will change the center of mass of the plume and its internal concentration distribution. When the loading period is lengthened, as in the application of EDB in both study areas, the result will be a plume or plumes that are larger than if the mass were added over a shorter time period.

The following assumptions regarding the hydrologic flow system were made as a first approximation for the mass transport of EDB in ground water for the mass-balance model: (1) the region of ground-water flow in both study areas is homogeneous, isotropic, and fully saturated; (2) steady-state flow conditions exist; and (3) lateral or transverse dispersion is negligible. In a later section of the report, dispersion in directions parallel and transverse to the principal direction of ground-water flow is considered. A flow net can be constructed based on these three assumptions, and any flow lines contained in the flow net would constitute imaginary impermeable boundaries (there would be no flow across a flow line). In such a system, transport of EDB is assumed to be restricted to flow tubes, which are the areas bounded by flow lines (fig. 6). It is also assumed that, within a flow tube, mixing in the transverse and vertical directions is complete.

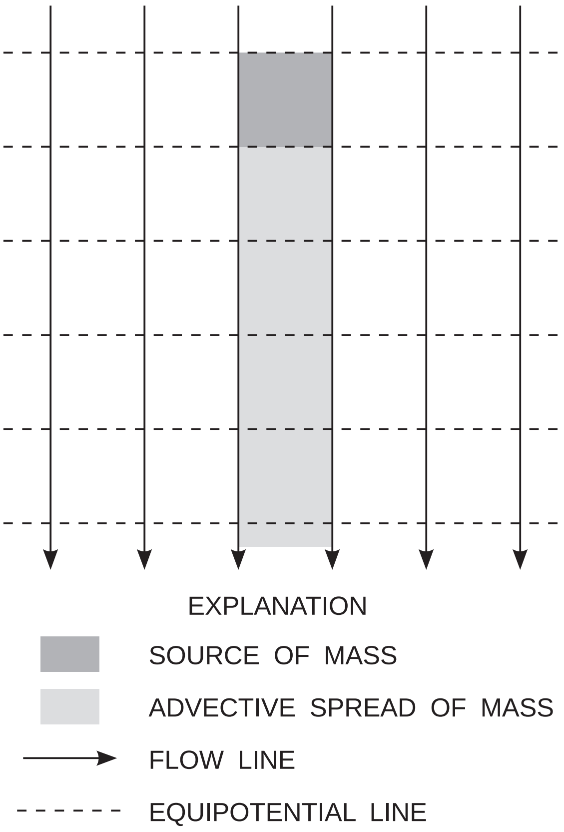


Figure 6. Mass spreading by advection, if hydrodynamic dispersion were negligible, in the surficial aquifer system in the Lake Francis and Lake Pierce study areas (modified from Domenico and Schwartz, 1990).

The average ground-water flow velocity in the two study areas was calculated by using Darcy’s law:

$$v = K(dh/dl)/n, \tag{8}$$

where

v is the average ground-water flow velocity,
K is the hydraulic conductivity,
dh/dl is the hydraulic gradient (change in water-table altitude with distance), and
n is the porosity, calculated from equation 7.

The average ground-water velocity in the Lake Francis study area is 0.6 m/d, calculated from a hydraulic conductivity of 24 m/d (the average of the saturated soil hydraulic conductivities in table 1), an estimated hydraulic gradient of 0.01, and a porosity of 0.40 (calculated from the average bulk density of the C horizon and equation 7). For the Lake Pierce study area, the average ground-water velocity is 1 m/d, based on a hydraulic conductivity of 23 m/d (table 1), an estimated hydraulic gradient of 0.02, and a calculated porosity of 0.43. It is assumed, as a first approximation, that advection is the only process for transport of EDB in ground water. Hydrodynamic dispersion in directions transverse to the principal flow direction is most likely of secondary importance with these relatively high ground-water flow velocities (Freeze and Cherry, 1979) and was not considered in the calculations. The magnitude and direction of advective transport, which is driven by the ground-water flow velocity, are controlled by the following factors (Domenico and Schwartz, 1990): (1) the hydraulic conductivity distribution within the flow field, (2) the shape of the water table or potentiometric surface, (3) the presence of additional sources or sinks (such as wells), and (4) the shape of the flow domain.

Transformation Processes

The amount of EDB lost as a result of chemical hydrolysis, microbial degradation, and nucleophilic substitution reactions involving HS^- can be treated as three parallel first-order rate reactions, as follows:

$$[\mathrm{EDB}] \xrightarrow{k_1} \text{reaction products} \tag{9}$$

$$[\mathrm{EDB}] \xrightarrow{k_2} \text{reaction products} \tag{10}$$

$$[\mathrm{EDB}] \xrightarrow{k_3} \text{reaction products} \tag{11}$$

where k_1, k_2, and k_3 are rate constants for the three parallel reactions. The rate law for parallel first-order reactions can be expressed as:

$$d[\mathrm{EDB}]/dt = -k_1[\mathrm{EDB}] - k_2[\mathrm{EDB}] - k_3[\mathrm{EDB}], \qquad (12)$$

$$d[\mathrm{EDB}]/dt = -(k_1 + k_2 + k_3)\,[\mathrm{EDB}] \qquad (13)$$

The apparent rate constant for all three reactions, $k(\mathrm{app})$, is equal to $(k_1 + k_2 + k_3)$, and the overall kinetic first-order rate expression is:

$$C = C_o\, e^{-k(\mathrm{app})\, t}, \qquad (14)$$

where

C is the concentration of EDB remaining after a specified time t,

C_o is the initial concentration of EDB in ground water beneath the application site, after accounting for losses from volatilization, partitioning between aqueous and gaseous phases, sorption on organic matter, and nonreversible binding to soils,

$k(\mathrm{app})$ is the apparent rate constant for the chemical and biological reactions controlling the degradation of EDB and is equal to the natural logarithm of 2 (0.693) divided by the half-life for each controlling reaction, and

t is the elapsed time between EDB injection at a buffer zone or push-and-treat application site and collection of the sample for analysis of EDB.

The apparent rate constant, $k(\mathrm{app})$, is controlled by the rates of the individual reactions.

Storage Processes

As a first approximation in the mass-balance model, it is assumed that 5 percent of the original amount of EDB applied is bound in some manner and is not available for further reactions. This estimate is based on the findings reported by Moye and others (1991) for experiments performed on samples of a soil from Highlands County with characteristics almost identical to those of the soils in the Lake Francis and Lake Pierce study areas.

Computational Mass-Balance Model Expression

A simple mathematical model was developed to calculate the concentration of EDB in ground water at a specific location and date. Computationally, the model consists of two expressions. First, the mass of EDB (M) remaining in the unsaturated zone beneath an application site is estimated as follows:

$$M = (\text{mass of EDB applied})(F_v)(F_H)(F_{om})(F_{st}), \qquad (15)$$

where

F_v is the fraction remaining in the soil gas phase after volatilization losses,

F_H is the fraction remaining after partitioning between the aqueous and gaseous phases according to Henry’s law,

F_{om} is the fraction remaining after sorption of EDB vapor on organic matter, and

F_{st} is the fraction of EDB available for transport to ground water after nonreversible binding reactions.

The values for the fraction of EDB available for transport to ground water are presented in table 5 for the various processes involving volatilization, partitioning between aqueous and gaseous phases, sorption on organic matter, and nonreversible binding to soils. The mass of EDB remaining (M) obtained using equation 15 is assumed to be solubilized in any available soil moisture and water percolating downward through the unsaturated zone to the water table. Therefore, it is also assumed that all water that solubilizes EDB in the unsaturated zone participates in the process of transporting EDB to the water table. The solubilized EDB is transported by preferential flow fingers to the water table in approximately 30 to 60 days, as was previously reported.

In the second expression in the model, the initial concentration of EDB in ground water (C_o) beneath an application site is calculated by dividing the mass of EDB remaining (M) by the volume of water in a flow tube:

$$C_o = \frac{M}{\text{volume of water in flow tube}}\,. \qquad (16)$$

The volume of water in a flow tube, in which EDB will be transported downgradient, is calculated as follows: the cross-sectional area of a flow tube (perpendicular to the principal ground-water flow direction) between any two adjacent flow lines is obtained by multiplying the width (plan-view distance between flow lines) by the vertical dimension of flow. When the third dimension is included, the distance from the sampling site to the application site, a three-dimensional flow tube can be described. The width of a flow tube in which EDB is transported is estimated by the longest dimension of a buffer zone application site that is perpendicular to the principal direction of ground-water flow. The vertical dimension of flow is estimated from information on the maximum depth at which EDB was detected in each study area. The volume of water in the flow tube is then calculated by multiplying the flow-tube cross-sectional area by the distance of the sampling site from the application site and multiplying that product by the porosity of the aquifer material.

Table 5. Factors used to account for loss in mass of 1,2-dibromoethane (EDB) resulting from various biogeochemical processes in mass-balance model

[For example, the factor of 0.90 for volatilization means that, after volatilization, 90 percent of the EDB applied is available for transport to ground water]

Process	Factor used to account for loss in mass of EDB
Transport:	
Volatilization (F_v)	0.90
Partitioning between aqueous and gaseous phases (F_H)	0.97
Sorption on organic matter (F_{om})	0.98
Transformation:	
First-order degradation by chemical hydrolysis and microbial reactions	$C = C_o e^{-k(\mathrm{app})t}$
where	
C is the concentration of EDB after time t (interval in years between sampling date and date of application),	
C_o is the initial concentration of EDB at time of application (after accounting for losses from volatilization, partitioning between aqueous and gaseous phases, sorption on organic matter, and nonreversible binding to soils), and	
$k(\mathrm{app})$ is the apparent rate constant = 0.693/half-life.	
Storage: Nonreversible binding to soils (F_{st})	0.95

As described above, the concentration of EDB in ground water (C) at a particular downgradient location is calculated by using equation 14. The calculations for the Lake Francis and Lake Pierce study areas are presented in the following sections.

The mass-balance approach for calculating the downgradient concentration of EDB in ground water relies on two basic assumptions that represent a simplification of a very complex system. The first assumption is that the remaining EDB in the unsaturated zone (M) is transported to ground water over a period of time that is less than the time required for ground water to travel from beneath an application site to the downgradient sampling site. Therefore, without knowledge of the exact residence time in the unsaturated zone or the precise timing of an instantaneous pulse of EDB, the contribution of M to the downgradient concentration of EDB is accounted for. Secondly, the EDB in the ground-water system is assumed to be well mixed both vertically and laterally within the flow tube. This assumption of a well-mixed condition in a homogeneous, isotropic aquifer under steady-state uniform flow will be explored in greater detail in the section of the report on hydrodynamic dispersion processes.

RESULTS OF MASS-BALANCE MODELING CALCULATIONS

The mass-balance model is used to calculate the maximum concentration of EDB in ground water at a specified location downgradient from an EDB application site. The results of the mass-balance calculations are described for the ground-water flow systems in each study area, along with a description of their applicability and the sensitivity of the mass-balance model to changes in input variables.

Lake Francis Study Area

In the Lake Francis study area (fig. 1), the direction of ground-water flow is oblique to the east- and north-trending limbs of buffer zone B111, buffer zone B80, and push-and-treat site PT157. The width of a flow tube is assumed to be the distance along a northeast-trending diagonal line that connects the outermost part of the two limbs of buffer zone B111. The volume of water in this presumed flow tube (9.38×10^9 L) can be calculated by multiplying its width (820 m) by the distance of the sampling point (well 911) from the application site (610 m), the depth of the ground-water flow tube (47 m), and the porosity of the aquifer material (0.40).

By use of a range of published values for the half-life of EDB in ground water, 0.5 to 5.0 years, a range of concentrations of EDB in ground water was calculated by using the mass-balance model developed in this study. The mass of EDB applied was 18,500 kg during 1962 through 1983. Calculated concentrations of EDB in ground water ranged from 24 to 460 μg/L (table 6). Mass-balance calculations using a half-life for EDB of 0.65 year produced a concentration of 39 μg/L (table 6), which agrees well with the measured maximum concentration of EDB in the aquifer of 37 μg/L. A half-life for EDB of 0.65 year is consistent with an EDB half-life of 1 to 2 years reported for chemical hydrolysis reactions in Florida ground water at 22 ^{o}C and a half-life of 3 to 6 months reported for microbial degradation reactions at 22 ^{o}C (Weintraub and others, 1986).

Table 6. Calculated concentrations of 1,2-dibromoethane (EDB) in ground water and mass of EDB remaining at the time of sampling using various half-lives of EDB in the mass-balance model for the Lake Francis and Lake Pierce study areas

	Lake Francis study area		Lake Pierce study area	
EDB half-life (years)	Mass of EDB remaining (kilograms)	Concentration (micrograms per liter)	Mass of EDB remaining (kilograms)	Concentration (micrograms per liter)
0.50	225	24	3.34	0.07
.65	370	39	13.5	.29
.75	474	50	26.2	.56
.85	580	62	46.3	.99
.90	632	67	58.5	1.3
1.0	739	79	88.1	1.9
1.2	949	100	170	3.6
1.5	1,250	130	346	7.4
2.0	1,740	190	766	16
2.5	2,200	240	1,310	28
5.0	4,270	460	4,700	100

Lake Pierce Study Area

The predominant direction of ground-water flow in the Lake Pierce study area is to the northeast, toward Lake Pierce (fig. 3). The width of a flow tube encompassing most of the mass of EDB applied (47,500 kg during 1963–83) is estimated to be 800 m, the approximate distance diagonally across buffer application site B109 (fig. 3). The volume of water in this flow tube is calculated to be 4.68×10^{10} L, which was obtained by multiplying the width of the flow tube (800 m) by the distance of the downgradient well 23901 from the application site (2,607 m), multiplying that product by the depth of ground-water flow containing EDB (50 m), and that product by the porosity of the aquifer material (0.45).

A half-life for EDB of 0.65 year resulted in a calculated concentration of 0.29 μg/L (table 6), which agrees well with the maximum concentration of 0.22 μg/L, which was measured in water from the downgradient well (well 23901, fig. 3) sampled in November 1986. This half-life of 0.65 year is the same value obtained for the Lake Francis study area.

In contrast to the decreasing trends in EDB concentrations in water from wells in the Lake Francis study area, water from wells that were sampled more than 10 times during 1983–87 in the Lake Pierce study area had an increase in EDB concentrations. The increase in EDB concentration during 1984 through 1987 is most likely related to the mass of EDB remaining from several large applications of EDB, to the time of transport from soil and ground water to the downgradient sampled wells, and to the rainfall distribution pattern. Prior to early 1978, approximately 34,000 kg of EDB was applied to the study area. Approximately 7,000 kg was applied in March 1978 as part of the 13,500 kg that was applied between March 1978 and mid-1983. The calculated mass of EDB remaining in mid-1984 is 8.54 kg, after accounting for losses resulting from chemical and microbial degradation reactions (EDB half-life of 0.65 year) and other processes, including volatilization, partitioning between aqueous and gaseous phases, sorption on soil organic matter, and storage in some nonreversibly bound fraction (equations 15 and 16). This remaining mass of EDB would have a concentration of 0.18 μg/L in ground water. This concentration is obtained by dividing the 8.54 kg of EDB remaining by the volume of water in the ground-water flow tube (4.68×10^{10} L).

The mass of EDB remaining after the aforementioned losses are taken into account is calculated to be 14.2 kg in November 1986, the date of the latest sampling of well 23901. This mass results in a ground-water concentration of EDB of 0.30 μg/L. An inherent assumption in these calculations is that the average transport time is about 7 years. The transport time is the interval in which EDB travels to the downgradient site following its injection into the soil at the upgradient application sites, a distance of 2,607 m. The large amount of EDB applied in 1978 was followed by a year of above-normal rainfall in 1979 (fig. 7), when rainfall was approximately 30 cm greater than the mean annual rainfall of 127 cm for 1951–80 (National Oceanic and Atmospheric Administration, 1982). The large amount of rainfall recorded in 1979 was preceded by 9 years of below-normal rainfall (fig. 7). The high volume of rainfall in 1979 may have solubilized and transported a larger than expected fraction of the mass of EDB applied in 1978 to the water table for further transport in ground water.

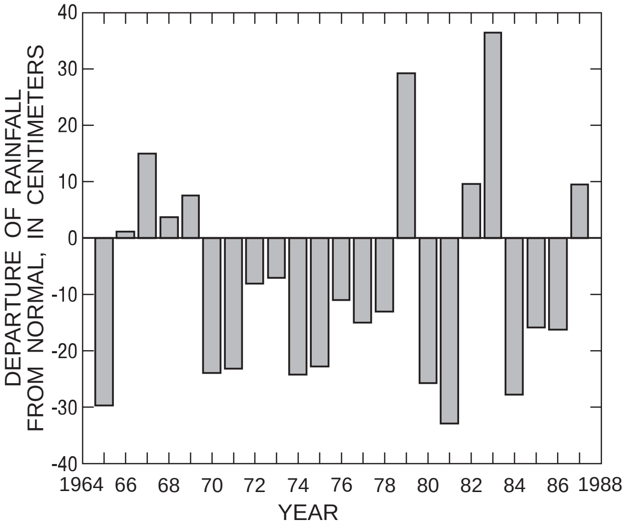


Figure 7. Annual departure of rainfall from the 1951–80 mean, Lake Alfred station, Polk County. Data from National Oceanic and Atmospheric Administration (1982).

The estimated EDB transport time of 7 years from the application site to the downgradient wells near Lake Pierce was based on the following conditions. First, in the 3 to 6 months between applications of EDB, the compound was dissolved in recharge water (rainfall). Next, water containing EDB percolated through the unsaturated zone along preferential flow fingers (Glass and others, 1988, 1989; Pendexter and Furbish, 1991) and reached the water table of the surficial aquifer in approximately 30 to 60 days following application (based on previously discussed estimates from Adams and Stoker, 1985). Once in the surficial aquifer, the water was assumed to move downgradient laterally at an average velocity of approximately of 1 m/d. The average flow velocity was calculated from Darcy's law (equation 8), $v = K(dh/dl)/n$, as presented in an earlier section of the report.

EDB has also been detected in water from wells tapping the Floridan aquifer system in the study area. Contamination of the deeper aquifer system most likely results from water moving laterally through the surficial aquifer and encountering depression and collapse features (sinkholes or breaches in the confining unit) where the upper part of the Floridan aquifer system is in direct contact with the lower part of the surficial aquifer (fig. 8).

Sinkholes, indicated by closed circular depressions on a U.S. Geological Survey topographic map of the 7.5-minute quadrangle containing the area, are very common in this region; at least 30 mappable surface karst features occur in the study area. Sinclair and others (1985) reported that limestone dissolution is rapid and that cover-subsidence sinkholes predominate in this area. Water in the Floridan aquifer system flows through numerous solution cavities of various sizes; as a result, an average velocity has less significance than average velocities for homogeneous unconsolidated aquifers because of the large range in possible velocities. However, if an average hydraulic conductivity of 10^{-3} m/s for karst limestone (Freeze and Cherry, 1979) is assumed along with an average effective porosity of 0.05, and a hydraulic gradient of 0.001 (Duerr and others, 1988), an average velocity of 1.7 m/d can be calculated. Based on this velocity, the average time required for ground water to travel from the vicinity of the application sites to the downgradient wells tapping the Floridan aquifer system is about 4 years. These calculations of ground-water flow velocity represent averages based on large ranges in hydraulic conductivity (five orders of magnitude, 10^{-1} to 10^{-6} m/s), porosity, and hydraulic gradient. These estimates of transport time through the different aquifers are presented only to demonstrate that a transport time for EDB of 7 years is a reasonable assumption. The effect of dispersion was not accounted for in the calculation of average time of transport of EDB. EDB could travel faster or slower than the average velocity of the water, depending on the magnitude of the longitudinal and transverse hydrodynamic dispersion coefficients.

EDB concentrations in water from surficial-aquifer well 17991 (fig. 3), located approximately 100 m downgradient from the eastern corner of buffer zone application site B109, ranged from 18 to 73 µg/L in eight samples of water collected between September 1984 and August 1987. The peak concentration of EDB (73 µg/L) was observed in August 1986. Unfortunately, adequate well construction information (total well depth, in particular) was not available for this well, and so detailed mass-balance calculations were not made. However, the limited information on EDB concentrations could indicate that a breakthrough of the center of mass of a plume of EDB has occurred. It is conceivable that the peak EDB concentration measured in 1986 corresponds to the peak amount of EDB applied to nearby application sites in 1978 (fig. 4).

To repeat, ground water sampled at the downgradient sites during 1984 may represent water beneath EDB application sites that received the contaminant throughout the time period from 1963 to early 1978. The calculated concentration of 0.18 µg/L is within the range of measured concentrations of 0.10 to 0.20 µg/L. Water sampled in late 1986 most likely represents the input of EDB to the water table from 1978 to 1983, which has not degraded substantially because of the relatively short time between application and sampling. As a result of the greater mass of EDB introduced to ground water during that period than in 1963 to early 1978, higher concentrations were produced. A calculated concentration of 0.30 µg/L, based on the mass-balance model, falls within the range of higher EDB concentrations observed in ground water from 1986 through 1987 (0.22 to 1.1 µg/L).

To further test this hypothesis, additional samples of ground water collected after 1987 were needed. Unfortunately, because of the installation of charcoal filters on most of the contaminated wells for the purpose of remediation, only a limited number of samples were collected by FDER and FHRS before sampling of untreated water was suspended in mid-1987.

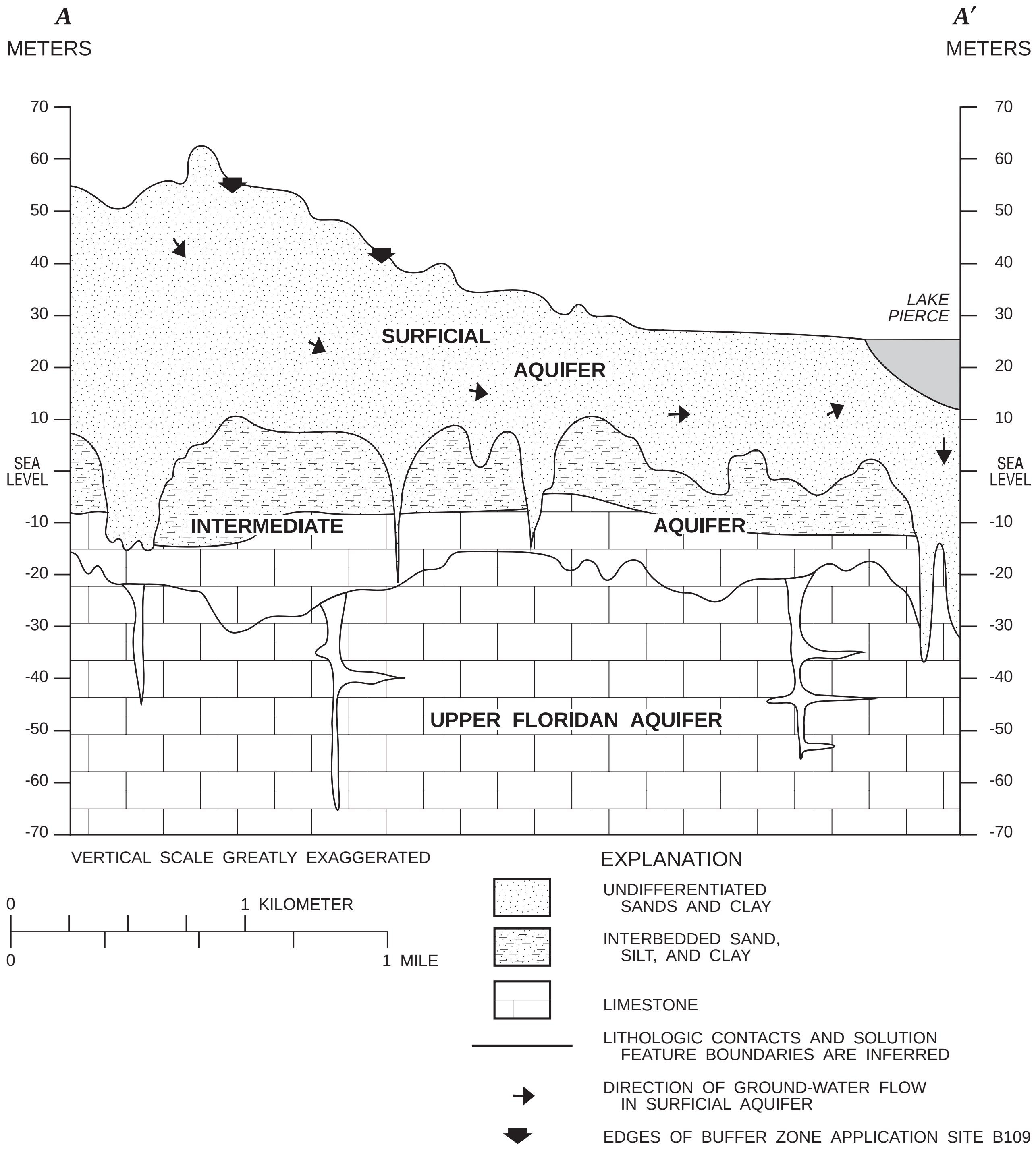


Figure 8. Generalized hydrogeologic section of the Lake Pierce study area (modified from Lee and others, 1991).

Sensitivity of Mass-Balance Model to Input Variables

The sensitivity of the mass-balance model to a particular input variable is a measure of the amount of influence that changing the value of that variable has on the calculated concentration of EDB in ground water. To determine the sensitivity of the mass-balance model, actual or estimated ranges of values for variables were evaluated for the Lake Francis study area. The range of values was expected to be representative of chemical and physical conditions in both study areas. The sensitivity of an input variable was obtained after assigning intermediate values to all other variables and comparing the calculated EDB concentrations when the two extreme values for the variable of interest were used. An important assumption in the sensitivity analyses is that there is no interdependence among variables in the model.

The changes in EDB concentration resulting from varying each input variable over its actual or estimated range (table 7) are shown in figure 9. EDB concentration in ground water is most sensitive to the range in half-life values. This sensitivity is a function of the order of magnitude difference between the extreme values; the difference between the extreme values for the other variables is about 20 to 40 percent. The values for the partitioning of EDB between the aqueous and gaseous phases (*H*) and the sorption of EDB on organic matter (K_{om}) were kept constant because these values resulted from calculations based on constants derived from the literature at a specific temperature of ground water. It was not possible to assign a range of values. However, because of the low sensitivity of the model to the 20 percent range of extreme values for volatilization, one would expect that the model would not be sensitive to small changes in the values for *H* and K_{om}. The results of the sensitivity analyses are dependent on the values selected as intermediate values and the independent variation of the input variables to the mass-balance model. These intermediate values represent best estimates of chemical, biological, and physical processes that are controlling the fate of EDB in ground water.

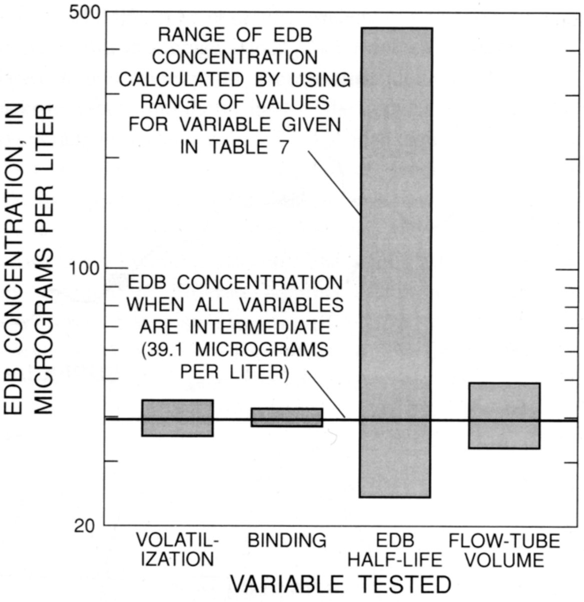


Figure 9. Simulated concentrations of 1,2-dibromoethane (EDB) in ground water in the Lake Francis study area based on sensitivity analyses of selected input variables for mass-balance model.

Table 7. Ranges of extreme values and intermediate values for selected input variables used in sensitivity analyses of mass-balance model

[EDB, 1,2-dibromoethane]

Input variable to mass-balance model	Range of values tested	Intermediate value
Volatilization, in percent..........	0–20	10
Partitioning between aqueous and gaseous phases	0.03	.03
Sorption on organic matter, in percent	1.2	1.2
Nonreversible binding, in percent............................	0–10	5
EDB half-life, in years	0.5–5.0	.65
Flow-tube volume, in liters	$7.50–11.3 \times 10^9$	9.38×10^9

Applicability of Mass-Balance Model Calculations

The mass-balance model calculations that used a half-life for EDB of 0.65 year resulted in concentrations that were in good agreement with the measured concentrations of EDB in ground water at downgradient sites in the Lake Francis and Lake Pierce study areas. This agreement implies that the maximum downgradient concentrations of EDB in ground water can be estimated fairly accurately by making some assumptions regarding the hydrologic flow system and by the quantification of EDB transport, transformation, and storage processes. Even with some of the uncertainties associated with extrapolating laboratory rate constants to field situations, and with an oversimplification of the hydrologic flow system, if application rates are known or can be estimated for a given contaminant, the mass-balance technique presented in this report can be a useful tool to estimate expected concentrations for a particular contaminant in ground water.

One of the problems associated with the delineation of contaminant distributions is the observation that water from adjacent or nearby wells that tap a similar depth interval in an aquifer can have widely different concentrations of a particular contaminant. In a study of the distribution of volatile organic compounds (VOC’s) in ground water beneath an abandoned landfill, Barbash and Barker (1985) reported that small-scale heterogeneity in the concentrations of VOC’s was significantly greater near their point of entry into the flow system than further downgradient. They reported that concentration-depth profiles of VOC’s were highly irregular, with concentrations often differing by one to four orders of magnitude between sampling points spaced only 1 m apart. In the Lake Francis study area in August 1984, one well produced water with an EDB concentration of 37 μg/L, whereas a nearby well (about 100 m away) produced water with EDB concentrations below the detection limit of 0.02 µg/L. If it is assumed that the sampling methods, well construction techniques, and depth of the sampling interval for both wells are nearly identical, then the differences in concentration may arise from a combination of physical and chemical processes in the aquifer.

According to the concepts and assumptions presented about the transport of EDB in the unsaturated zone in preferential flow fingers and transport of EDB in ground water through flow tubes, the concentration of EDB in a particular flow tube depends on the rate of transport of EDB through the unsaturated zone to that part of the water table where the flow tube originates. If flow fingers develop beneath an application buffer zone in one place and, for the sake of example, no flow fingers form in an interval of 10 m directly adjacent to this first location, then it is possible for a narrow flow tube to develop that has an elevated concentration of EDB, whereas the adjacent flow tube may have no detectable EDB. At a downgradient site where, for example, 37 µg/L EDB had been measured in ground water, the sampling interval of a well could have been situated precisely along the flow tube that had intersected the upgradient preferential flow finger carrying EDB. Ideally, the width of a flow tube that is transporting EDB is proportional to the total width of the buffer zone that is perpendicular to the flow direction. The mass associated with this segment would therefore be proportional to the total mass of EDB applied along the entire application zone.

For both study areas, the concentrations calculated by using reported half-lives for EDB of 1 to 2 years (based on laboratory measurements of first-order chemical hydrolysis rate constants) were greater than the measured concentrations. As mentioned above, the hydrologic conditions presented in the mass-balance model are an oversimplification of the flow system. The mass transport processes included in the model assumed that hydrodynamic dispersion (particularly in directions transverse to the principal flow direction) was negligible as a first approximation, and dispersion was not considered in the mass-balance model. To gain some insight into how the process of hydrodynamic dispersion may affect the transport and fate of EDB in ground water at downgradient sites in the two study areas, the following section presents an analytical solution to the three-dimensional advection-dispersion equation using estimates of the coefficients of hydrodynamic dispersion in the longitudinal and transverse directions.

HYDRODYNAMIC DISPERSION AND MASS TRANSPORT OF 1,2-DIBROMOETHANE

This section of the report examines the effect of hydrodynamic dispersion on the EDB concentration in ground water in the two study areas. An analytical solution to the three-dimensional advection-dispersion equation will be used to estimate the maximum concentration of EDB at selected downgradient sites and to compare this prediction with measured values. For a rigorous treatment of the topic of hydrodynamic dispersion, the reader is referred to Domenico and Schwartz (1990).

Hydrodynamic dispersion spreads and dilutes contaminants in an aquifer system. As ground water moves through tortuous, branching, and interfingering pores of different sizes between sediment grains, it mechanically mixes. Dispersion results from this mixing and from molecular diffusion in the pore water. As a result of dispersion, a plume of contamination spreads, both in the direction of ground-water flow and, to a lesser extent, perpendicular to the flow direction.

If a nonreactive tracer is introduced as an instantaneous point source to the water table (fig. 10), into a uniform flow regime, it theoretically spreads in all directions in a horizontal plane as it moves along the flow path. The mass of tracer would occupy an increasing volume of the porous medium even though the total mass does not change. Although the aquifer material is homogeneous and isotropic, the process of mechanical dispersion is directionally dependent and anisotropic. For purposes of this example, it is assumed that there is no significant density contrast between the contaminant and the ground water in the surrounding flow regime. Although figure 10 shows only the two-dimensional map view of the plume, the tracer plume expands in three dimensions and develops the shape of an ellipsoid as it is transported through the aquifer system. This shape results from dispersion being stronger in the direction of flow (longitudinal dispersion in the *x* direction) than in directions transverse to the principal flow direction (in the *y* and *z* directions).

To mathematically model the transport of a tracer (contaminant) in three dimensions, it is necessary to consider both longitudinal and transverse hydrodynamic dispersion in addition to advection. The three-dimensional advection-dispersion equation used to model transport of a reactive solute (such as EDB) in a ground-water flow system can be represented as follows:

$$D_x(\partial^2 C/\partial x^2) + D_y(\partial^2 C/\partial y^2) + D_z(\partial^2 C/\partial z^2)$$

$$- v_x(\partial C/\partial x) - r/n \;=\; \partial C/\partial t, \qquad (17)$$

where

C	is the concentration of the reactive solute,
v_x	is the advective velocity of ground water,
D_x, D_y, and D_z	are the coefficients of hydrodynamic dispersion in the x, y, and z directions from the center of gravity of the contaminant mass,
x, y, and z	are space coordinates,
t	is time,
r	is the first-order kinetic expression for degradation, $e^{-k(\text{app})t}$,
k(app)	is the first-order degradation constant 0.693 divided by the half-life, and
n	is the porosity.

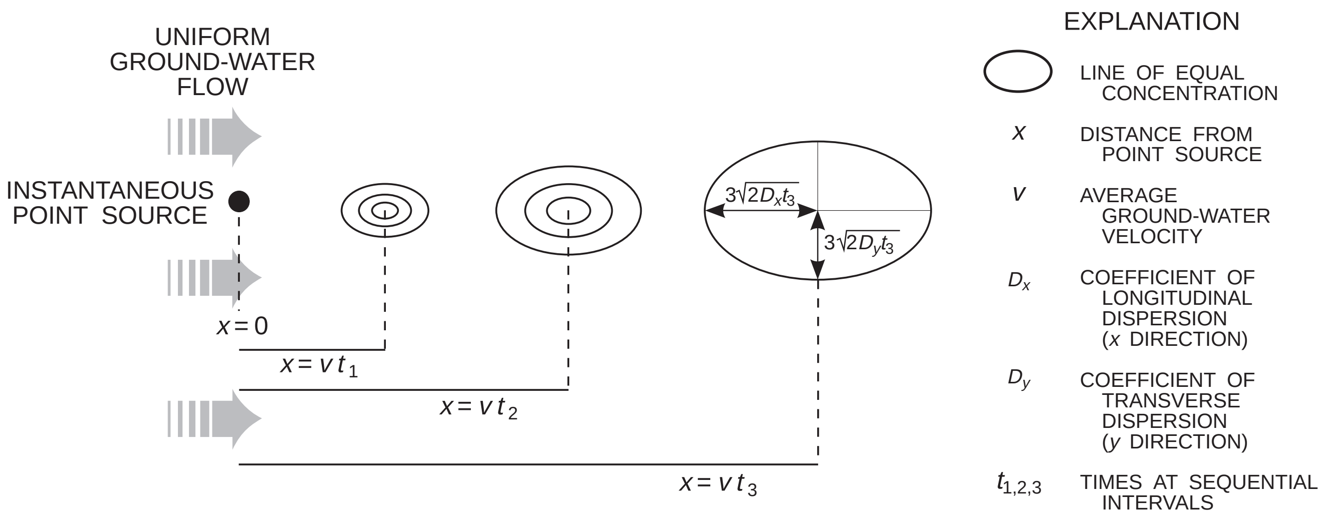


Figure 10. Map view of the plume developed from an instantaneous point source of contamination at three different times (modified from Domenico and Schwartz, 1990).

Analytical Solution to Advection-Dispersion Equation

An analytical solution to the above advection-dispersion equation was formulated by Baetsle (1969). His model provides the concentration distribution resulting from an instantaneous contaminant source originating at a point (x=0, y=0, z=0) rather than from a continuous source. Baetsle's model has been used successfully to obtain estimates of migration patterns for leachate from buried wastes and from small contaminant spills (Freeze and Cherry, 1979).

Determining the effects of advection and dispersion on the movement of EDB in ground water in Florida presents a more complex problem than that described by Baetsle. The manner in which EDB was applied results in a complex mass loading rate to ground water that would be similar to a series of instantaneous pulse-type point-source contamination problems. A new supply of EDB was injected below the ground surface every 6 months (during 1962–83) at buffer zones. At individual push-and-treat sites, treatment generally consisted of a one-time application of a large amount of EDB. Many point sources of contamination could originate as flow fingers transporting EDB from these application sites to the water table. The mass of EDB is assumed to have been carried away from these point sources in the aquifer by a steady-state uniform flow field, moving in the x direction, in a homogeneous isotropic medium. The concentration distribution of the mass of EDB at time t, as the mass is transported through the aquifer system, is given in the Baetsle (1969) model as

$$C(x,y,z,t) = \frac{M}{8(\pi t)^{3/2}(D_x D_y D_z)^{1/2}} \exp\{-((x-vt)^2/4D_x t) - (y^2/4D_y t) - (z^2/4D_z t) - k(\text{app})t\} \qquad (18)$$

where

M is the mass of contaminant (EDB) introduced at the point source and is commonly expressed as the product of the initial concentration C_o and the initial volume V_o,
D_x, D_y, and D_z are the coefficients of hydrodynamic dispersion in the x, y, and z directions from the center of gravity of the contaminant mass,
v is the velocity of EDB movement,
x, y, and z are space coordinates,
t is time, and
k (app) is the first-order, overall rate constant for EDB transformation (0.693 divided by the overall half-life).

The position of the center of gravity of the contaminant mass at time t will lie along the flow path in the x direction at coordinates

$$(x_t, y_t, z_t), \text{ where } y_t = z_t = 0 \text{ and } x_t = vt = q t/n,$$

where

v is the average linear velocity,
q is the specific discharge, and
n is porosity (equation 8).

The maximum concentration is located at the center of gravity of the contaminant plume, where $x = vt$ and $y = z = 0$. The solution to this equation can also be obtained as the product of three one-dimensional solutions (Domenico and Schwartz, 1990).

Calculated Maximum Concentrations of 1,2-Dibromoethane in Ground Water at Downgradient Sites

From equation 18, the maximum or peak concentration that occurs at the center of gravity (mass) of the plume (where $y = z = 0$ and $x = vt$), and for which spreading occurs in the direction of flow, is given by

$$C_{\max} = \frac{M\, e^{-k(\mathrm{app})t}}{8(\pi t)^{3/2}(D_x D_y D_z)^{1/2}} \quad . \qquad (19)$$

If the plume is assumed to have started as a point, then its dimensions are

$$3\sigma_x = 3(2D_x t)^{1/2};\ \ 3\sigma_y = 3(2D_y t)^{1/2};$$
$$3\sigma_z = 3(2D_z t)^{1/2}, \qquad (20)$$

where σ is the standard deviation so that $3\sigma_x$, $3\sigma_y$, and $3\sigma_z$ represent three spreading lengths of an ellipsoid within which about 99.7 percent of the mass of contaminant (EDB) is contained. A cross section of this ellipsoid in the x,y plane is shown in figure 10.

To calculate the maximum concentration expected at the center of mass of the ellipsoid at sites downgradient from the sources in each study area, the following steps were used. The surficial aquifer material was assumed to be isotropic and homogeneous. The time (t) required for transport of EDB following an injection at an application site was obtained by using the following expression (Domenico and Schwartz, 1990):

$$t = R_f x / v_w, \qquad (21)$$

where

R_f is the retardation factor and is equal to $1 + [(1-n)/n]\rho K_d$,
n is the porosity,
ρ is the density of the aquifer solids, typically 2.65 g/cm^3,
K_d is the distribution (sorption) coefficient,
x is distance between sampling point and application site, and
v_w is average velocity of ground-water flow.

The maximum sorption coefficient for EDB on organic matter is 0.58 mL/g (Chiou and others, 1979); however, a value of zero is used for K_d because there is virtually no organic carbon in the saturated aquifer material and hence no sorption of EDB. Therefore, the velocity of EDB transport is the same as the velocity of ground-water flow. The values of t for the sites located downgradient from application sites in both study areas are given in table 8.

The coefficient of hydrodynamic dispersion in the x direction was obtained by using the expression,

$$D_x = \alpha_x v_x + D^*, \qquad (22)$$

where

α_x is the dispersivity in the x direction (longitudinal),
v_x is the ground-water velocity along a flow line (Darcy's law, equation 8), and
D^* is the bulk diffusion coefficient.

Table 8. Observed maximum concentrations of 1,2-dibromoethane (EDB) in the Lake Francis and Lake Pierce study areas and maximum concentrations calculated by using the specified ground-water velocity and coefficients of hydrodynamic dispersion

[µg/L, micrograms per liter; m/d, meters per day; m^2/d, square meters per day]

Study area	EDB transport time (years)	Observed maximum EDB concentration (µg/L)	Calculated maximum EDB concentration (µg/L)	Average ground-water velocity (m/d)	Coefficients of hydrodynamic dispersion D_x (m^2/d)	D_y (m^2/d)	D_z (m^2/d)
Lake Francis	2.8	37	79	0.6	0.6	0.10	0.10
Lake Pierce	7.1	.22	.24	1.0	1.0	.10	.10

A value of 1 m was selected for α_x on the basis of natural-gradient tracer studies in a sand aquifer at Cape Cod (Garabedian, 1987). The average ground-water velocities in the Lake Francis and Lake Pierce flow systems, as discussed above, are 0.6 and 1 m/d, respectively. Measured intra-particle diffusivities of $2–7 \times 10^{-16}$ m^2/d were reported by Steinberg and others (1987) for the radial diffusion of EDB from soils into aqueous solution. These parameter values indicate that molecular diffusion is insignificant compared to dispersion; therefore, the longitudinal dispersion coefficient, D_x, can be estimated as 0.6 and 1 m^2/d for the Lake Francis and Lake Pierce flow systems, respectively. Expressions similar to equation 22 were used to estimate the transverse coefficients of hydrodynamic dispersion in the y and z directions, D_y and D_z. As a first approximation, they were estimated to be one-tenth of the coefficient of hydrodynamic dispersion in the direction of flow, D_x, based on field experiments in a sand aquifer (Sudicky, 1986). Garabedian (1987) reported that transverse dispersion coefficients were about 1/50 of longitudinal dispersion at the Cape Cod site.

The calculated and observed maximum EDB concentrations ($C_{\max}$) in ground water at selected sites downgradient from application sites are presented in table 8. These are the same sites that were used in the mass-balance model. Also included in table 8 are the coefficients of hydrodynamic dispersion (D_x, D_y, and D_z) and average ground-water velocity that provided the closest agreement between $C_{\max}$ and the observed maximum EDB concentrations during the sampling period. On the basis of the mass-balance model, a half-life of 0.65 year was used in the calculation of $C_{\max}$ for both study areas.

Good agreement (within 40 percent) between calculated and observed maximum EDB concentrations for the ground-water flow system in the Lake Francis study area was obtained by using longitudinal (D_x) and transverse coefficients of hydrodynamic dispersion (D_y and D_z) of 0.6 and 0.1 m^2/d, respectively. The calculated maximum EDB concentration is approximately twice the observed maximum EDB concentration of 37 µg/L. Better agreement between calculated and observed maximum concentrations of EDB could be obtained by using the same D_x of 0.6 m^2/d and D_y and D_z values of 0.2 m^2/d. A calculated $C_{\max}$ of 40 µg/L was obtained for the downgradient site by using the corrected mass of EDB applied at the upgradient buffer zone in November 1983. However, the use of higher values of transverse coefficients of hydrodynamic dispersion does not seem to be a realistic alternative because the ratio of the coefficients of longitudinal to transverse dispersion would be about 3.

In contrast to the Lake Francis ground-water flow system, the best agreement between calculated and observed maximum concentrations of EDB in the Lake Pierce ground-water flow system was obtained when values of D_y and D_z were 0.1 m^2/d (table 8). One would intuitively expect that the ratio of the coefficients of longitudinal to transverse dispersion would be the same in both study areas, given that both areas contain similar surficial aquifer material composed of fairly uniform sands and that dispersivity is a property of the aquifer. If values of D_y and D_z of 0.06 m^2/d (one-tenth the longitudinal dispersion coefficient, D_x) had been used to calculate $C_{\max}$ in the Lake Francis study area, values of $C_{\max}$ would have been approximately an order of magnitude higher than the observed maximum concentration of 37 µg/L.

Several possible explanations may account for the discrepancy between the calculated and observed maximum EDB concentrations in ground water in the Lake Francis study area. First, the sampling interval at well 911 (fig. 1) may not have been in the center of mass of the EDB contamination plume at the time of sampling, and the sample may have represented a more dilute part of the plume. Second, the average ground-water velocity used in the calculation of $C_{\max}$ could have been too high. If an average ground-water velocity of 0.4 m/d had been used along with the following values for the coefficients of dispersion, in square meters per day, (D_x=0.4, D_y=D_z=0.04), the calculated $C_{\max}$ would have been 30.2 µg/L. This value is in good agreement with the observed maximum concentration of EDB of 37 µg/L. If the center of mass of the EDB contamination plume was sampled at well 911, then the average ground-water velocity and coefficients of dispersion were likely within the range bracketed by the values presented. A third explanation is that differences in properties of the surficial aquifer between the two study areas may have resulted in different ratios for the coefficients of longitudinal and transverse dispersion in the two areas. Although the sands present in both areas are fairly uniform in size, differences in stratification could result from the many collapse features that are present in the Lake Pierce study area. Without additional information on the properties of the surficial aquifer in both areas, none of the above explanations could be ruled out.

The above explanations are based on the following assumptions: (1) the measured EDB concentrations in water from the sampled wells represent actual concentrations in the aquifer, (2) the half-life of 0.65 year is a reasonable estimate of the EDB degradation rate in soil and ground water, and (3) losses of EDB from the system prior to reaching the water table can be estimated from volatilization, sorption on organic matter, and nonreversible binding reactions. If any of these assumptions are not valid, then calculations of the maximum concentration would be severely affected.

The maximum concentration of EDB at the center of mass of a contaminant plume resulting from each upgradient application of EDB (1962–83) is shown in figure 11 for the selected downgradient sites in the two ground-water flow systems. The $C_{\max}$ values shown in figure 11 were calculated from equation 18 by using the

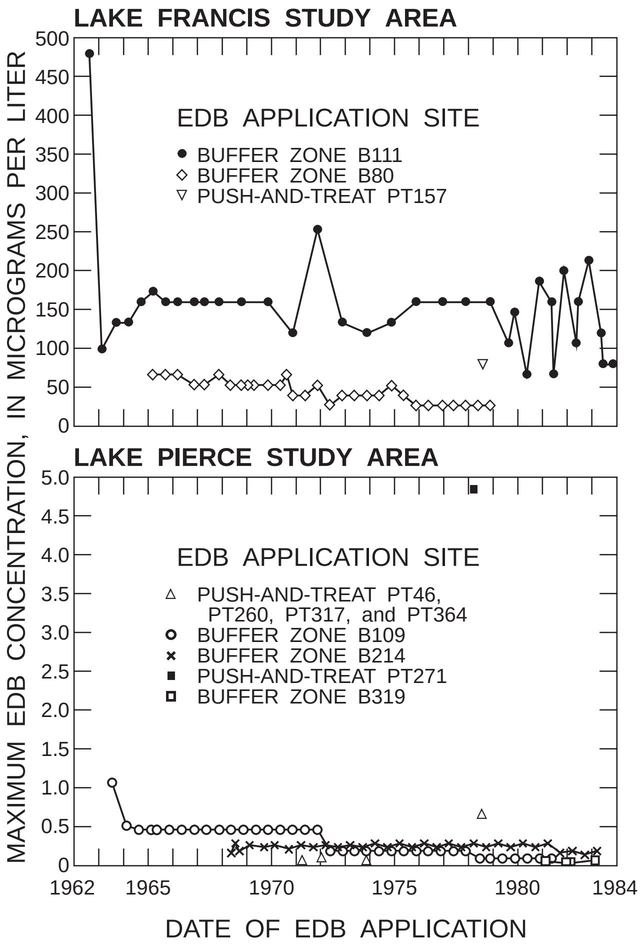


Figure 11. Calculated maximum concentration of 1,2-dibromoethane (EDB) in the center of mass of a contaminant plume in ground water resulting from EDB applications made during 1962–83 for the Lake Francis and Lake Pierce study areas.

values for average ground-water velocity, EDB transport time, and the coefficients of hydrodynamic dispersion given in table 8. These calculated maximum concentrations of EDB would result if the entire mass of each EDB application (corrected for losses due to volatilization, sorption, and nonreversible binding to soils) reached the water table at the same time. This probably did not happen. With the development of preferential flow fingers, it is likely that there were many "point" sources of EDB reaching the water table at different times following each application. Each of these point sources of EDB could result in separate contaminant plumes, with corresponding maximum concentrations at different points in time at a downgradient site.

The information presented in figure 11 can help to provide an explanation for the observed decreasing trends in EDB concentrations with time in ground water from the Lake Francis study area and the increasing trends observed in the Lake Pierce study area. By the use of a calculated average ground-water velocity of 0.6 m/d, a travel time of 2.8 years was obtained for the transport of EDB from the application sites B111 and B80 (fig. 1) to the downgradient sampling site (well 911) in the Lake Francis study area. Therefore, because samples were collected from 1983 to 1987, the peak concentration of EDB from the last application in November 1983 could have passed the sample well in 1985. By 1987, the trailing edge of the EDB contamination plume (or plumes) could have passed the sampled well, resulting in a decreasing trend in the measured concentration of EDB.

A travel time of 7.1 years was calculated for the transport of EDB from beneath the application site B109 (fig. 3) to the downgradient site (well 23901) in the Lake Pierce study area. EDB concentrations of approximately 0.30 μg/L at the sampled well could have been maintained for many years by the EDB applied periodically at buffer zones B109 and B214 (fig. 11). However, even if only a fraction of the large amount of EDB that was applied in 1978 at push-and-treat application site PT271 (fig. 3) reached the water table, the $C_{\max}$ calculated from applications of EDB at buffer site B109 would be expected to increase during the period of sampling from 1983 through 1987.

Sensitivity of Analytical Model to Input Variables

The sensitivity of the analytical model of Baetsle (1969) to the advection-dispersion equation can be measured by the amount of influence the changing of the value of an input variable has on the calculated maximum concentration of EDB in ground water ($C_{\max}$). To evaluate the sensitivity of the model (calculated values of $C_{\max}$) to variations in model parameters, data were used for the most recent application of EDB (280 kg active EDB) at buffer zone B214 (March 1983) in the Lake Pierce study area (fig. 3). The range of values for hydrologic and (bio)chemical variables used in this sensitivity analysis is considered to be representative of conditions for both study areas (table 9). Intermediate values (table 9) were assigned to all other variables when extreme values for the model parameter of interest were used to calculate $C_{\max}$. The sensitivity of the model to the input variable being evaluated was determined by comparing the model results ($C_{\max}$ values) for the two extreme values for the variable being evaluated. As with the sensitivity analyses for the mass-balance model reported above (table 7), it is assumed that there is no interdependence among variables in the model for the sensitivity analyses.

Table 9. Ranges of extreme values and intermediate values for selected input variables used in sensitivity analyses of analytical model

[D_x, coefficient of longitudinal hydrodynamic dispersion; D_y, D_z, coefficients of transverse hydrodynamic dispersion in the *y* and *z* directions; EDB, 1,2-dibromoethane]

Input variable to analytical model	Range of values tested	Intermediate value
Mean ground-water velocity (v_x), in meters per day	0.3–1.2	1.0
D_x, in square meters per day	0.3–3.0	1.0
D_y, in square meters per day	0.05–0.5	.1
D_z, in square meters per day	0.05–0.5	.1
EDB half-life, in years	0.5–5.0	.65

All values for the input variables were varied over an order of magnitude, with the exception of the longitudinal ground-water velocity (v_x). The range of values for v_x was 0.3 to 1.2 m/d, which was believed to represent the range of ground-water flow velocities in the two study areas. The model calculated maximum EDB concentration (C_{max}) in ground water was most sensitive to the EDB half-life (fig. 12), as was the case for the mass-balance model. When the value for the half-life of EDB in ground water ranged from 0.5 to 5.0 years, C_{max} ranged from 0.02 to 150 µg/L.

The sensitivity analyses revealed some interesting information about the analytical model. First, there are a number of possible combinations of the values for the longitudinal and transverse dispersion coefficients (D_x, D_y, and D_z) that result in a C_{max} that closely matches the observed maximum EDB concentration in ground water (0.22 µg/L) when the EDB half-life is assigned an intermediate value of 0.65 year. This variety of possible combinations indicates the relatively low sensitivity of the analytical model to the values for the dispersion coefficients. Second, the model is very sensitive to the EDB half-life; when a half-life of 2.0 years (three times the intermediate value) is used, the C_{max} value is 33 µg/L, which is more than two orders of magnitude greater than the observed EDB concentration in ground water. Therefore, an accurate estimate of the apparent rate constant for the transformation reactions of EDB in ground water is needed if this analytical solution is used to calculate maximum concentrations of EDB in ground water.

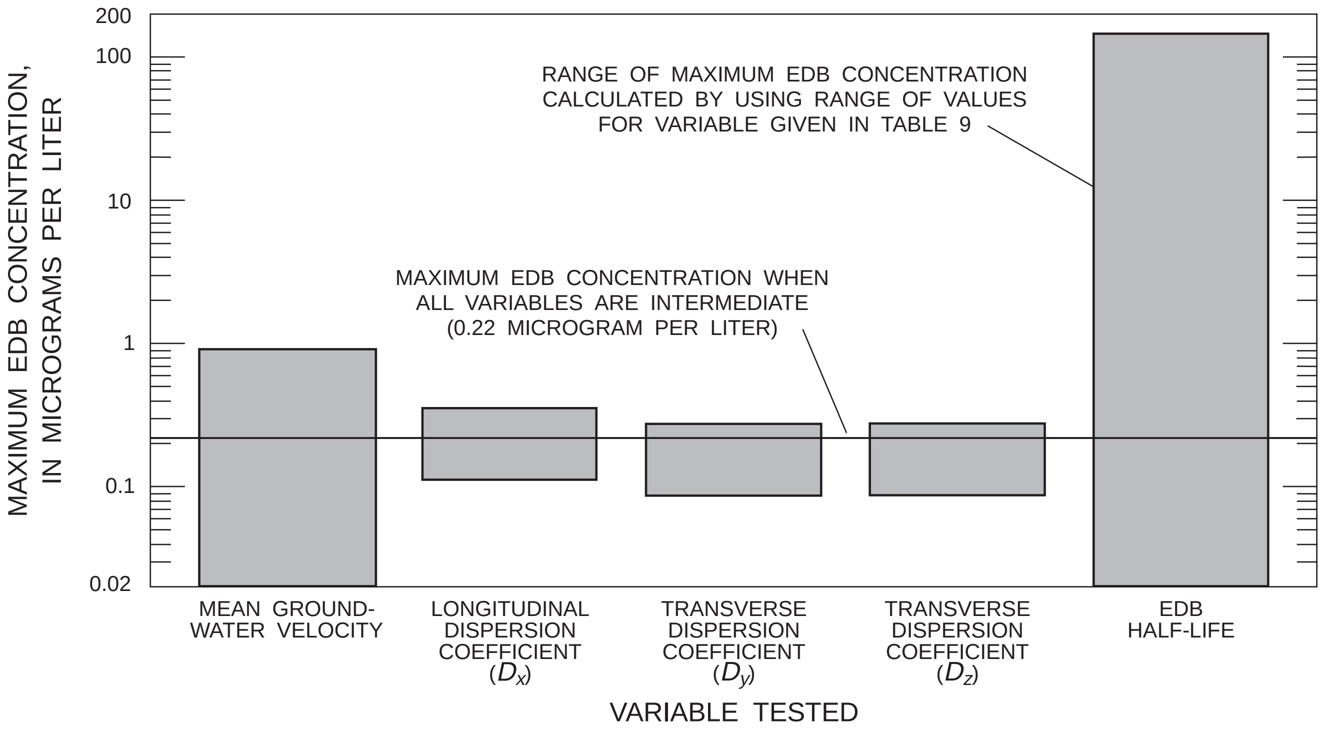


Figure 12. Range of simulated maximum concentrations of 1,2-dibromoethane (EDB) in ground water in the Lake Pierce study area based on sensitivity analyses of selected input variables for analytical model.

SUMMARY AND CONCLUSIONS

In Florida, large quantities of EDB were applied as a soil fumigant from the early 1960's to 1983 to highly permeable, sandy soils that contain little or no organic matter. As a result of the high water solubility and low vapor pressure of EDB and the low sorption capacity of the soils, the prolonged use of this compound resulted in widespread contamination of ground water in agricultural areas of Florida, especially in central Florida. Laboratory experiments have shown that EDB can degrade fairly rapidly to other products by microbial activity (3–6 months at 22 °C) and chemical reactions (1–6 years at 20 °C). Where EDB has been used as a soil fumigant, however, it has been found to persist for as many as 20 years in soils and in underlying ground water. The unexpected persistence of EDB is controlled by a complex interaction of chemical, physical, biological, and hydrological processes.

A mass-balance model was developed to estimate the maximum EDB concentration in ground water resulting from known application rates of EDB in the Lake Francis and Lake Pierce study areas of central Florida. The study areas have hydrology representative of other local ground-water flow systems in the area. The mass-balance model incorporates information on biogeochemical processes controlling the transport, transformation, and storage of EDB in soil and ground water along with the hydrological characteristics of each ground-water flow system. The following processes were quantified in the model: volatilization, diffusion of EDB vapor in soils, partitioning between aqueous and gaseous phases, sorption of EDB vapor on organic carbon and soil particles, chemical and biological transformation reactions, and nonreversible binding of EDB to soils.

As a first approximation, the following assumptions were made regarding the ground-water flow systems in the two study areas for the mass-balance model calculations: (1) advection is the only significant mass-transport process for EDB in ground water; (2) the aquifer is homogeneous, isotropic, and fully saturated; (3) steady-state flow conditions exist; and (4) transport of EDB is restricted to flow tubes where complete mixing occurs.

The maximum EDB concentration in each study area was calculated by dividing the mass of EDB remaining on a given date (as calculated from the mass-balance model) by the volume of ground water associated with a particular flow tube. The model calculations based on an EDB half-life of 0.65 year were in good agreement with the observed maximum concentrations of EDB in ground water at downgradient sites in the Lake Francis and Lake Pierce study areas. This half-life agrees well with reported values of 1 to 2 years for chemical hydrolysis reactions and 3 to 6 months for microbiological degradation reactions at 20 to 25 °C. This agreement indicates that it may be possible to estimate the maximum downgradient concentrations of EDB in ground water fairly accurately by using this mass-balance model, making some assumptions regarding the hydrologic flow system, and quantifying EDB transport, transformation, and storage processes. Even with some of the uncertainties in extrapolating laboratory rate constants to field situations involving biogeochemical processes and with an oversimplification of the hydrologic flow system, if application rates are known or can be estimated for a given contaminant, the mass-balance technique presented in this report can be a useful tool to estimate expected concentrations for a particular contaminant in ground water.

Maximum concentrations of EDB in ground water were also calculated by using an analytical solution to the three-dimensional advection-dispersion equation for an idealized situation involving instantaneous point sources of EDB entering the ground-water flow system. Coefficients of hydrodynamic dispersion in the *x* (longitudinal) direction and in the *y* and *z* (transverse) directions were estimated by using data from other field studies in ground-water systems with similar aquifer properties. The complex loading function for EDB, resulting from multiple EDB applications per year over a 20-year period and the potential for development of preferential flow fingers in the unsaturated zone, presented a difficult set of conditions to model. However, a peak or maximum concentration of EDB in ground water was calculated for each application of EDB at selected downgradient sites in each study area.

For the ground-water flow system in the Lake Francis study area, a good agreement (within 40 percent) between calculated and measured maximum EDB concentrations in the center of mass of a contaminant plume (monitored from 1983 through 1987) was obtained when an average ground-water velocity of 0.6 m/d, a coefficient of longitudinal dispersion of 0.6 m^2/d, and coefficients of transverse dispersion of 0.1 m^2/d were used in the analytical solution. In contrast, in the Lake Pierce ground-water flow system, the best agreement (within 10 percent) between calculated and measured maximum EDB concentrations in the center of mass of a contaminant plume was obtained when an average ground-water flow velocity of 1 m/d, a coefficient of longitudinal dispersion of 1 m^2/d, and coefficients of transverse dispersion of 0.1 m^2/d were used in the solution. The many sinkhole-related collapse features that are present in the Lake Pierce study area could cause aquifer properties, such as stratification of sediments, to vary between the two areas, which could account for the differences in the coefficients of dispersion. Another factor that could account for differences in the coefficients of dispersion between the two study areas is that the observed maximum concentration might not have been representative of the center of mass of the contaminant plume. The use of similar (same order of magnitude) coefficients of longitudinal and transverse dispersion in the analytical model for the two ground-water flow systems would have resulted in good agreement (within 10 percent) between calculated and observed maximum concentrations of EDB in ground water at the downgradient sites.

To adequately describe the fate in soils and ground water of EDB and other nonpolar organic compounds with similar chemical and physical properties, many complex biogeochemical processes must be understood and quantified. The nature of transport of EDB through the unsaturated zone by preferential flow fingers severely complicates the prediction of the movement and fate of EDB in ground water because these flow fingers can result in the introduction of many point sources of EDB to the water table over a period of time. Although the methods for estimating the concentrations of EDB in ground water described in this report can provide a useful tool for monitoring the transport, transformation, and storage of this compound in soil and ground water, additional data are needed to further test and refine these methods. Continued monitoring of EDB in ground water in selected wells in the two ground-water flow systems would provide data needed to further test these methods.

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