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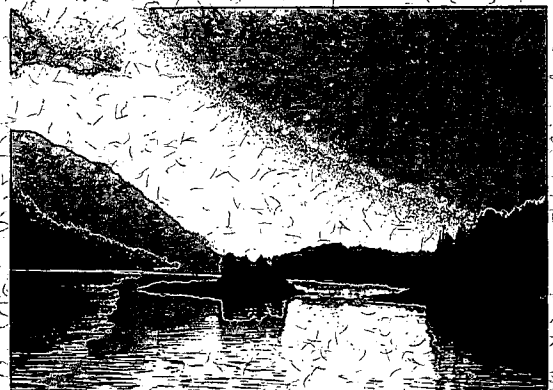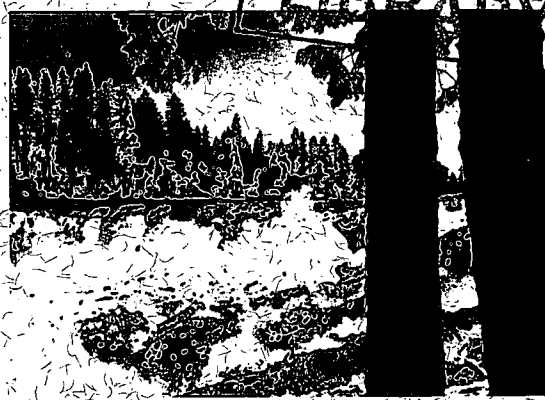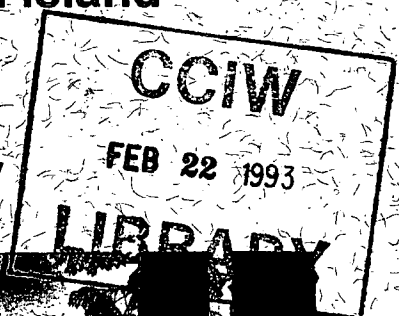SCIENTIFIC SERIES NO. 194

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The Fate and Simulation of Aldicarb in the Soil and Groundwater of Prince Edward Island

J.P. Mutch,* R.E. Jackson,† M.W. Priddle,* and D.I. Bray ‡

*National Water Research Institute
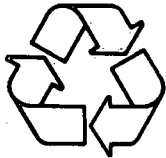Canada Centre for Inland Waters
Burlington, Ontario

† Intera Inc.
Austin, Texas

‡ Department of Civil Engineering
University of New Brunswick
Fredericton, New Brunswick

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Abstract

Aldicarb (Temik) is a systemic pesticide that has been used in the Maritimes primarily on potato crops to control aphids and the Colorado potato beetle. Aldicarb possesses the three characteristics necessary for a chemical to be considered as a serious potential threat to ground-water supplies. It is highly toxic, mobile, and persistent in the environment.

Aldicarb was first detected in domestic wells on Long Island, New York, in 1979. Aldicarb has since been detected in domestic wells in a number of U.S. states and Canadian provinces, including Prince Edward Island (PEI). Three field sites were established on PEI to investigate the processes controlling the fate of aldicarb in the local sandstones. The field sites were instrumented and hydraulically tested, and a five-year (1985–89) ground water quality monitoring program was conducted. Results indicate that aldicarb residues are persisting much longer than had been expected. Aldicarb concentrations were high (maximum = 16.4 ppb) and relatively consistent over the five-year period, despite the fact that there were only one or two pesticide applications at the field sites during this time.

Field data suggest that a relationship may exist between high levels of aldicarb and nitrate. In 10 of the 11 samples where aldicarb was found in excess of its maximum acceptable concentration (9 ppb), nitrate was also in excess of its maximum acceptable limit (10 mg/L NO_3- as N). Simulations with PHREEQE (a geochemical reaction model) suggest that the oxidation of ammonium-based fertilizer applied to the field sites may be inhibiting the degradation of the aldicarb residues.

A one-dimensional solute transport model, LEACHMP, was chosen to investigate the processes that are most influential in controlling the fate of aldicarb in the unsaturated portion of the PEI sandstone. Attempts to calibrate the model by minimizing the differences between predicted and observed field data were unsuccessful. The inability of the model to reproduce observed concentrations, and the persistent nature of the pesticide in the field suggest that there may be a storage mechanism at work that acts to retain the nondegraded pesticide, slowly releasing the pesticide to the water table over time. LEACHMP was also used in a sensitivity study. The total aldicarb concentration predicted by the model was found to be most sensitive to the degradation rate constants, the date of application, and the dispersivity value.

Résumé

L'aldicarbe (Temik) est un pesticide systémique qui a été employé dans les Maritimes, principalement dans les champs de pommes de terre pour lutter contre les pucerons et le doryphore. Il a les trois caractéristiques voulues pour constituer une menace sérieuse pour les eaux souterraines. Il est très toxique, mobile et persistant dans l'environnement.

L'aldicarbe a été décelé pour la première fois dans des puits à Long Island (New York) en 1979. Il a depuis été retrouvé dans des puits d'un certain nombre d'États américains et de provinces canadiennes, dont l'Île-du-Prince-Édouard (Î.-P.É.). Trois stations d'étude ont été établies dans l'Île-du-Prince-Édouard pour obtenir plus de données sur les processus déterminant le devenir de l'aldicarbe dans les formations de grès de la région. Ces stations ont été équipées de divers instruments, ont été soumises à des essais hydrauliques et ont fait l'objet d'un programme de surveillance de la qualité de l'eau pendant cinq ans (1985–1989). Les résultats obtenus indiquent que la persistance des résidus d'aldicarbe est beaucoup plus élevée que prévue. Les concentrations d'aldicarbe sont demeurées élevées (maximum de 16,4 ppb [parties par milliard]) et ont varié relativement peu au cours de la période d'étude, malgré le fait qu'il n'y a eu qu'un épandage ou deux de pesticide aux emplacements d'étude pendant cette période.

Les résultats semblent indiquer la possibilité d'un rapport entre les concentrations élevées d'aldicarbe et de nitrates. Dans 10 des 11 échantillons où la concentration de l'aldicarbe dépassait la concentration acceptable (9 ppb), celle des nitrates (NO_3-) dépassait aussi la limite, qui est de 10 mg/L (en N). Les simulations faites avec le modèle PHREEQE (un modèle des réactions géochimiques) indiquent que l'oxydation de l'engrais à base d'ammonium épandu à ces endroits pourrait inhiber la dégradation des résidus d'aldicarbe.

Un modèle unidimensionnel du transport des solutés (LEACHMP) a été choisi pour étudier les processus influant le plus fortement sur le devenir de l'aldicarbe dans la partie non saturée de l'aquifère dans le grès à l'Île-du-Prince-Édouard. On a essayé sans succès d'étalonner le modèle à prévoir les concentrations mesurées, ajoutée à la rémanence observée du pesticide sur le terrain, indique la possibilité d'un mécanisme de stockage qui conserverait le pesticide à l'état non dégradé et le libérerait lentement dans la nappe phréatique. Le modèle LEACHMP a également été employé pour une étude de la sensibilité. Ses prévisions pour la concentration totale d'aldicarbe se sont révélées particulièrement sensibles aux constantes pour la vitesse de dégradation, à la date d'épandage et à la valeur pour la dispersivité.

Acknowledgments

INTRODUCTION

The widespread use of agricultural chemicals poses a serious threat of contamination to groundwater supplies. The contamination of groundwater by agricultural chemicals presents additional problems not generally associated with the more obvious sources of pollution such as landfill leachate, chemical or petroleum spills, or industrial discharges. These sources are typically considered as quasi-point sources of pollution and can often be traced to a single source. It may then be possible to isolate and contain the source, eliminating any further pollution. Remedial action may also be taken to remove or lessen the effects of the pollutants that have entered an aquifer.

The areal extent to which agricultural chemicals are applied shifts these contaminant sources from quasi-point to nonpoint sources of contamination. In the event of groundwater contamination, the contaminant cannot be traced to a single source, making containment of the source and remedial action (e.g., pumping and treatment) impractical.

When faced with the possibility of groundwater contamination from nonpoint sources, the emphasis must be placed on prevention rather than on remedial action after the contamination has occurred. Prevention of groundwater contamination by agricultural chemicals requires that the physical, chemical, and biological processes involved in the fate and migration of these chemicals in the subsurface be thoroughly understood before these chemicals are applied.

It is too late to apply this reasoning to the application of the pesticide Temik (active ingredient: aldicarb) to potato fields on Prince Edward Island (PEI). Temik (aldicarb) has been applied to potato crops on Prince Edward Island since 1978 and, as a result, a number of domestic wells have been found to contain residues of the pesticide (Matheson *et al.* 1987).

A postmortem study of the fate and migration of aldicarb in the sandstone aquifer of Prince Edward Island has been undertaken by Environment Canada and the University of New Brunswick. The results of a portion of this study, along with numerical simulations of the physical and geochemical processes that control the fate of aldicarb in the subsurface, are presented in this report.

A GENERAL DESCRIPTION OF ALDICARB

A chemical must possess three characteristics before it is considered to be a serious threat to groundwater supplies. It must be highly toxic or carcinogenic, mobile, and persistent in the environment. Aldicarb possesses all three of these characterstics.

Aldicarb (2-methyl-2-[methylthio]propionaldehyde O-[methylcarbamoyl]-oxime) is the active ingredient in the systemic pesticide Temik, developed and manufactured by Union Carbide Agricultural Products Company, Inc. (now Rhone Poulenc). Temik belongs to the oxime carbamate insecticide family and is one of the most toxic pesticides registered for agricultural use today (Dierberg and Given 1986; Matheson *et al.* 1987). Aldicarb is effective as an insecticide because it acts as an inhibitor of the cholinesterase enzyme, which is necessary for the proper functioning of the nervous system (Rothschild *et al.* 1982; Moye and Miles 1988). The oral LD_{50} (rats) for aldicarb is 0.9 mg/kg (Ware 1978).

Aldicarb also has a high dermal toxicity (LD_{50} = 5 mg/kg for rabbits [Ware 1978]) and is formulated as a granular pesticide to reduce the risk of exposure during application. The granules are incorporated into the soil, where they dissolve in the soil moisture, mobilizing the active ingredient (aldicarb) in the soil water. Aldicarb is taken up by the plant through its root system and is distributed throughout the portion of the plant above ground surface. Pests are killed as they begin to ingest the plant. Systemic pesticides must possess high water solubilities to function effectively; aldicarb has a solubility of 6000 mg/L at 25°C (Carsel *et al.*1985). This property is indicative of the mobility of the pesticide

Upon dissolution, the degradation of aldicarb may follow two possible pathways: oxidation and hydrolysis. The parent pesticide (aldicarb) may be quickly oxidized to aldicarb sulfoxide (2-methyl-2-[methylsulfinyl]propionaldehyde O-[methylcarbamoyl]-oxime). This oxidation reaction generally occurs quickly,

and the parent pesticide is rarely found in sampling programs. Aldicarb sulfoxide may then be oxidized to aldicarb sulfone 2-methyl-2-[methyl-sulfonyl]propionaldehyde O[methylcarbamoyl]oxime) (Figure 1). Aldicarb sulfone is also known by the name aldoxycarb. These two transformation products (daughter products) are also highly toxic, mobile, and persistent in the environment, and, therefore, must be considered in any study of aldicarb. The solubilities and oral LD_{50} (rats) values for aldicarb sulfoxide and aldicarb sulfone are 28 000 and 7800 mg/L (Carsel et al. 1985) and 0.9 and 24 mg/kg, respectively (Jones 1986). In this report, aldicarb is abbreviated as AS, aldicarb sulfoxide as ASO, and aldicarb sulfone as ASO_2.

The second degradation pathway for aldicarb is via hydrolysis of the three aldicarb species (parent pesticide and two daughter products) to their respective oxime and nitrile species. The hydrolysis products of the three aldicarb species are much less toxic (see Figure 1) and are no longer a major environmental concern.

The rate of the detoxifying hydrolysis reaction is dependent on a number of physical and chemical conditions and will be highly variable from one location to another, and also from one time to another, at a given site (Jones 1986; Moye and Miles 1988). Lightfoot et al. (1987) found that aldicarb was most persistent in acidic soils (pH = 5–6) with low soil temperatures. Jones (1986), in summarizing the work conducted on aldicarb degradation in both the saturated and unsaturated zones, reported hydrolysis half-lives ranging from less than two weeks to more than two years.

Aldicarb, as Temik, was first registered for use in the United States in 1970. Primary target pests included nematodes, mites, and aphids, and application rates ranged from approximately 2 to 11 kg of active ingredient (a.i.) per hectare (Moye and Miles 1988). The application of aldicarb is presently restricted to emergence applications in the United States.

In Canada, aldicarb is registered for application at planting only, and a minimum 90-day application-to-harvest interval must be observed. A number of U.S. states and Canadian provinces have enacted additional legislation to govern the application of aldicarb. This legislation often requires that applicators of the pesticide be registered with a government agency. It may also restrict the amount of aldicarb that can be applied, the timing of the application, the distance from the nearest domestic well for which it can be applied, and the timing between successive applications of the pesticide.

CONTAMINATION OF GROUND WATER BY ALDICARB

Aldicarb was first detected in domestic well water on Long Island, New York, in 1979. Prior to this date, aldicarb had been widely used on the majority of the more than 8000 ha in active potato production on Long Island (Pacenka et al. 1987). A sampling program conducted in 1979 found that 76 (23%) of the 330 wells tested in the survey contained aldicarb levels in excess of the 7 ppb total toxic residue (TTR: concentration of AS +ASO +ASO_2) drinking water guideline recommended for aldicarb and established by the National Academy of Sciences for the State of New York (Moye and Miles 1988). The recommended drinking water guideline of 10 ppb set by the Environmental Protection Agency (EPA) Health Advisory has been accepted by all other U.S. states. A larger sampling program on Long Island found that 1121 (13.5%) of the 8404 wells tested were in excess of the 7 ppb recommended guideline level, with the highest detected concentration being 515 ppb (Moye and Miles 1988). The results of the sampling programs on Long Island led the manufacturer, Union Carbide, to withdraw the pesticide from the Long Island market in February 1980 (Wartenberg 1988).

Several factors may have contributed to the leaching of aldicarb to the water table on Long Island. Aldicarb was applied at high rates (5.6–7.8 kg/ha a.i.) on successive years to sandy soils with low organic matter contents and shallow water table depths. Applications occurred at planting (and also at emergence), which coincided with heavy spring rainfall, suggesting high mobility with little attenuation of the pesticide. In addition, soil temperatures, pH, and microbial activity levels were low, leading to slow degradation rates and greater persistence in the soil environment (Harkin et al. 1986).

Aldicarb contamination of groundwater has also been a problem in the Central Sands area of Wisconsin. Sixty-nine (19%) of the 363 wells tested in a survey of Wisconsin well water contained detectable levels of aldicarb, with 5% in excess of the 10 ppb guideline. The maximum concentration detected was 111 ppb (Moye and Miles 1988).

Conditions similar to those found on Long Island also exist in Wisconsin. However, the average annual precipitation is much lower in Wisconsin, and the soil and groundwater tend to be more alkaline.

HYDROLYSIS ⟶

CH₃ O
| ||
CH₃-S-C-CH=N-O-C-NH-CH₃   ⟹   CH₃-S-C-CH=NOH   ⟹   CH₃-S-C-C≡N
| | |
CH₃   CH₃   CH₃
(with CH₃ above each C)

Aldicarb
(0.9 mg/kg)

**Aldicarb
Oxime**
(2380 mg/kg)

**Aldicarb
Nitrile**
(570 mg/kg)

O CH₃ O
|| | ||
CH₃-S-C-CH=N-O-C-NH-CH₃   ⟹   CH₃-S-C-CH=NOH   ⟹   CH₃-S-C-C≡N
| | |
CH₃   CH₃   CH₃

**Aldicarb
Sulfoxide**
(0.9 mg/kg)

**Aldicarb
Sulfoxide
Oxime**
(8060 mg/kg)

**Aldicarb
Sulfoxide
Nitrile**
(4000 mg/kg)

O CH₃ O
|| | ||
CH₃-S-C-CH=N-O-C-NH-CH₃   ⟹   CH₃-S-C-CH=NOH   ⟹   CH₃-S-C-C≡N
|| | || | || |
O CH₃   O CH₃   O CH₃

**Aldicarb
Sulfone**
(24 mg/kg)

**Aldicarb
Sulfone
Oxime**
(1590 mg/kg)

**Aldicarb
Sulfone
Nitrile**
(350 mg/kg)

Total Aldicarb

Hydrolysis Products

Figure 1. Degradation pathways of aldicarb (X mg/kg - acute oral LD₅₀ [rats] (after Jones 1986).

The higher pH of the soil and groundwater favours faster degradation of aldicarb and its metabolites, and, as a result, the contamination in Wisconsin has generally been confined to shallow aquifers in areas where the pH remains low (Harkin et al. 1986).

On a larger scale, a review of sampling programs in 34 U.S. states, involving over 28 000 different potable wells, found aldicarb TTR levels above the EPA recommended concentration of 10 ppb in 2735 wells (9.7%) in 8 of the 34 states (Moye and Miles 1988).

Detection of aldicarb residues in domestic well water has also been reported in several Canadian provinces, including Prince Edward Island. Aldicarb was first used on PEI in 1978, and by 1983, it was estimated that between 5000 and 10 000 kg of active ingredient was applied to 3000 ha of potatoes annually (Matheson et al. 1987). On Prince Edward Island, aldicarb is applied to potato crops to control aphids, flea beetles, and the Colorado potato beetle. Application rates are low (1.8–2.3 kg/ha a.i.) compared to the application rates in other areas.The pesticide is applied to the soil in bands along with the seed potato at planting and is incorporated to a depth of approximately 10 cm.

The Environmental Protection Service (EPS) of Environment Canada and the PEI Department of Community and Cultural Affairs conducted a joint study to assess the presence of aldicarb in the groundwater of Prince Edward Island (Matheson et al. 1987). The study conducted between June 1983 and November 1984 consisted of the analysis of water samples from 103 domestic wells. Aldicarb residues were found in 20 (19%) of the wells tested. All levels, however, were found to be below the Canadian maximum acceptable concentration (MAC) of 9 ppb (Health and Welfare Canada 1988).The maximum concentration detected was 5.4 ppb, and the majority of the measured values were in the range of 1.3–2.2 ppb. Many of the factors contributing to the leaching of aldicarb on Long Island and in Wisconsin also apply to the situation on PEI. Although application rates were much lower than those on Long Island, the pesticide was applied at planting to soils of low pH, temperature, and organic matter content (Matheson et al. 1987).

Aldicarb use on Prince Edward Island has declined sharply in recent years as reports of aldicarb contamination of groundwater have been publicized and legislative restrictions have been imposed on its application.

OBJECTIVES OF STUDY

The objectives of this study are to investigate the fate and migration of aldicarb in the sandstone aquifer of Prince Edward Island and to determine the physical, chemical, and biological processes that are most influential in controlling the fate of the pesticide in the subsurface environment.

Specific objectives of this report are

1. to present the results of a five-year groundwater/aldicarb monitoring program at three field sites on Prince Edward Island;

2. to determine the local hydrogeological properties of the field sites;

3. to investigate the influence of the addition of ammonium fertilizer on the persistence of aldicarb with the use of an equilibrium geochemical reaction model, PHREEQE; and

4. to model processes involved in the transport and transformation of aldicarb in the unsaturated zone of the Prince Edward Island sandstone aquifer with LEACHM (Leaching Estimation And CHemistry Model) and to determine which of the processes may be most influential in the leaching of aldicarb to the water table.

A brief discussion of the major physical and chemical processes that control the fate of a pesticide in the subsurface follows in Chapter 2. This background material is provided as a review of the processes that must be considered in the study of the fate of aldicarb and in the modelling simulations that are discussed in a later chapter. A review of the results of previous studies conducted on the pesticide aldicarb is also presented to provide insight into the processes that may be most influential in controlling the fate of aldicarb for the conditions found on Prince Edward Island.

Chapter 3 details the development of the three field sites established on Prince Edward Island and discusses the methods used in, and the results obtained from, the five-year program undertaken to monitor aldicarb concentrations in the groundwater at the three field sites. The results of the groundwater monitoring program (presented in Chapter 3) provide the data base necessary for the calibration and performance testing of the unsaturated zone pesticide transport model (LEACHM), which was used to simulate the fate of aldicarb under the conditions found

in the sandstone aquifer on Prince Edward Island. A description of LEACHM and the results of the calibration and performance testing efforts are presented in Chapter 4. The influence of the oxidation of ammonium-based fertilizers on the persistence of aldicarb is also investigated in Chapter 4 with a geochemical reaction model (PHREEQE).

Theory of Transport and Transformation in the Unsaturated Zone

The transport and transformation of pesticides in the unsaturated zone are controlled by many physical, chemical, and biological processes. An adequate knowledge of these processes must be gained before any attempt is made to simulate the fate of aldicarb in the subsurface. The unsaturated zone is a three-phase system consisting of a solid (soil matrix), liquid (soil solution), and gaseous (soil atmosphere) phase, the composition and properties of which may be highly heterogeneous. Phenomena such as adsorption, surface tension, and dispersion result from the presence of the three phases and the interactions between them. At present, an understanding of the resulting phenomena is incomplete, and simplifications are often required in the mathematical representation of the system if these processes are to be simulated.

The transport and transformation of a chemical in the unsaturated zone are controlled by two main groups of processes. The first group consists of processes and mechanisms that control the transport of chemicals through the unsaturated porous media, while the second group is composed of processes that attenuate the movement of a chemical. These two groups are discussed in the following sections.

TRANSPORT OF SOLUTES IN A POROUS MEDIUM

Three mechanisms involved in the transport of solutes (e.g., pesticides) are advection (mass flow), liquid diffusion/dispersion, and vapour diffusion.

The first, advection (mass flow), considers the passive transport of dissolved solutes with the bulk flow of water. In the unsaturated zone, emphasis is placed on the vertical movement (leaching) of solutes towards the water table. Secondary processes, such as surface runoff, erosion, and volatilization, may become significant in the transport of some solutes under certain conditions. However, Donigian and Rao (1986) quote several references in concluding that runoff and erosional losses of pesticides in agricultural applications generally account for only a small percentage of the total pesticide application. This finding is supported by Carsel et al. (1988) and Jones et al. (1986).

Water flow in the unsaturated zone, as is the case with saturated flow, occurs due to the presence of a potential energy gradient. Flow occurs in the direction of the decreasing energy potential, and the rate of flow (flux) is proportional to the potential gradient.

In the unsaturated zone, the soil water is subjected to negative (subatmospheric) pressure potentials arising from the affinity of water for the surfaces of the soil particles. The negative suction potentials (ϕ) are generally reported as equivalent positive values and are referred to as matric suctions (ψ), signifying that the positive suction values actually represent negative matric potentials ($-\phi = \psi$). With this convention in mind, the flow of water in the unsaturated zone occurs from areas of low matric suction to areas of high matric suction. The flow of water occurs in both the pore spaces of those pores that remain saturated at a given matric suction and also along the hydration film covering the solid particles in those pores that are no longer saturated (Hillel 1980b).

The most significant difference between saturated and unsaturated flow is the dependence of the unsaturated hydraulic conductivity on the matric potential of the soil. As conditions change from saturated to unsaturated, the matric potential becomes important. Capillary forces holding water in the larger pores are exceeded as suction forces develop, and water in the largest, most conductive pores is the first to drain. As suction continues to develop, the capillary forces holding water in successively smaller pores are exceeded, and they in turn drain, further reducing the size of the conducting pathways and the hydraulic conductivity of the soil.

To complicate matters further, the conductivity curve (relationship between the hydraulic conductivity [K], and the matric suction [ψ]) is hysteretic, with different curves for wetting and drying fronts (Fig. 2a). The same phenomenon is observed in the retentivity curve relating matric suction (ψ) to the volumetric soil-water content (θ) (Fig. 2b). The conductivity and retentivity curves shown in Figure 2 are complex for a given soil. Simplified empirical equations describing these relationships have been developed by measuring these parameters in the laboratory or under field conditions. Hillel (1980b) reviews some of these relationships.
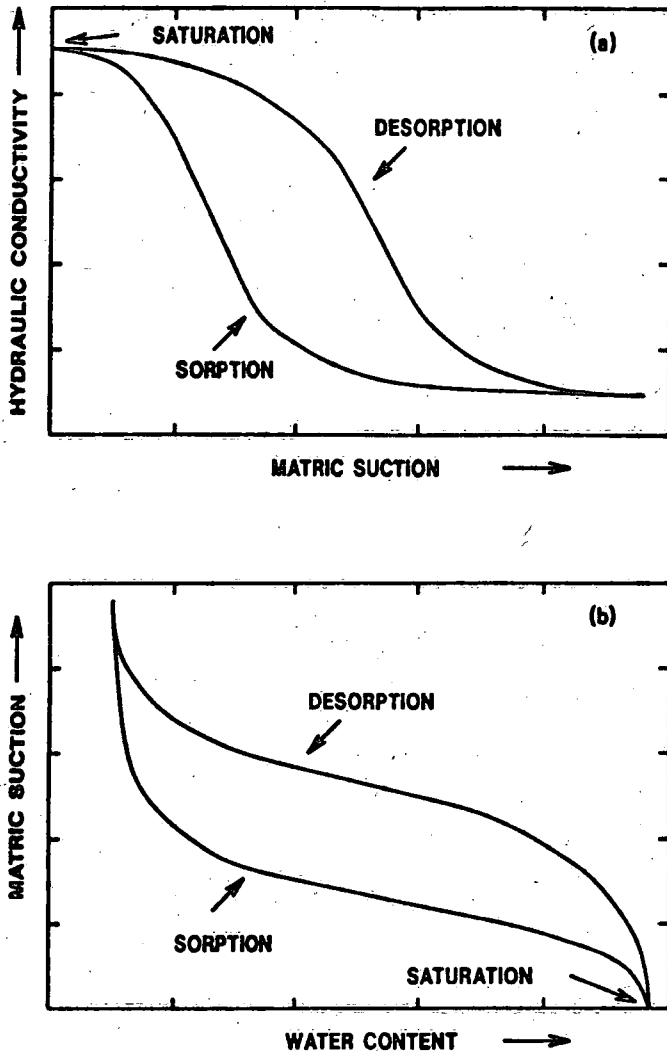
Figure 2. Typical characteristic curves for both sorption and desorption in a soil: (a) hydraulic conductivity curves and (b) retentivity curves (after Hillel 1980b)

$$\frac{\partial \theta}{\partial t} = \frac{\partial h}{\partial t} \cdot C(\theta) = \frac{\partial}{\partial z}(K(\theta) \cdot \frac{\partial H}{\partial z}) \pm S\ (z,t)\ (1)$$

where

h	= the soil-water pressure head (H-z),
$C(\theta)$	= the differential water capacity,
$K(\theta)$	= the hydraulic conductivity,
θ	= the volumetric water content,
H	= the hydraulic head,
z	= the depth,
t	= time, and
$S(z,t)$	= possible sources and sinks for water gain or loss.

The convective flux of solutes (e.g., pesticides) in the soil solution is determined by assuming that the convective flux of a solute is proportional to the solute concentration in the bulk soil solution. Diffusive and dispersive fluxes are also included to account for chemical and mechanical mixing of the solute in the solution. A more detailed discussion of the derivation of this equation can be found in Hillel (1980b). The general form of the solute transport equation is given by

$$\frac{\partial (c \cdot \theta)}{\partial t} = \frac{-\partial (q \cdot c)}{\partial z} + \frac{\partial}{\partial z}(D_d\ (\theta,v)\cdot\frac{\partial c}{\partial z})\ (2)$$

where

c	= the dissolved solute concentration,
q	= the flux across a unit area per unit time, and
$D_d(\theta,v)$	= the diffusion/dispersion coefficient, which is a function of the water content (θ) and the average linear groundwater velocity (v).

Empirical regression equations have also been proposed to facilitate the development of conductivity and retentivity relationships based on a few pertinent soil parameters (Hutson and Cass 1987; Wagenet and Hutson 1987).

Once the conductivity and retentivity relationships for a soil have been established, the advective flow equation can be developed. Hillel (1980b) and Wagenet and Hutson (1987) describe Richards' development of the convective flow equation for unsaturated water flow (now known as Richards equation), however, a detailed discussion is not presented here. The approach couples the continuity equation with Darcy's law to describe water flow in the unsaturated zone. The final form of the one-dimensional transient equation is given as

ATTENUATION PROCESSES

Additional terms must be added to equation (2) to account for the processes that attenuate the transport of the pesticide. The transport equation is given by

$$\frac{\partial (c \cdot \theta)}{\partial t} = \frac{-\partial(q \cdot c)}{\partial z} + \frac{\partial}{\partial z}(D_d\ (\theta,v)\cdot\frac{\partial c}{\partial z}) \pm S\ (3)$$

where

S = a source/sink term for the pesticide.

Attenuation can occur as the result of one or more of the following groups of processes:

1. partitioning of the solute,

2. transformation or degradation of the solute, and

3. plant processes.

Partitioning of the Solute

The presence of a chemical in a three-phase system, such as an unsaturated soil, will result in the partitioning of the solute between its liquid and solid phases and its liquid and gaseous phases.

Partitioning of a solute between its dissolved and solid phases may occur by the adsorption of the solute to the surface of soil minerals and/or organic matter present in the soil matrix. The processes involved in the adsorption of organic and inorganic solutes are varied and complex and prevent the development of a detailed mathematical description of adsorption. However, a number of simplified adsorption isotherms (including Langmuir, Freundlich, and BET) have been developed to relate the sorbed concentration to the dissolved concentration in the liquid phase (Bohn et al. 1979).

It is often assumed that the adsorption relationship for pesticides is linear, reversible, and instantaneously at equilibrium at low concentrations (Carsel et al. 1984; Jury 1986; Wagenet and Hutson 1987). The mass of pesticide sorbed, c_s, is related to the dissolved concentration, c, by a distribution (or partition) coefficient, K_D.

$$c_s = K_D \cdot c \tag{4}$$

The amount, composition, and cation exchange capacity of the clay fraction strongly affect the adsorption of inorganic cations and organic molecules with permanent positive charges (such as paraquat and diquat), but no correlation has been observed between the percent clay and the amount of nonpolar organic adsorption (Jury 1986). A positive linear relationship does appear to exist between the organic matter content of the soil and the adsorption of organics (Jury 1986). The distribution coefficient, K_D, defining the partitioning of the sorbed and dissolved states of the chemical is related to the amount of organic matter present in a soil (Karickhoff et al. 1979) and is given by

$$K_D = K_{oc} \cdot f_{oc} \tag{5}$$

where

K_{oc} = organic carbon partition coefficient, defined as the mass of pesticide sorbed per gram of organic carbon, divided by the mass of pesticide per gram of solution, and

f_{oc} = fractional organic carbon content.

Jury (1986) reviews the practical limitations of using these adsorption representations. The adsorption models are assumed to be linear. However, no single K_D value describes the partitioning between the sorbed and dissolved states over the entire range of possible concentrations. The results of experiments conducted by Karickhoff et al. (1979) on the sorption of hydrophobic compounds (water solubilities between 500 ppt and 1800 ppm) on pond and river sediments indicate that the linear adsorption isotherm is a good approximation for the observed sorption of trace concentrations of the compounds studied (aromatic and chlorinated hydrocarbons).

Adsorption isotherms are assumed to be reversible. However, most organic and many inorganic compounds exhibit a hysteretic adsorption–desorption isotherm. They provide a greater resistance to desorption than to adsorption and are, therefore, at least partially irreversible (Jury 1986). Reversible models overestimate the amount of desorption as the chemical is leached through the system. The amount of chemical actually remaining sorbed to the soil particles (and out of the aqueous phase) tends to be higher than that predicted by these adsorption models.

The third assumption is that the adsorption processes reach equilibrium instantaneously. The validity of this assumption is dependent on the kinetics of the adsorption process and on the residence time of the adsorbing solute. In some instances, the residence time may be too short to establish equilibrium, and the actual adsorption would be lower than that predicted by the models.

The solute is also partitioned between its liquid and gaseous phases. Liquid–vapour partitioning is similar to liquid–solid partitioning. The concentration of the chemical in the gaseous phase, c_g, is linearly related to the chemical concentration in the liquid phase, c, by Henry's law,

$$c_g = K_H \cdot c \tag{6}$$

where

K_H = a dimensionless partition coefficient known as Henry's constant.

Although the partitioning of the solute between its solid and liquid phase depends on the chemical involved, it is typically more important in the attenuation of a solute than is the liquid–vapour partitioning of the chemical.

Transformation and Degradation

Transformation and degradation processes encompass the chemical and biological processes that control the fate of the chemical. In this report, *transformation* refers to the alteration of a compound that is of environmental concern to a compound (a daughter product) with properties distinct from the parent compound, but which is also of environmental concern because of its high toxicity, mobility, and persistence in the environment. *Degradation* refers to the alteration of a compound where the resulting compound (degradation product) is no longer of environmental concern.

The processes controlling the transformation and degradation of a chemical are of prime importance in determining the contamination potential of a chemical, as these processes are responsible for determining the persistence of the chemical in the soil environment. Even if conditions exist that will transport a chemical to the water table, a chemical will not be considered as a potential contamination risk if it does not persist long enough to reach the water table.

Transformation and degradation processes are superimposed on the transport processes, and the contamination potential of a nonpersistent chemical is highly dependent on the timing of the rainfall and/or irrigation events in relation to the application date. If contamination is to occur, the chemicals must move quickly through the unsaturated soil profile. Sufficient mobility must be given to the chemical during its effective lifetime in the environment to move it through the soil profile. As the persistence of the chemical is increased, the timing of rainfall and irrigation events becomes less critical in determining the contamination potential of the chemical.

Transformation and degradation of a chemical may be either biologically or nonbiologically mediated. For biologically mediated processes, the chemical reactions are catalyzed by enzymes and may include biologically mediated hydrolysis and oxidation–reduction (redox) reactions. These reactions occur at higher rates in the surface and root zone layers where microbial populations are higher (Jury and Valentine 1986). The most significant factors influencing biologically mediated processes are those factors that control the

availability of the substrate and the size and activity of the microbial population.

Nonbiologically mediated processes include chemical and photochemical reactions. Chemical hydrolysis and redox reactions may occur without the aid of biological catalysts, while photochemical reactions require the adsorption of light (photons) to catalyze the reactions. Photochemical reactions are, therefore, potentially important only at or near the soil surface. Chemicals incorporated into the soil are not significantly affected by photochemical reactions (Valentine 1986).

Difficulties arise when trying to determine the degradation rate of a chemical. It is often difficult to distinguish between biotic and abiotic processes without extensive laboratory studies. Many possible pathways and fates exist for chemicals in the soil, and it is possible that the disappearance of a portion of the chemical may be misinterpreted as transformation or degradation when, in fact, the disappearance may be due to other processes (e.g., permanently bound chemical residues). In such cases, the degradation and transformation rate constants will be overestimated.

Degradation and transformation rate constants are difficult to determine, and, as a result, most mathematical representations are greatly simplified, lumping the processes together and representing them as either first-order or second-order rate reactions that account for the overall effective disappearance of the chemical.

First-order reaction equations are commonly used, even when experimental data indicate that a more complex relationship may exist. First-order reaction rates are often used because the determination of a first-order rate constant is relatively simple (Valentine and Schnoor 1986), requiring only the measurement of the chemical concentration over time.

The limitations imposed by these rate constants must be recognized. The assumptions and simplifications inherent in these rate constants prevent their use from providing anything more than empirical approximations. First-order equations, which consider only the chemical concentration, are more site specific than higher order equations, where consideration is given to other factors in addition to the chemical concentration when determining the rate constant.

If the degradation/transformation pathway includes more than one transformation or degradation

step, consideration of the individual rate constants for each step (rather than a single, lumped degradation/transformation step) will produce results that are more accurate and less site specific.

The determination of rate constants is generally performed in the laboratory, where conditions are controlled, but may vary greatly from conditions found in the field. A more accurate approximation will result if the rate constants are determined under field conditions, where they may simply represent the effective disappearance of the pesticide.

Plant Processes Influencing Chemical Transport

Processes that occur in the soil (i.e., transport, sorption, transformation, and degradation of solutes) also occur within plants (Donigian and Rao 1986). Transport mechanisms within the plant result from the same pressure gradients as those in the soil. The plants passively extract water from the soil, but actively control the transpiration loss forced by atmospheric and soil-water potential gradients. Nutrients and other chemicals dissolved in the soil water are taken up at the same time by specific and nonspecific selection processes. The extraction of water and the uptake of chemicals by the plant influence the fate of chemicals in the soil. The withdrawal of water and chemicals will affect both the water and chemical content of the soil and, hence, the convective and diffusive transport of solutes in the saturated and unsaturated zones. Hillel (1980a), however, states that the processes of water and nutrient uptake by plants are largely independent, with specific selection of chemicals by plants dominating.

A REVIEW OF PREVIOUS ALDICARB STUDIES

As stated previously, the degradation of aldicarb follows two possible pathways: hydrolysis and oxidation. In addition, the transport of the pesticide may become attenuated by either sorption and/or volatilization. The following subsections present a review of some of the major findings of previous studies on the mechanisms involved in the attenuation of aldicarb.

Degradation of Aldicarb

The hydrolysis of aldicarb and its two daughter products results in a significant decrease in the toxicity of the resulting degradation products. Zhong *et al.*

(1986) found from column studies that little difference existed between the hydrolytic degradation rates in sterilized and unsterilized soil samples for each of the three aldicarb species, thus indicating that hydrolysis of aldicarb is predominantly a chemically catalyzed reaction.

Jones (1986), in reviewing the results of field studies conducted in 16 states over a period of six years, found that the half-life of the total toxic residue (TTR) ranged from two weeks to three months in the unsaturated zone, and from three days to several years in the saturated zone.

The hydrolysis of aldicarb may be either acid or base catalyzed, and it has been found that the base hydrolysis rates are more rapid than those for acid hydrolysis (Lightfoot *et al.* 1987). For the case of alkaline hydrolysis, the first-order rate constants for the three aldicarb species were ranked in the following order: $ASO_2 > ASO >> AS$ (Miles and Delfino 1985; Moye and Miles 1988). The transition zone from alkaline to acid hydrolysis occurs in the pH range 4 to 6, with the result that within this range, the hydrolysis of aldicarb will be minimal. Hydrolysis rates vary widely with the pH of the solution and were found to be first-order with respect to the hydroxyl ion concentration for the base hydrolysis of AS, ASO, and ASO_2 (Lightfoot *et al.* 1987).

Miles and Delfino (1985) and Lightfoot *et al.* (1987) also found that hydrolysis rates are significantly dependent on the temperature. As a general rule, the rate of most chemical reactions doubles for every 10°C rise in temperature. However, in the case of aldicarb, the rate of the hydrolysis reaction increases by a factor ranging from 3 to 5 for a 10°C rise in temperature (Lightfoot *et al.* 1987). Lightfoot *et al.* (1987) developed functions relating both the acid and base hydrolysis rates of ASO and ASO_2 to the pH and temperature in distilled water. These equations are given below, where the temperatures are in degrees Kelvin and the resulting rate constants have units of days^{-1}. The equations were determined from experiments conducted over a temperature range from 14°C to 60°C and over a pH range of 3.0 to 9.0.

Base-catalyzed hydrolysis:

$$K_2 = \exp(30.00 - 14150/T + 1.793 \cdot pH) \qquad (7)$$

$$K_3 = \exp(30.68 - 14740/T + 2.081 \cdot pH) \qquad (8)$$

Acid-catalyzed hydrolysis:

$$K_2 = \exp(32.34 - 9432/T - 1.673 \cdot pH) \qquad (9)$$

$$K_3 = \exp(27.97 - 8963/T - 1.255 \cdot pH) \qquad (10)$$

where

K_2 = the rate constant for the hydrolysis of ASO to a less toxic degradation product, and

K_3 = the rate constant for the hydrolysis of ASO_2 to a less toxic degradation product.

Ou et al. (1985b) found that ASO_2 experienced a more rapid degradation in surface soils than in subsurface soils. Ou et al. (1985b) state that ASO_2 degrades much faster under anaerobic conditions than under aerobic conditions. Further work by Ou et al. (1988) indicates that both the hydrolysis and oxidation of aldicarb are significantly higher in surface soils than in subsurface soils, and that the rate constants for oxidation and hydrolysis show a distinct variability with depth.

Oxidation is the major transformation pathway for aldicarb in the shallow soil environment. Aldicarb is rapidly oxidized to ASO and is subsequently more slowly oxidized to ASO_2. The oxidation reaction does not result in the detoxification of aldicarb, as the two daughter products, ASO and ASO_2, are also highly toxic, mobile, and persistent.

Investigations into the mechanisms involved in aldicarb degradation found that the oxidation processes are primarily microbially catalyzed. The oxidation processes were almost entirely eliminated when soil samples were sterilized prior to testing (Lightfoot et al. 1987). Miles and Delfino (1985) reached similar conclusions for the oxidation of AS to ASO. Several species of common soil fungi were shown to be capable of oxidizing AS to ASO (Ou et al. 1985a). Oxidation of the aldicarb species is,

therefore, most pronounced in the surface layers of the soil. Microbial populations generally decline rapidly with depth, and the oxidation rate of the aldicarb species was also observed to decrease with depth (Ou et al. 1985a).

Sorption of Aldicarb

As a general rule, the amount of sorption of a chemical is inversely proportional to its solubility (Moye and Miles 1988). The three aldicarb species (AS, ASO, and ASO_2) all have solubilities in excess of 6000 mg/L, and would, therefore, not be expected to be strongly sorbed. Pesticides are generally most strongly sorbed to the organic matter in a soil (Moye and Miles 1988; Karickhoff 1984), and the soil distribution coefficient (K_D) defining the partitioning of the pesticide between its dissolved and sorbed states is, therefore, related to the soil organic carbon partition coefficient (K_{oc}) as is given in equation (5).

Moye and Miles (1988) present figures indicating that the K_{oc} values for AS, ASO, and ASO_2 are all low (4.3–6.5, 0.0–1.7, and 1.7–2.2, respectively), and that significant sorption of the three aldicarb species should occur only in soils with large organic matter contents. Miles and Delfino (1985), Richey et al. (1977), Zhong et al. (1986), and Lemley et al. (1988) all support the claim that the sorption of aldicarb will be significant only in highly organic soils.

Volatilization

Published values for the vapour pressure of aldicarb at 25°C range from 1.0×10^{-4} mm Hg (Dierberg and Given 1986) to 1.0×10^{-6} mm Hg (Ou et al. 1985a). All authors agree that volatilization losses of aldicarb are minor. In an experiment conducted by Supak et al. (1977), volatilization losses of AS accounted for only 0.08% to 0.2% of the AS added to the soils.

Field Investigations

SITE DESCRIPTION

Three field sites were established on Prince Edward Island (Figure 3) to investigate the fate and migration of aldicarb in the sandstone aquifer and the overlying till. The three sites are located in eastern Prince County, the main potato-growing region on PEI. The main field site is located on the southern shore of PEI, north of Hwy 10 between Tryon and Augustine Cove. This site will be referred to as the Augustine Cove (AC) site. The second site is located inland on Hwy 109 south of Kensington between Freetown and Kelvin Grove. This site will be referred to as the Mill Valley (MV) site. The third site is located on Hwy 2 between Kensington and Summerside. The site is approximately 4 km west of Kensington near the community of New Annan, and will be referred to as the New Annan (NA) site.

The selection of the field sites was based on (1) the availability of accurate information on pesticide and fertilizer application rates and dates of application, (2) good cooperation with farm managers, and (3) in the case of the Augustine Cove site, evidence of aldicarb residues in a domestic well surrounded by the field in question.

The climate on Prince Edward Island is cool and humid. The surrounding water bodies regulate the temperature, producing long and relatively mild winters with short, moderately warm summers and gradual transition periods between the two. The average total precipitation for the 30-year period 1941 to 1970 is 1059.2 mm, with an estimated water equivalent snowfall accounting for approximately one quarter of the precipitation. Mean monthly temperatures range from -6.8°C in February to 19.1°C in July (MacDougall et al. 1981). Figures 4 and 5 present a 30-year average for the total monthly precipitation and water equivalent of snowfall, and the mean monthly air temperature, respectively.

The bedrock underlying PEI consists of a sequence of Permo-Carboniferous sandstone redbeds ranging in age from Carboniferous (Upper Pennsylvanian) to middle Early Permian (van de Poll 1983).

Regionally, the bedrock is either flat-lying or dips gently to the east, northeast, or north. There has

been little structural deformation in the bedrock, however, steeply dipping joints in excess of 75° are common (van de Poll 1983; Lapcevic and Novakowski 1988).

Van de Poll (1983) has divided the redbeds into four megacycles (I to IV) of fining upward terrestrial redbeds. The bedrock beneath the Augustine Cove field site belongs to the Megacyclic Sequence II (fossils present), and the bedrock under the Mill Valley and New Annan sites belongs to the Megacyclic Sequence III (fossils absent). Sandstone is the dominant rock type underlying most of PEI, with a texture ranging from very fine (pale orange) to very coarse (dark purplish red). The coarse sandstones are often interbedded with conglomerates (mud pellet and pebble-cobble) and mudstone breccia. The fine-grained sandstones may be interbedded with siltstone or claystone. The clastic fraction (70%) is composed of 45%–60% angular to subangular quartz, 20%–30% feldspar, 10%–20% lithic fragments, 5%–10% mica, and 5% specular hematite. The matrix, the remaining 30%, is largely hematitic clay-silt with considerable carbonate content (van de Poll 1983).

The surface relief on Prince Edward Island is gently undulating with a maximum amplitude of less than 60 m, and approximately 75% of the land area is less than 45 m above sea level (MacDougall et al. 1981). The bedrock is covered by a relatively thin layer (1–5 m) of glacial deposits. The deposits are primarily basal till of local origin, and these deposits cover approximately 75% of PEI. The till is characteristically reddish brown in colour, strongly acidic, and usually compact and dense. The texture is dominantly a sandy loam, but also includes loamy sands, loams, and clay loams (MacDougall et al. 1981). The soil covering the three field sites is classified as a Charlottetown Series soil (MacDougall et al. 1981). The Charlottetown Series soil is an Orthic Humo-Ferric Podzol derived from a reddish brown, medium to strongly acid, fine, sandy loam. The surface soil is well drained, while the subsoil varies from moderately to poorly drained. The root depth for the soil varies from 50 to 75 cm, and organic matter contents are low to medium (MacDougall et al. 1981). Soil organic carbon values were determined for samples taken from the Augustine Cove and Mill Valley sites, and the value of the fraction of organic carbon,
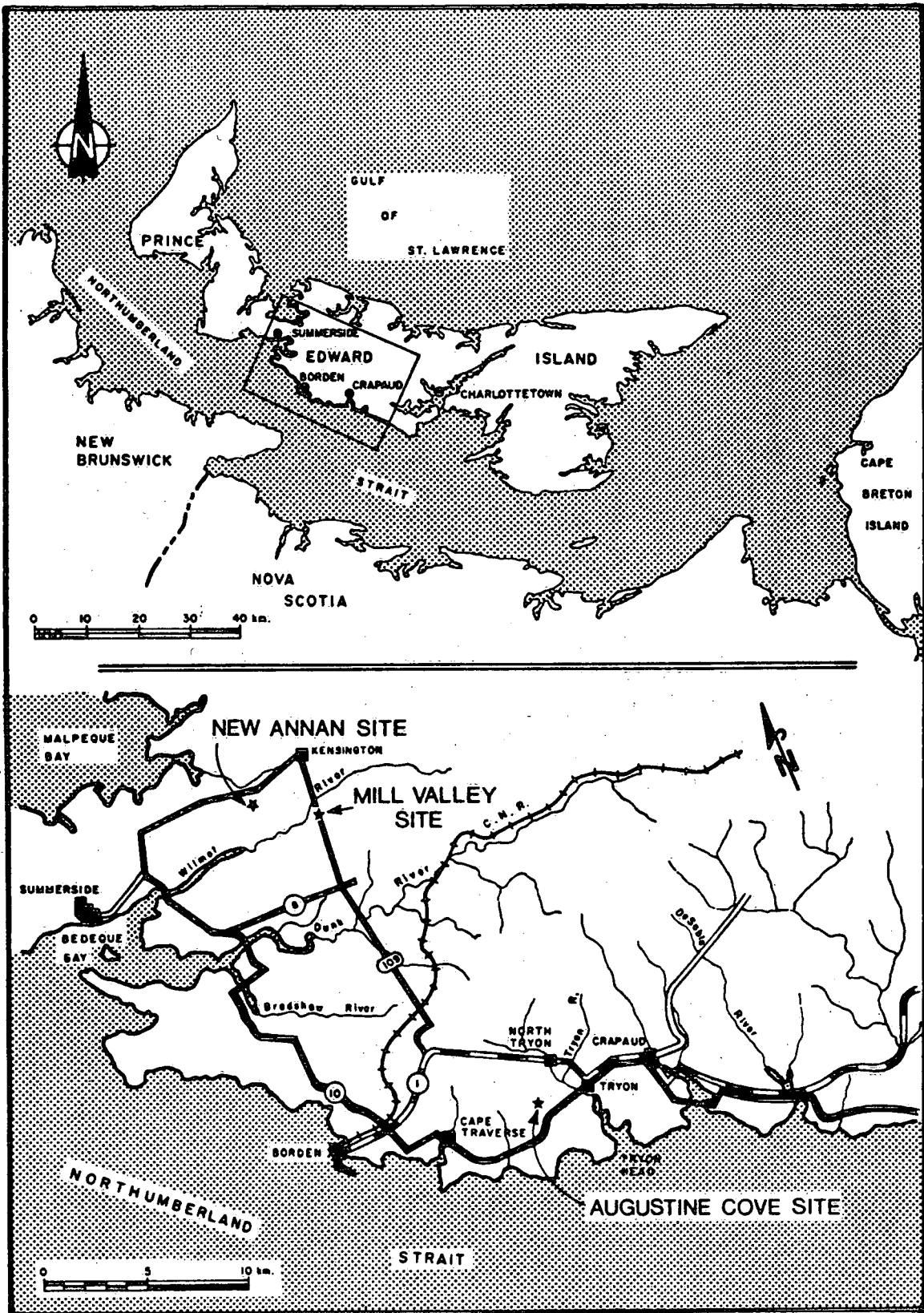
Figure 3. Location of field sites on Prince Edward Island (after Priddle *et al.* 1987).
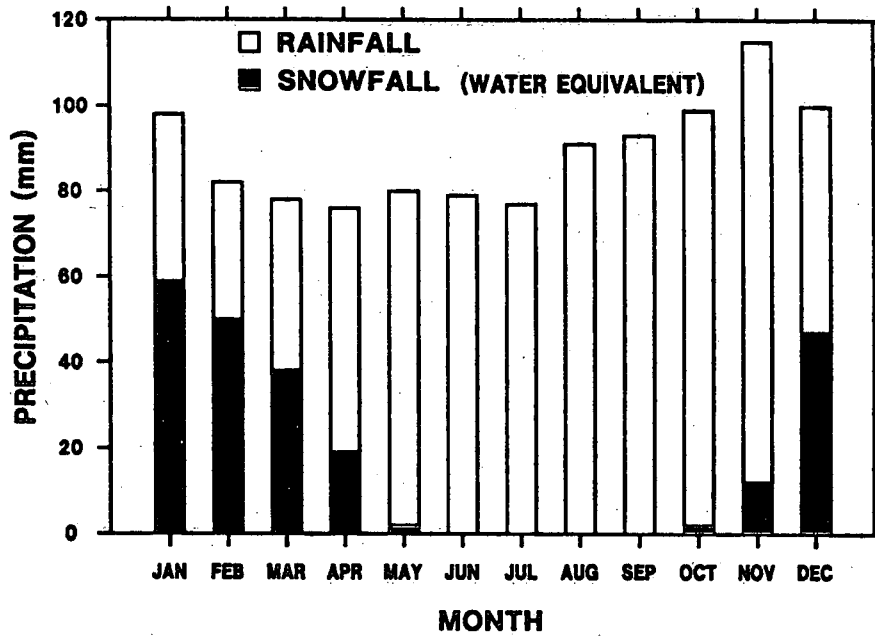
Figure 4. Mean monthly total precipitation and water equivalent snowfall for Charlottetown, PEI (1941–1971) (after MacDougall *et al.* 1981).
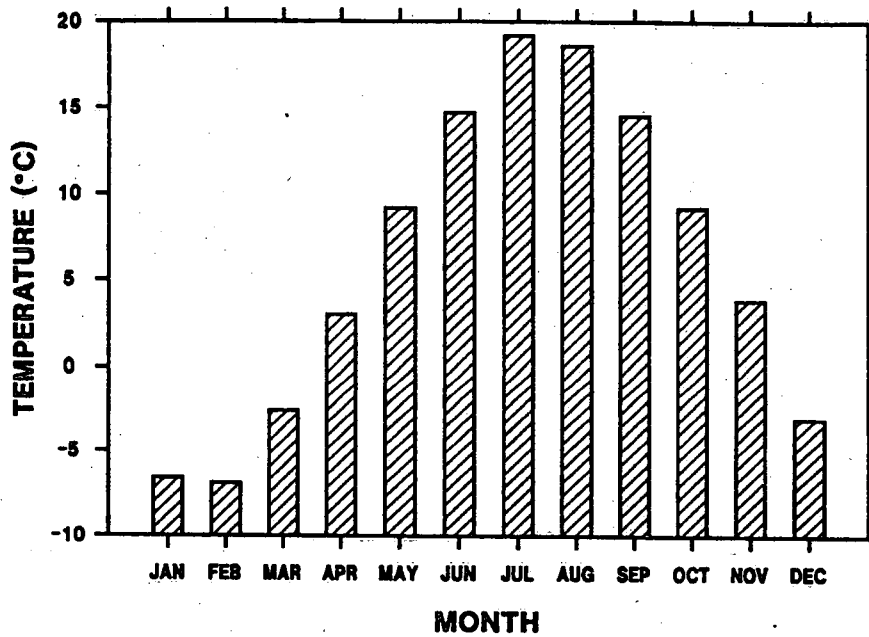
Figure 5. Mean monthly temperature for Charlottetown, PEI (1941–1971) (after MacDougall *et al.* 1981).

Table 1. Soil Parameters—Charlottetown Series Soil[*]

Profile #1

Chemical Parameters

Horizon	Depth (cm)	pH	Organic matter (%)	C.E.C. (Me/100g)	Available P (ppm)	K	Ca
Ae	0–10	4.4	0.7	4.9	8	17	130
Bf	10–20	4.1	4.4	13.9	24	33	62
Bm1	30–45	4.0	1.2	8.3	17	33	20
Bm2	45–60	4.1	ND	ND	17	32	30
Btj	60–90	4.2	ND	ND	ND	ND	ND

Hydraulic Parameters

Horizon	Depth (cm)	Water (% by volume) at tensions indicated					Hydraulic conductivity (cm/h)	Bulk density (g/cm³)
		0 bars	0.06 bars	1/3 bars	1 bars	15 bars		
Ae	0–10	59	39	34	24	3	3.2	1.32
Bf	10–20	61	44	39	34	14	11.5	1.05
Bm2	45–60	47	40	36	34	12	0.7	1.33
Btj1	60–90	35	31	28	26	19	0.4	1.62
Btj2	90–120	ND	ND	ND	ND	ND	ND	1.86

Particle Size

Horizon	Depth (cm)	Gravel (%)	Sand (%) 1–2 (mm)	0.5–1 (mm)	0.25–0.5 (mm)	0.1–0.25 (mm)	0.05–0.1 (mm)	Total	Silt (%)	Clay (%)
Ae	0–10	11	0	1	5	32	20	58	37	5
Bf	10–20	22	0	1	4	29	18	52	39	9
Bm1	30–45	25	1	2	6	27	18	54	37	9
Bm2	45–60	40	1	2	5	27	17	52	37	11
Btj1	60–90	23	1	2	5	27	18	53	34	13
Btj2	90–120	17	1	3	6	27	16	53	34	13

[*]After MacDougall et al. 1981.

C.E.C. = cation exchange capacity by $Ca(OAc)_2$ + $CaCl_2$ at pH 7.

ND = not determined.

f_{oc}, was found to be below 0.020 in all samples, with the exception of one, and declined sharply below the root zone (Table A-1, Appendix A). Table 1, taken from a survey of Prince Edward Island soils (MacDougall et al. 1981), presents further details on the Charlottetown Series soil.

Essentially all water used for domestic and industrial purposes on Prince Edward Island is supplied from these sandstone units (Francis and Gale 1988). The units are fractured with a significant fracture permeability. They also possess an intergranular porosity that averages 16% (Francis and Gale 1988). The fractures significantly influence the hydrogeological properties and, thus, generally control groundwater flow in the sandstone aquifer. The degree to which the fractures control groundwater flow depends upon the frequency, continuity, and aperture of the fractures. In a study of the Winter River basin (north-central PEI), Francis et al. (1984) state that "fractures were the primary source of permeability and that variations in their properties controlled both fluid flux and fluid velocity in the aquifer."

Fractures in the sandstone decrease in both number and aperture with depth, and, as a result, the permeability of the aquifer decreases with depth. Zones in the aquifer closest to the surface are the most productive, but are also the most readily contaminated (Francis 1989).

Carr (1969) measured the intergranular (matrix) hydraulic conductivity of the PEI sandstone in the laboratory and found hydraulic conductivities ranging from 1.0×10^{-7} m/s to 5.0×10^{-6} m/s. Hydraulic conductivity values determined for the siltstone/claystone core samples taken from the Winter River basin were less than 5.0×10^{-10} m/s. Sandstone samples from the same area had hydraulic conductivity values in the range 1×10^{-8} to 1×10^{-7} m/s (Francis 1989). The average bulk hydraulic conductivity (includes conductivity contributions from the fractures) for a

Table 2. Shallow Piezometer Installation Details

Augustine Cove			Mill Valley			New Annan		
Piez. no.	Top of pipe elev. (m)	Depth to mid-screen (m)	Piez. no.	Top of pipe elev. (m)	Depth to mid-screen (m)	Piez. no.	Top of pipe elev. (m)	Depth to mid-screen (m)
AC1	19.48	18.80	MV12	24.14	18.80	NA1A	29.74	10.97
AC2	19.37	12.70	MV13	24.14	12.70	NA1B	29.73	12.15
AC25	19.53	8.51	MV38	24.06	9.90			
AC3	17.28	16.70	MV14	20.37	18.80	NA2C	27.34	13.10
AC4	17.73	12.70	MV15N	20.36	12.28			
AC34	17.32	10.20	MV37N	19.60	9.92			
AC5	12.36	9.60	MV16	12.10	9.60	NA3	21.66	12.20
AC6	12.10	6.60	MV17	11.74	5.60			
AC35	12.53	3.50						
AC7	10.94	6.60	MV18N	11.67	4.45	NA4A	19.59	9.14
AC8	11.15	3.60	MV19	12.05	9.60	NA4B	19.63	12.20
AC36	11.25	2.90						
AC9	10.12	5.10	MV20	13.02	9.60	NA5A	18.56	8.53
AC10	11.39	3.60	MV21	12.66	5.00	NA5B	18.61	13.11
AC30	11.23	10.50						
AC22	20.02	16.90	MV39	25.00	13.20			
AC23	19.96	9.10	MV40	21.00	12.91			
AC24	19.93	5.60	MV41	13.15	6.07			
AC26	17.52	10.00						
AC27	10.14	9.50						
AC28	10.42	6.60						
AC29	9.63	2.20						
AC31	11.26	10.60						
AC32	11.37	6.50						
AC33	11.13	2.30						

series of 32 pump tests on PEI was 1.9×10^{-5} m/s (Carr 1971).

The three field sites on PEI used in this study were instrumented for geochemical and hydraulic testing. Figures 6a and 6b show a plan view and cross section of the Augustine Cove site, respectively. Five pairs of piezometers (one shallow and one deep) were originally installed at the Augustine Covesite in June 1985. An additional 15 piezometers were installed in June 1986. Six of the piezometers were shallow water table piezometers, with five of the six piezometers placed next to each of the original five pairs (nests A, B, C, E, and F in Figure 6a). The sixth (AC26) was placed by itself on the boundary of the field. The remaining piezometers were placed along the boundary of the field in nests of three (nests D, G, and H in Figure 6a). Piezometers were installed with an air rotary drill rig and were constructed of 50-mm diameter Schedule 40 PVC with either a 1.0- or 1.5-m length of #6 slot screen. The screens were packed with #2 silica sand and capped with a 1-m bentonite seal. The remainder of the hole was backfilled with native material collected during drilling (Priddle et al. 1988). Figure 7 illustrates a typical piezometer installation, and Table 2 gives further details on the piezometers.

Three deep, inclined (60°–65°) holes were drilled in 1987 to depths between 30 and 35 m below ground surface to investigate the fractured nature of the bedrock at the site. The holes (DAC1-DAC3 in Figure 6a) were cased through the overburden and were hydraulically tested and then instrumented with either a four- or five-interval multilevel sampling system (Solinst Canada Ltd., Glen Williams, Ont.). Further details on the boreholes and multilevel sampling systems are given in Table 3 and also in Lapcevic and Novakowski (1988).

Ten piezometers were installed at the Mill Valley site in June 1985 in a manner similar to that described for the piezometers at Augustine Cove. Only three piezometers were installed in 1986 because of problems with access to the field (Priddle et al. 1988). Five additional piezometers were installed with air rotary in 1987 to replace piezometers that were damaged or destroyed over the previous two years. Figures 8a and 8b show a plan view and cross section of the Mill Valley site, respectively.

Eleven piezometers were installed at the New Annan site in September 1986. Piezometers were installed with air rotary in a manner similar to the installation at the Augustine Cove site. The locations of the piezometer installations are shown in Figure 9.

Figure 6. The Augustine Cove field site showing (a) a plan view and map of the water table in metres above mean sea level and (b) a cross section (ABCD) with an equipotential map of hydraulic head in metres above mean sea level. Average of two water level measurements in June 1987 (after Priddle *et al.* 1988).
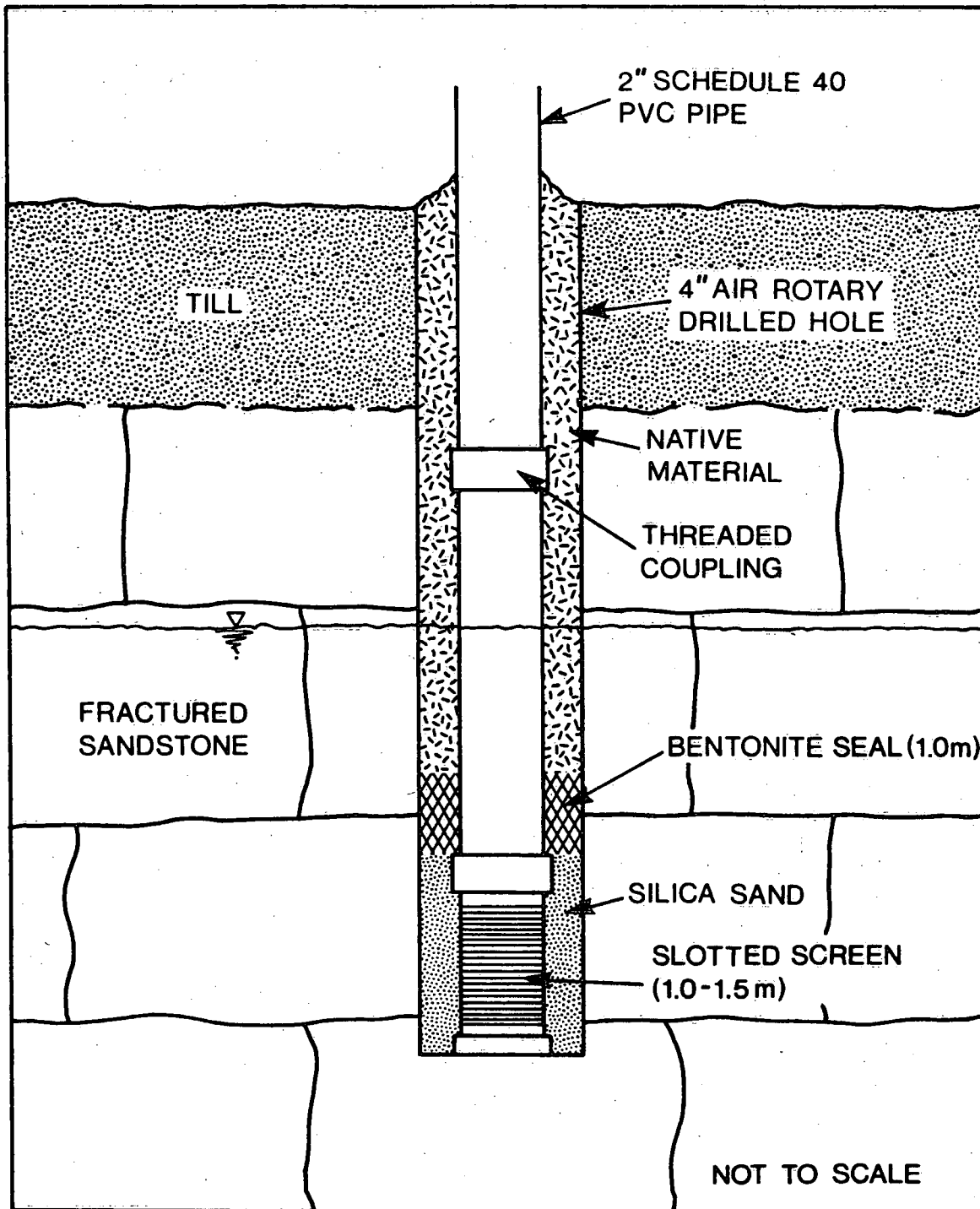
Figure 7. Schematic of a typical piezometer installation (after Priddle *et al.* 1989).

The diagram labels, from top to bottom, include:
- 2" SCHEDULE 40 PVC PIPE
- TILL
- 4" AIR ROTARY DRILLED HOLE
- NATIVE MATERIAL
- THREADED COUPLING
- FRACTURED SANDSTONE
- BENTONITE SEAL (1.0m)
- SILICA SAND
- SLOTTED SCREEN (1.0-1.5 m)
- NOT TO SCALE

Figure 8. The Mill Valley field site showing (a) a plan view and map of the water table in metres above mean sea level and (b) a cross section (JLM) with an equipotential map of hydraulic head in metres above sea level—September 1986 (after Priddle *et al.* 1988).
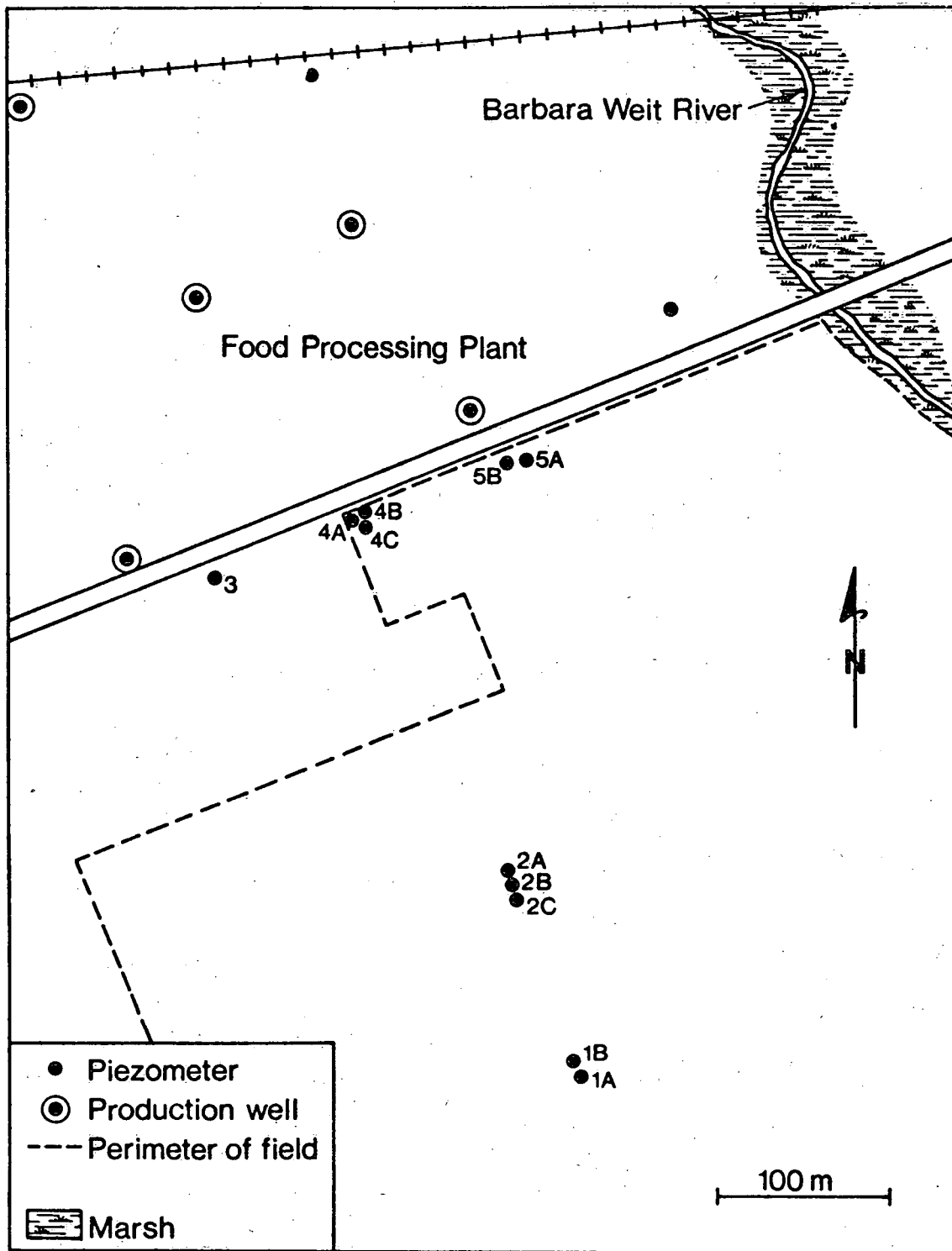
Figure 9. Plan view of the New Annan field site showing the location of piezometers.

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Table 3. Summary of Inclined Borehole Characteristics and Multiple Interval Monitoring System Setup[*]

			Borehole characteristics			
Borehole no.	Diameter (mm)	Inclination (from ground surface)	Surface elevation[1] (m)	Total length[2] (m)	Casing length (m)	Depth to bedrock[3] (m)
DAC1	76	65°	16.33	41.45	9.52	4.7
DAC2	76	60°	9.33	29.26	5.09	1.8
DAC3	76	60°	10.20	29.26	5.89	3.4

			Multiple level monitoring system			
Borehole no.	Interval no.	Depth[4] (mbgs)	Elevation[5] (masl)	Entry port (masl)	Interval length (m)	Interval volume (L)
DAC1	1	35.41 – 32.25	-15.76 – -12.90	-14.07	3.16	5.68
	2	31.27 – 27.48	-12.01 – -8.58	-9.19	3.79	6.83
	3	27.02 – 24.19	-8.16 – -5.59	-6.72	2.83	5.10
	4	23.72 – 17.50	-5.18 – 0.47	-2.35	6.23	11.22
	5	17.04 – 7.80	0.89 – 9.26	3.71	9.24	16.62
DAC2	1	26.10 – 25.33	-13.28 – -12.61	-12.71	0.77	1.39
	2	24.87 – 20.17	-12.21 – -8.13	-9.51	4.71	8.48
	3	18.62 – 14.83	-6.80 – -3.51	-4.10	3.79	6.83
	4	14.37 – 3.65	-3.12 – 6.17	-0.42	10.72	19.29
DAC3	1	26.87 – 26.09	-13.07 – -12.40	-12.50	0.77	1.39
	2	25.64 – 20.36	-12.00 – -7.43	-9.30	5.28	9.50
	3	19.38 – 16.20	-6.59 – -3.83	-5.21	3.19	5.73
	4	15.74 – 3.51	-3.43 – 7.16	4.47	12.23	22.02

[*]After Lapcevic and Novakowksi 1988.
[1]Metres above mean sea level.
[2]Metres below ground surface (down inclination of borehole).
[3]Approximate overburden-bedrock contact based on core samples (metres below ground surface).
[4]Depth in metres below ground surface (mbgs).
[5]Elevation in metres above sea level (masl) taking into account the inclination of the holes.

HYDROGEOLOGY OF FIELD SITES

Water Levels

Water levels were taken periodically during the course of the five-year groundwater quality monitoring program. The hydraulic heads for the Augustine Cove, Mill Valley, and New Annan sites are presented in Appendix B (see Tables B-1, B-2, and B-3, respectively). A continuous recording observation well was installed at the Augustine Cove site (near nest B, see Figure 6a) in 1986, and the hydrograph of the water table from the well for the period November 1986 through October 1988 is presented in Figure 10. The continuous record demonstrates the cyclic nature of the water table, with variations of up to 4 m observed over the course of one year.

The groundwater flow pattern at the Augustine Cove site appears to be more complicated than at the Mill Valley or New Annan sites. Two distinct groundwater flow patterns can be inferred from the water table contours and equipotential plots prepared for the Augustine Cove site. The first period, June 1987 (see Figures 6a and 6b), is representative of a period with a low water table. During periods with a low water table, it appears that the stream running along the eastern boundary of the field is a losing stream, and that water from the stream is directly recharging the fractured sandstone aquifer. The water table contours and hydraulic heads suggest that groundwater may be flowing through a highly fractured zone running roughly parallel to the stream and extending out of the plane of the paper in Figure 6b near piezometers AC5 and AC6 (nest C). Groundwater may then be discharged through the highly fractured zone that may extend to the southeast corner of the field.

In contrast, the groundwater flow pattern inferred from Figures 11a and 11b is representative of a period with a high water table (May 1988). During these periods, the groundwater flow pattern shows recharge occurring in the upland areas with a subsequent discharge to the stream. Using the high hydraulic gradients that can be calculated from Figure 11a, it has been estimated that ground-water velocities may be
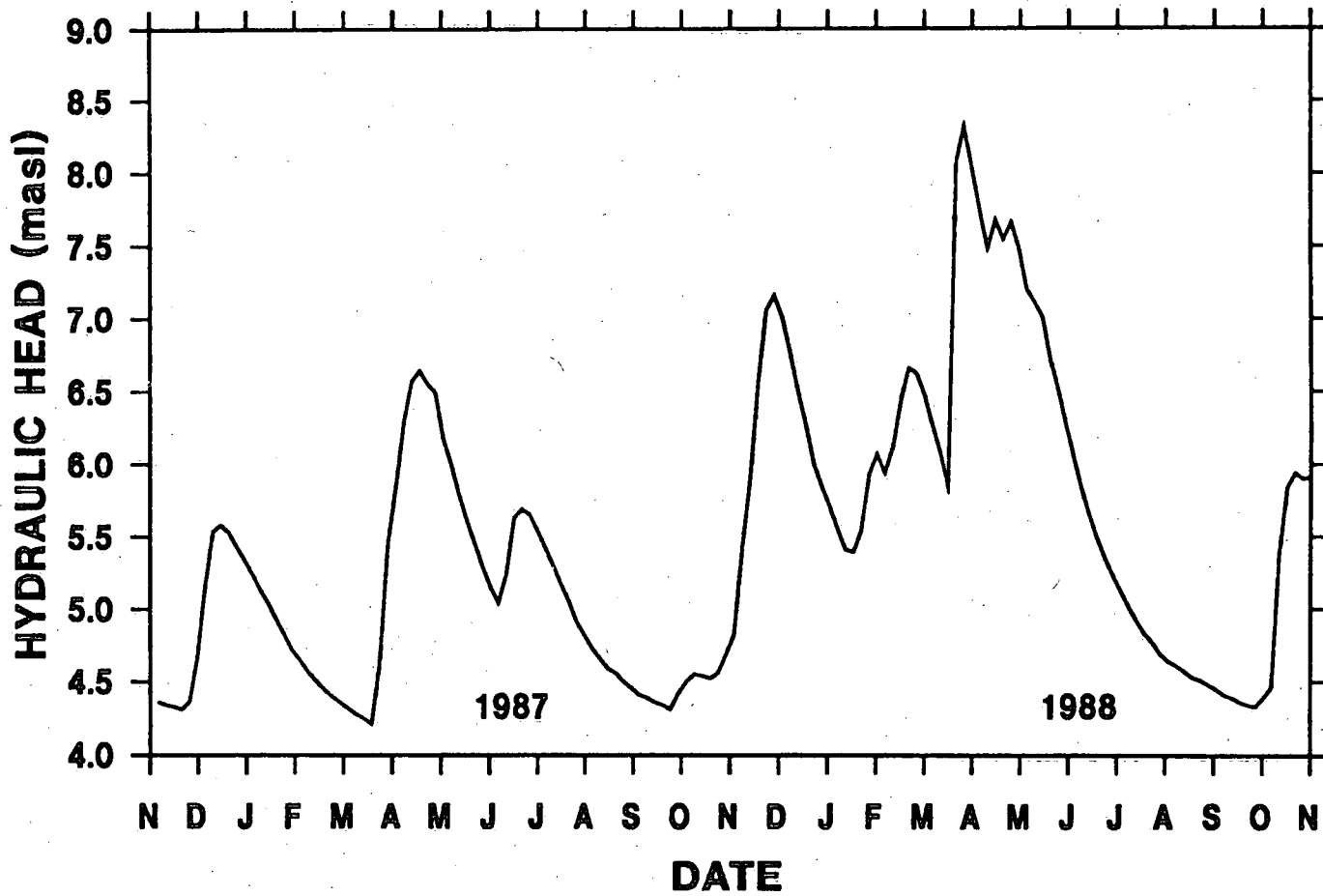
Figure 10. Hydrograph of continuous recording observation well (Augustine Cove, November 1986–November 1988).
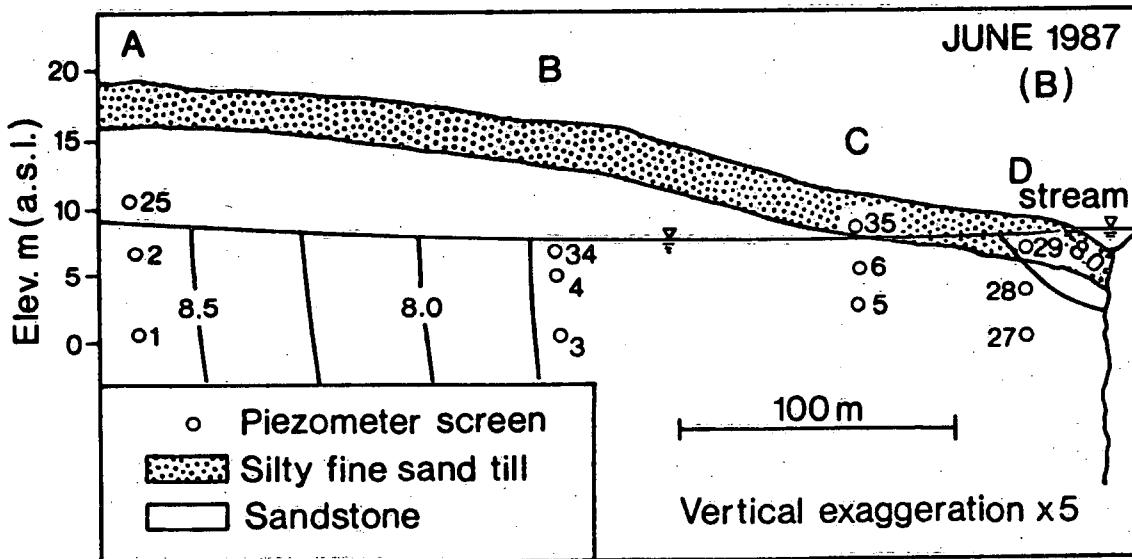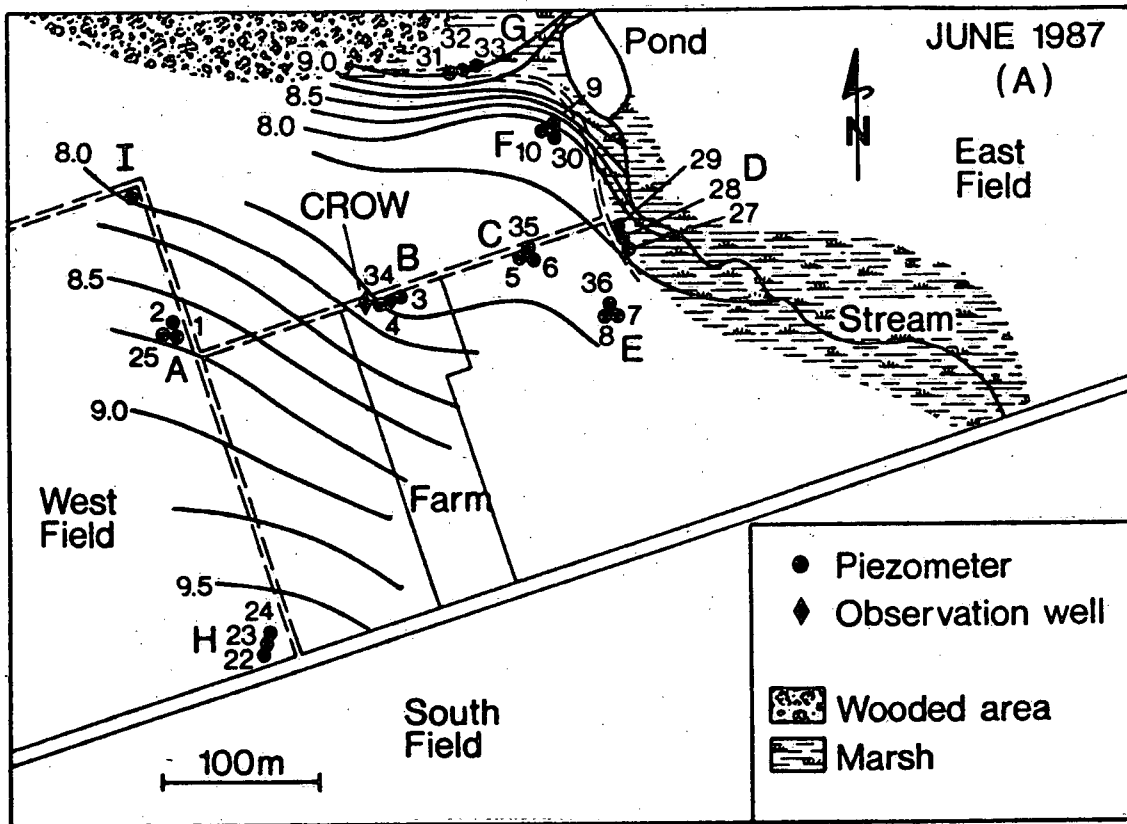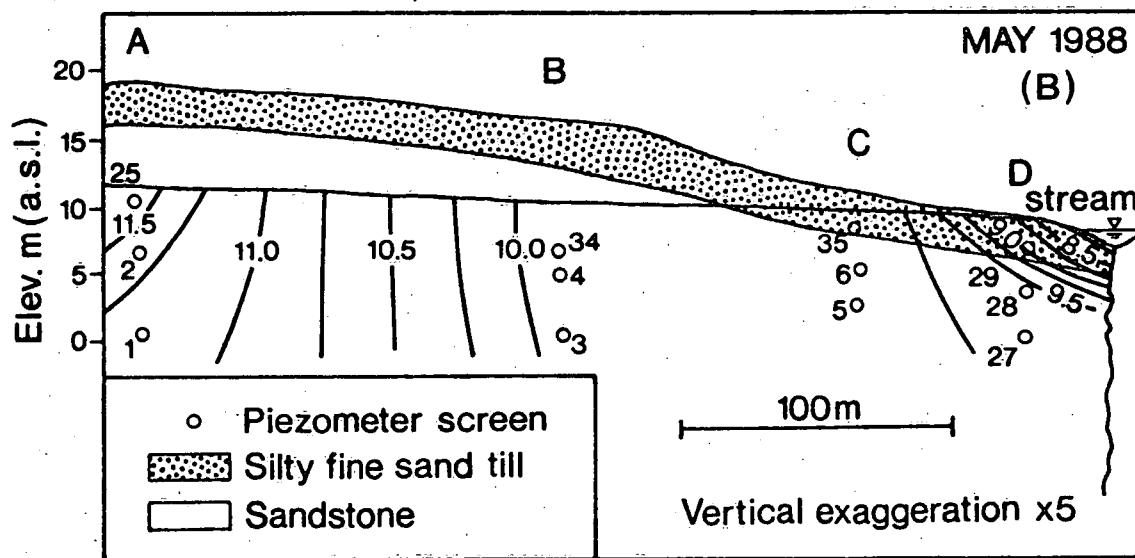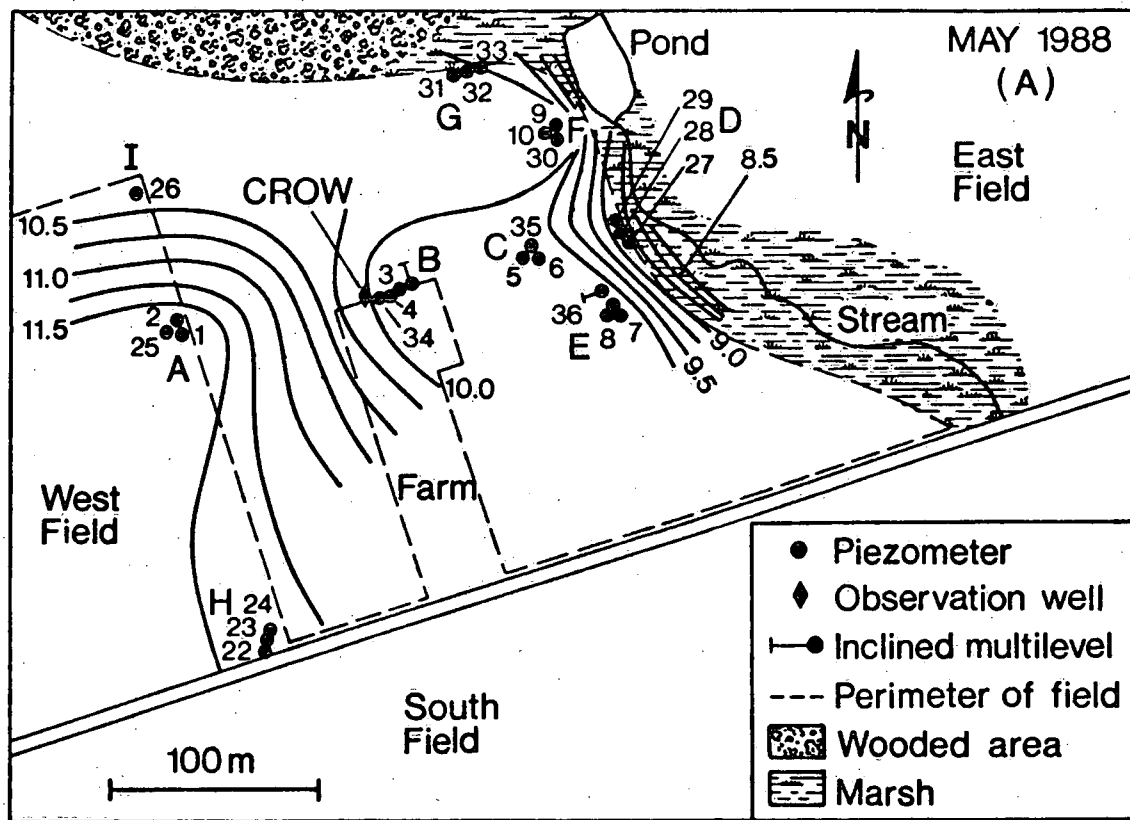
Figure 11. The Augustine Cove field site showing (a) a plan view and map of the water table in metres above mean sea level and (b) a cross section (ABCD) with an equipotential map of hydraulic head in metres above mean sea level— May 1988 (after Priddle *et al.* 1988).
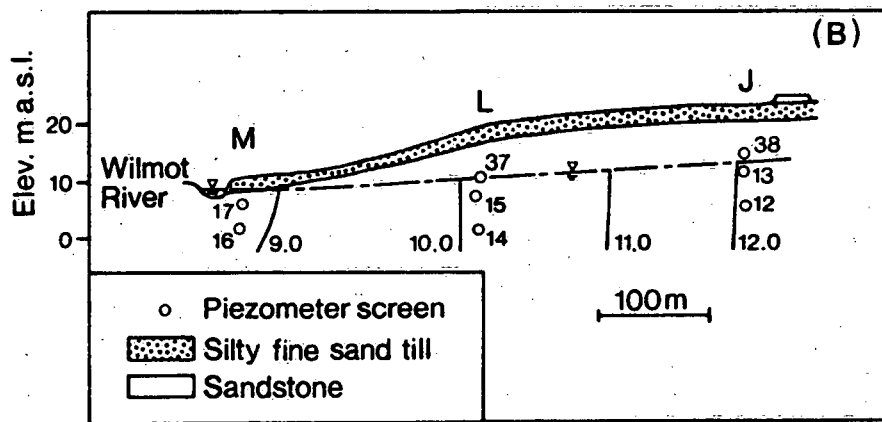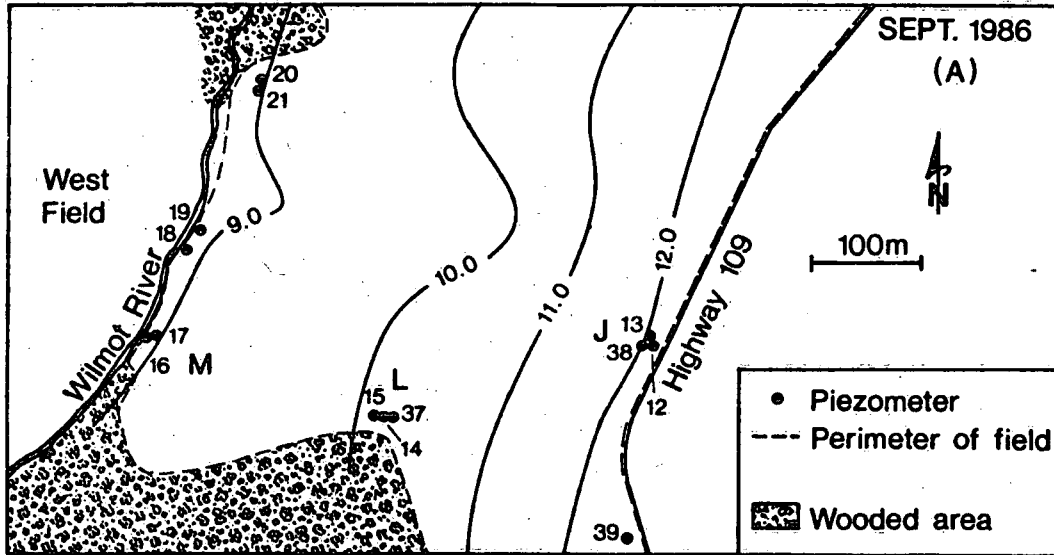
as high as 3 m per day, assuming an effective fracture porosity of 1% (Jackson et al. 1989). It appears probable that the high water table flow regime occurs each spring, but that the low water table flow regime is more representative for the remainder of the year.

Slug Tests

Slug tests were conducted in the piezometers at all three field sites. In addition, open-hole slug tests were performed on the three inclined boreholes at the Augustine Cove site prior to the instrumentation of these holes with a multilevel sampling system.

Single piezometer slug tests were performed according to the method of Patterson and Devlin (1985). Water was withdrawn from each piezometer and stored for later use in the slug tests. This avoided possible contamination of the well had water from another source been used. Water levels were allowed to return to static conditions before the slug tests were performed. A pressure transducer connected to a strip chart recorder measured the response in the piezometer to the addition of a slug of water.

Open hole slug tests were performed in the three inclined boreholes at the Augustine Cove site immediately after the drilling and development of the holes. A double-packer apparatus was used to isolate and hydraulically test intervals within the borehole. Overlapping intervals were tested over the entire length of the borehole, providing a complete profile of the transmissivities within the borehole. A more detailed description of the slug test field methods is given in Lapcevic and Novakowski (1988).

Data from slug tests performed on the shallow piezometers produced plots with steep curves, making curve matching difficult for the Cooper et al. (1967) procedure (applicable for confined conditions only). A few of the tests provided results that could be matched with the Cooper et al. (1967) type curves, but the majority of the tests were analyzed using the Hvorslev (1951) procedure (applicable for water table conditions only). Results from the shallow piezometer slug tests are presented in Appendix B (Tables B-4, B-5, and B-6 for the Augustine Cove, Mill Valley, and New Annan sites, respectively).

Hydraulic conductivities at Augustine Cove ranged from 2.4×10^{-6} m/s to 6.0×10^{-4} m/s and, in general, increased with proximity to the stream (with the exception of AC9 and AC30). It was observed that hydraulic conductivities tended to decrease with depth. Analysis of the 1986 data indicates that semiconfined conditions existed in the areas surrounding piezometers AC1, AC3, and AC27, and may be due to a semiconfining siltstone bed noticed in the borehole logs (Priddle et al. 1987). Hydraulic conductivities at the Mill Valley site ranged from 4.5×10^{-5} m/s to 1.0×10^{-3} m/s and, similar to the Augustine Cove site, tended to increase with proximity to the stream and decrease with depth. Hydraulic conductivities at the New Annan site were typically an order of magnitude smaller than at the other sites, ranging from 1.5×10^{-7} m/s to 3.1×10^{-5} m/s.

Slug tests were performed on 32 intervals in the three inclined boreholes (DAC1–DAC3) at the Augustine Cove site prior to the instrumentation of these holes. The results are summarized in Table 4.

Test results were analyzed with both Cooper et al. (1967) and Hvorslev (1951) procedures. In general, the hydraulic conductivities calculated by the two methods of analysis were within an order of magnitude of each other. Hydraulic conductivities varied from 1.0×10^{-7} m/s to 3.0×10^{-4} m/s with a geometric mean of 3.6×10^{-5} m/s (Lapcevic and Novakowski 1988). This compares favourably with the mean of 1.9×10^{-5} m/s obtained by Carr (1969) in the analysis of 32 pump tests conducted on PEI. Variations in the hydraulic conductivities can most probably be attributed to differences in lithology, fracture frequency, and aperture (Lapcevic and Novakowski 1988).

The hydraulic conductivities obtained with a packer spacing of 1.5 m, covering predominantly mudstone for the Augustine Cove mudstone units ($\approx 1 \times 10^{-6}$ m/s), differ from those obtained by Francis (1989) in siltstone and claystone core samples ($\approx 5 \times 10^{-10}$ m/s) and reported in Lapcevic and Novakowski (1988). The difference arises from the fact that the tests conducted at the Augustine Cove site were performed in situ with a packer spacing of 1.5 m, which is much larger than the lithologic features observed in the core samples (Lapcevic and Novakowski 1988).

The trend of decreasing hydraulic conductivities with depth, seen in the shallow piezometers, was not observed in the results of the slug tests in the open bore holes.

Pumping Tests

Three short-term (<6 h) pumping tests were conducted in two of the three inclined open boreholes (DAC2 and DAC3) prior to the instrumentation of these holes. A packer was positioned and inflated

Table 4. Summary of Slug Tests and Short-term Pumping Tests on the Inclined Boreholes—Augustine Cove[*]

Summary of slug tests in inclined boreholes

Borehole number	Number of tests	Hydraulic conductivity[1] (Hvorslev) (m/s)	Hydraulic conductivity[1] (Cooper) (m/s)	Storativity[1]
DAC1	12	9.5E-6	1.7E-6	6.8E-6
DAC2	10	3.2E-5	1.1E-5	9.6E-7
DAC3	10	2.7E-5	3.6E-6	4.6E-6

Pump test results in open boreholes

Test no.	Well no.	Well type	Interval[2] (masl)	Flow rate (m³/s)	Radial distance[3] (m)	Transmissivity (m²/s)	Storativity
2	DAC3	P	-7.06 – 5.10	3.9E-4	1.4E-3	2.2E-5	9.2E-2
	AC31	O	0.67	-	6.0	2.6E-4	1.2E-2
	AC32	O	4.91	-	7.2	NA	NA
3	DAC3	P	-7.66 – 15.1	3.9E-4	1.4E-3	9.4E-5	7.8E-1
	AC31	O	0.67	-	6.0	1.0E-4	2.7E-4
	AC32	O	4.91	-	7.2	3.1E-4	9.0E-3

[*]After Lapcevic and Novakowski 1988.
[1]Geometric mean.
[2]Pumped interval or evaluation of mid-screen in observation wells (screen lengths in observation wells: 1.0 –1.5 m).
[3]Radial distance from pumping well.
P = pumping well.
O = observation well.
NA = not analyzed (insufficient data).

over the least permeable zone in each hole, effectively dividing the hole into two intervals. A 1.5-HP construction pump was used to maintain a high, constant flow rate for the duration of each test. Tests were conducted with the inlet line of the construction pump positioned both above and below the low permeability zone in each borehole, and the drawdown was observed in two shallow piezometers located near the pumping well. The tests were designed to determine if these low permeability zones acted as confining layers. Drawdown in the pumping well was monitored with a pressure transducer and strip chart recorder, while the drawdown in the piezometers was measured with water level tapes.

No response was observed in the shallow piezometers (AC7 and AC8, see Figure 6a for locations) when water was pumped from below the low permeability claystone layer in DAC2, indicating that this claystone layer may be acting as a confining layer in the vicinity of DAC2 (Lapcevic and Novakowski 1988).

The results of two pumping tests conducted in DAC3 are also presented in Table 4. In Test #3, performed below the low permeability claystone layer, a response was observed in the two shallow observation piezometers (AC31 and AC33) located near DAC3, both of which were screened above the low permeability zone. This indicates that the claystone

does not act as a confining layer, and that at least in the vicinity of DAC3, the profile is representative of a single aquifer (Lapcevic and Novakowski 1988).

The response observed in AC31 and AC32 was analyzed using the Theis method for those tests where sufficient data were available. The analysis provided transmissivities in the range of 1.0×10^{-4} m²/s to 3.1×10^{-4} m²/s and a storativity range of 1.2×10^{-2} to 2.7×10^{-4} (see Table 4).

GEOCHEMISTRY OF FIELD SITES

Tests were conducted at the three field sites to investigate the geochemical properties of the aquifer. As many geochemical tests as possible were conducted in the field to define the in situ conditions and to avoid chemical changes that could occur during storage and transportation of the samples to the laboratory prior to analysis. Approximately two to three well volumes were purged from the 50-mm diameter piezometers before beginning the geochemical testing to ensure that the water being tested was representative of that found in the aquifer.

The discharge line from a Teflon/stainless steel submersible bladder pump (Well Wizard, QED Systems, Ann Arbor, Mich.) was connected directly to a flow cell containing three electrode ports. Electrodes

placed in these ports allowed certain parameters to be determined in the groundwater prior to its exposure to the atmosphere. The pumping rate through the flow cell was approximately 300 mL per minute. Measurements taken in the flow cell included pH, redox potential (E_H), specific conductance, and temperature.

A glass pH electrode was calibrated using a double buffer (pH = 4 and 7 or pH = 7 and 10) technique prior to any measurement and again after a measurement was taken (pH = 7 only). The platinum redox electrode was checked at the beginning of each sampling day by measuring the redox potential of Light's (1972) solution and ensuring that it was within an acceptable range. These two electrodes were operated from an Orion 231 pH/mV meter (Orion, Cambridge, Mass.).

Specific conductance and temperature measurements were taken with a YSI specific conductance meter (YSI Scientific, Yellow Springs, Ohio). No field calibration was required for the operation of this meter.

Ammonia (NH_3) measurements were taken with an Orion 701 meter (Orion, Cambridge, Mass.) and an NH_3 specific electrode. A 50-mL sample of ground water was collected and 0.5 mL of 10 M NaOH was added to the sample. The solution was placed on a magnetic stirrer and the NH_3 electrode was introduced into the solution. The Orion 701 meter was calibrated to a zero setting, and 5 mL of an NH_3 standard was added to the solution. The resulting change in potential of the solution was noted, and the ammonium concentration of the sample was determined from a calibration table in the NH_3 electrode manual.

A 50-mL sample was also collected, after being passed through a 0.45-m filter, to determine the alkalinity of the ground water. The initial pH of the solution was recorded, and aliquots of a standardized acid (H_2SO_4) ranging from 100 to 1000 μL were added. The pH was recorded after each addition of acid until the pH fell below 4.2. The alkalinity was then determined from a plot of pH versus millilitres of standardized acid used.

The discharge line from the submersible pump was then connected to an Orbisphere Model 2606 oxygen meter (Orbisphere Labs, Geneva, Switzerland), and the flow rate was reduced to approximately 100 mL per minute. After allowing the probe to stabilize, the dissolved oxygen level was recorded. The re-

maining geochemical tests were performed in the laboratory.

Groundwater samples were collected and analyzed for aldicarb as well as major cations and anions. Samples taken for aldicarb analysis were collected in 60-mL amber bottles. A 0.45-m filter apparatus was connected to the discharge line of the submersible pump, and the sample bottles were rinsed three times with the filtered groundwater prior to taking the sample. As a preservation technique, 100 μL of dilute phosphoric acid was added to the bottle to lower the pH of the sample to approximately 5. The bottles were filled and capped, avoiding the entrapment of any air, and stored in the dark at approximately 4°C until analysis could be performed.

Samples for the determination of major ions were collected in 500-mL sample bottles. The filter apparatus remained in place for the collection of the cation sample. This sample was acidified to approximately pH = 3 with the addition of 0.5 mL of HNO_3 to prevent possible mineral precipitation. The anion sample was neither filtered nor acidified. All bottles were rinsed three times with the ground water being sampled prior to collection of the sample.

Dedicated pumps were not used in the sampling procedure. Therefore, the Teflon/stainless steel pump was cleaned by flushing it with distilled water prior to placing it in the next well. Samples of the cleaning water, as well as field blanks for quality control, were taken, stored, and analyzed in the same manner as the aldicarb samples.

Geochemical Results

Water samples were collected and analyzed for ground-water chemistry over the five-year period (1985–1989). In situ measurements were taken for pH, E_H, specific conductance (SC), alkalinity (HCO_3^-), dissolved oxygen (DO), temperature, and ammonia (NH_3). Samples were collected and analyzed in the laboratory for NO_3^--N at all three sites and for DOC, Fe^{2+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, SiO_2, SO_4^{2-}, and Cl^- at the Augustine Cove site. The results of both the in situ measurements and laboratory analysis for the three sites can be found in Appendix C (Tables C-1, C-2, and C-3). Statistical summaries of the in situ and laboratory geochemical results for the three sites are presented in Tables 5 through 8, and the major findings are discussed below.

The pH of the groundwater at the Augustine Cove (AC) site tends to be lower than that of the Mill

Table 5. Statistical Summary of in situ Geochemical Results—Augustine Cove, 1985-1988

	pH	E_H	SC	Temp.	DO	NH_3	HCO_3^-
Number of samples	37	37	28	16	31	21	34
Mean	7.0	417 mV	330 µS	11.6°C	5.8 mg/L	0.2 mg/L	105 mg/L
Standard deviation	0.6	153 mV	75 µS	2.9°C	4.0 mg/L	0.2 mg/L	57 mg/L
Relative standard deviation	9%	37%	23%	25%	69%	100%	54%
Median	6.9	440 mV	310 µS	12.0°C	8.0 mg/L	0.1 mg/L	104 mg/L
Maximum	8.2	690 mV	490 µS	16.0°C	10.0 mg/L	0.6 mg/L	265 mg/L
Minimum	5.6	120 mV	230 µS	7.0°C	0.2 mg/L	0.0 mg/L	<1 mg/L

Table 6. Statistical Summary of Laboratory Geochemical Results—Augustine Cove, 1985-1988

	NO_3^--N	DOC	Fe^{2+}	Ca^{2+}	Mg^{2+}	Na^+	K^+	SiO_2	SO_4^{-2}	Cl^-
Number of samples	64	27	16	27	27	27	27	16	27	27
Mean	7.6 mg/L	2.4 mg/L	2.3 mg/L	43.7 mg/L	5.0 mg/L	8.7 mg/L	0.76 mg/L	12.9 mg/L	13.8 mg/L	16.0 mg/L
Standard deviation	5.4 mg/L	3.3 mg/L	3.8 mg/L	12.0 mg/L	1.9 mg/L	3.0 mg/L	0.22 mg/L	2.8 mg/L	8.9 mg/L	4.6 mg/L
Relative standard deviation	71%	138%	165%	27%	38%	34%	29%	22%	64%	29%
Median	9.0mg/L	0.9mg/L	0.0mg/L	41.0mg/L	4.5mg/L	8.1mg/L	0.81mg/L	13.3mg/L	14.7mg/L	15.5mg/L
Maximum	22.0mg/L	11.0mg/L	11.0mg/L	68.7mg/L	9.1mg/L	16.9mg/L	1.1mg/L	18.2mg/L	35.8mg/L	28.5mg/L
Minimum	0.0mg/L	0.0mg/L	0.0mg/L	26.3mg/L	2.5mg/L	<0.5mg/L	0.34mg/L	8.6mg/L	0.0mg/L	10.2mg/L

Table 7. Statistical Summary of Geochemical Results—Mill Valley, 1985-1988

	pH	E_H	SC	DO	NO_3^--N	HCO_3^-
Number of samples	15	15	10	18	27	16
Mean	7.8	505 mV	288 µS	7.5 mg/L	6.7 mg/L	120 mg/L
Standard deviation	0.3	35.5 mV	45.6 µS	2.5 mg/L	3.1 mg/L	98.1 mg/L
Relative standard deviation	4%	7%	16%	33%	46%	82%
Median	7.8	490 mV	280 µS	9.0 mg/L	6.6 mg/L	90 mg/L
Maximum	8.1	570 mV	410 µS	10.0 mg/L	13.8 mg/L	490 mg/L
Minimum	7.2	460 mV	230 µS	1.6 mg/L	<0.2 mg/L	65 mg/L

Table 8. Statistical Summary of Geochemical Results—New Annan, 1985-1988

	pH	E_H	SC	DO	NO_3^--N	HCO_3^-
Number of samples	10	10	10	10	18	10
Mean	7.6	487 mV	513 µS	6.8 mg/L	14.5 mg/L	184 mg/L
Standard deviation	0.34	35.6 mV	193 µS	2.6 mg/L	8.1 mg/L	79.3 mg/L
Relative standard deviation	4%	7%	38%	38%	56%	43%
Median	7.8	490 mV	500 µS	8.0 mg/L	14.0 mg/L	161 mg/L
Maximum	7.9	530 mV	900 µS	9.0 mg/L	30.0 mg/L	322 mg/L
Minimum	6.8	400 mV	320 µS	0.5 mg/L	0.4 mg/L	166 mg/L

Valley (MV) or New Annan (NA) sites. The respective mean pH values were 7.0, 7.8, and 7.6. No pH measurement at the Mill Valley site and only one at New Annan had values below 7.2, while samples from 15 of the 25 piezometers at the Augustine Cove site had pH levels at or below 7.2 at some point during the monitoring program. The minimum pH recorded at the Augustine Cove site was 5.6. The thickness of the fractured sandstone in the unsaturated zone is greater at the Mill Valley and New Annan sites than at the Augustine Cove site. The acidic recharge waters have a longer residence time in the thicker unsaturated zones. This allows for greater neutralization of the recharge water by the natural carbonate of the sandstone before it reaches the water table. The lowest pH values generally occurred in the shallowest piezometers at all three field sites, and although pH values varied over a wide range, a decreasing trend was noticed with distance along the flow path.

The groundwater at the three sites contained appreciable dissolved oxygen. The mean dissolved oxygen values for the three sites were 5.8 mg/L (AC), 7.5 mg/L (MV), and 6.8 mg/L (NA), while mean E_H values were 417 mV (AC), 505 mV (MV), and 487 mV (NA), indicating that highly oxygenated conditions existed at all three sites.

Exceptions to the preceding statements were noted in the Augustine Cove piezometers located near the losing stream, most notably AC5 and AC27, but also included were AC28 and AC30 to AC32 (see Figure 6a for location of these wells). The groundwater quality in these piezometers is more representative of the stream than of the groundwater from the surrounding recharge areas. Dissolved oxygen levels were below 1.0 mg/L, and E_H levels were generally below 200 mV. The ground water in all piezometers near the stream, with the exception of AC28, contained DOC levels in excess of 6.0 mg/L. They were also found to contain detectable iron (1.0–11.0 mg/L). The reducing conditions in the piezometers near the stream are consistent with what would be expected in the water from a stream that had just passed through a marsh, as is the case just upstream from the Augustine Cove field site.

The high values of DOC and iron, and the low values of dissolved oxygen in the wells closest to the stream, when compared to the conditions existing in the rest of the field, account for a large portion of the high relative standard deviations for these measurements (see Tables 5 and 6).

Bicarbonate concentrations ranged from less than 1 mg/L to 265 mg/L (AC), from 65 mg/L to 490 mg/L (MV), and from 116 mg/L to 322 mg/L (NA), with mean values of 105 mg/L (AC), 120 mg/L (MV), and 184 mg/L (NA), respectively. The concentration values for HCO_3^- given in Tables 5, 7, and 8 were determined from the alkalinity values measured by acid titration in the field. The bicarbonate concentrations reported in these tables correspond to alkalinities of 86.1 mg/L (AC), 98.9 mg/L (MV), and 150.9 mg/L (NA) as $CaCO_3$.

Alkalinities were higher at the Mill Valley and New Annan sites than at the Augustine Cove site. The greater neutralizing capacity is evident with higher pH values at these two sites. It would be expected, therefore, that aldicarb degradation would occur at a greater rate in the groundwater under the Mill Valley and New Annan sites because of the more favourable conditions that exist for the base hydrolysis of the aldicarb residues.

Nitrogen fertilizers (NH_4NO_3 and $[NH_4]_2HPO_4$) have been applied to the field sites (Table 9). In the oxygen-rich groundwater of the sites, nitrification of the applied NH_4^+ should occur according to the equation

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O. \qquad (11)$$
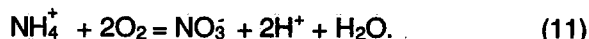
A significant portion of the ammonium applied with the seed potatoes at planting is nitrified within 60 days under the conditions found on Prince Edward Island (Priddle et al. 1988).

More nitrogen fertilizers have been applied to the New Annan and Augustine Cove sites than to the Mill Valley site over the period 1983–1989 (see Table 9). As would be expected, nitrate levels were highest at the sites with the greatest application of nitrogen fertilizers (New Annan > Augustine Cove > Mill Valley). The values for nitrate were 14.5 mg/L NO_3^--N at New Annan, 7.6 mg/L NO_3^--N at Augustine Cove, and 6.7 mg/L NO_3^--N at Mill Valley. Approximately 72% of the samples analyzed from New Annan and 40% of those from Augustine Cove had nitrate levels equal to or in excess of the drinking water standard of 10 mg/L NO_3^--N Only 15% of the Mill Valley samples were in excess of this level. The mean value for nitrate at the Augustine Cove site (Table 6) is much reduced by the absence of nitrate in the piezometers near the stream as a result of the reducing conditions that exist in these piezometers. The wide range of values of nitrate at Augustine Cove

Table 9. Fertilizer and Aldicarb Applications (1983–1989)[*]

Fertilizer (as N), pesticide (a.i.) and lime applications	Year	Amount applied (kg/ha)		
		Augustine Cove	Mill Valley	New Annan
Ammonium nitrate	1989	-	206	-
Ammonium nitrate	1988	-	206	206
Ammonium nitrate	1987	52	-	-
Aldicarb	1986	2.0	2.0	-
Ammonium nitrate		210	206	-
Urea		-	82	-
Aldicarb	1985	-	2.2	-
Ammonium nitrate		-	27	-
Limestone		2128	-	-
Dolomite		112	-	-
Ammonium nitrate	1984	-	27	206
Diammonium phosphate		54	-	-
Aldicarb	1983	2.0	-	2.0
Ammonium nitrate		190	27	206
Urea		5.9	-	-

[*]After Priddle et al. 1989.
Ammonium nitrate - NH_4NO_3
Diammonium phosphate - $(NH_4)_2HPO_4$
Dolomite - $CaMg(CO_3)_2$
Limestone - $CaCO_3$
Urea - $CO(NH_2)_2$
a.i. - active ingredient

is reflected in the high relative standard deviation as seen in Table 6.

The production of protons (H^+) due to the oxidation of NH_4^+ lowers the pH of the water and inhibits the degradation of aldicarb. Neglecting any geochemical neutralizing reactions that may occur to lessen the impact of nitrification on the pH of the groundwater, Priddle et al. (1987) calculated that the consumption of 8 mg/L O_2 would nitrify only 10% of the fertilizer applied to Augustine Cove and would lower the pH of the groundwater to 3.6 in a worst-case scenario.

It is evident that the persistence of aldicarb residues may be affected to a significant degree by the nitrification of ammonium-based fertilizers due to the effect of this process on the pH of the water. The results of a five-year aldicarb residue monitoring program and the correlation between the aldicarb and nitrate residues are presented in the following subsection.

Aldicarb Residue Concentrations and Speciation

Aldicarb was applied to the Augustine Cove site in 1983 and 1986, to the Mill Valley site in 1985 and 1986, and to the New Annan site in 1983. The pesticide, fertilizer, and lime application rates for the

field sites are presented in Table 9. Tables C-4, C-5, and C-6 in Appendix C contain the results of the five-year aldicarb monitoring program. Total aldicarb ($ASO + ASO_2$) concentrations are presented in these tables along with the ratio of aldicarb sulfone to the total aldicarb concentration (ASO_2/total aldicarb), which defines the speciation of the aldicarb residues.

For discussion purposes, the conditions found at the Augustine Cove site are represented graphically by the results from four piezometers (AC4, AC6, AC7, and AC9). The conditions existing at the Mill Valley site are characterized by the results from three piezometers (MV14, MV17, and MV21) and from a spring that discharges to the stream at the bottom of the field. The location of the piezometers and the spring are shown in Figures 6a and 8a. Only three sets of aldicarb samples were taken for the New Annan site, so no definite trends can be established for this site. The aldicarb and nitrate results for New Annan are not plotted, but are presented in Tables C-3 and C-6 in Appendix C.

Total aldicarb concentrations for the Augustine Cove and Mill Valley sites are presented in Figures 12 and 13. The parent aldicarb is quickly oxidized to ASO and is rarely detected in groundwater. As a result, total aldicarb is taken as the sum of ASO and ASO_2. The concentrations of total aldicarb in the groundwater at the Augustine Cove site were higher than at Mill Valley, despite the fact that aldicarb was applied

to the Mill Valley site on two successive years (1985 and 1986). The greater depth to the water table and the more alkaline conditions (and higher pH values) at the Mill Valley site are the most probable reasons for the lower concentrations of total aldicarb at Mill Valley.

The effect of the depth to the water table on the total aldicarb concentration is also evident within the Augustine Cove field site itself. Concentrations of aldicarb in the upland recharge areas (i.e., AC4), with an unsaturated zone depth of approximately 10 m, were lower than those in the lowland discharge areas (i.e., AC6, AC7, and AC9). The shallowest piezometer (AC9) showed the highest concentration.

The pronounced drop that appears in the concentration of total aldicarb at the Augustine Cove site (Figure 12) after the first sampling point is most probably due to the infiltration of highly contaminated shallow ground water during the drilling of the boreholes, followed by a rapid flushing of this water and a return to concentration levels more characteristic of the depth of each piezometer. This process is not evident at the Mill Valley site (Figure 13) and may be due to the short period of time between the pesticide application and the installation of the piezometers. Most of the pesticide would still be held in the upper portions of the unsaturated zone and would not have had sufficient time to contaminate the shallow ground water to any extent. Any aldicarb that was present in the infiltrating shallow ground water may have been diluted to a sufficient extent on mixing with the deeper ground water so that the aldicarb concentration peak was not detectable.

The daughter products, ASO and ASO_2, are highly mobile and are considered to be relatively nonretarding (retardation factors of 1.25 and 1.26 for ASO and ASO_2, respectively), yet they show a remarkable persistence. The concentrations at Augustine Cove remained relatively constant over the five-year sampling period despite the fact that only one pesticide application occurred (mid-May 1986) during this period. Slightly more variability was evident at the Mill Valley site, where two pesticide applications occurred on successive years (1985 and 1986).

With the exception of MV17 and the spring, little evidence of contamination existed at the Mill Valley site prior to sampling in May 1988. The concentration of 7.7 µg/L of total aldicarb found in MV17 in June/July 1987 was the maximum concentration found in any piezometer at the Mill Valley site during any sampling

period prior to May 1988 by a factor of more than two. Concentrations were also relatively high in the spring at the bottom of the field. Based on limited data, it is inferred that the spring maintained an average concentration of 4.4 µg/L total aldicarb prior to May 1988. The fracture system supplying the spring may be acting in a manner similar to that of a tile drain under portions of the Mill Valley site. The fracture system may be collecting infiltrating water and transporting it laterally with discharge occurring at the spring rather than allowing deeper infiltration of the recharge water.

The concentrations of total aldicarb in May 1988 were the highest of any sampling date during the monitoring program despite the fact that it had been two years since the last application of aldicarb to either field. It appears that aldicarb is being stored in the unsaturated zone of the two fields, possibly via matrix diffusion, and that during periods of high recharge, large amounts of the pesticide are being carried to the water table. At other times in the year when the recharge is greatly reduced, a smaller, steadier flux of pesticide is supplied from the unsaturated zone to the water table.

At Mill Valley, it is possible that during spring recharge the capacity of the fracture system supplying the spring is greatly exceeded. The high concentrations of pesticide being leached from the unsaturated zone during spring melt may follow discharge pathways (in addition to those located near the spring and MV17) that are not normally activated during the rest of the year. Evidence of this is indicated by the increase in total aldicarb concentrations for all piezometers in the discharge area in May 1988.

Aldicarb concentrations were also determined from unsaturated soil samples taken from Augustine Cove in 1988 (Table C-7, Appendix C). Aldicarb residues were found in only one-third of the samples taken in the unsaturated zone, and concentrations were low (all ≤ 1 µg/L). Little aldicarb appears to remain in the first 3 m. Seven samples were collected at differing depths within this 3-m interval, and only one contained aldicarb residues (0.5 µg/kg).

The number of samples taken from the unsaturated zone in this study was small, and the observations noted above must be viewed with this in mind. A more extensive sampling of the unsaturated zone is required before any concrete conclusions can be drawn about the presence of aldicarb residues in the unsaturated zone. This would include sampling the unsaturated fractured sandstone.
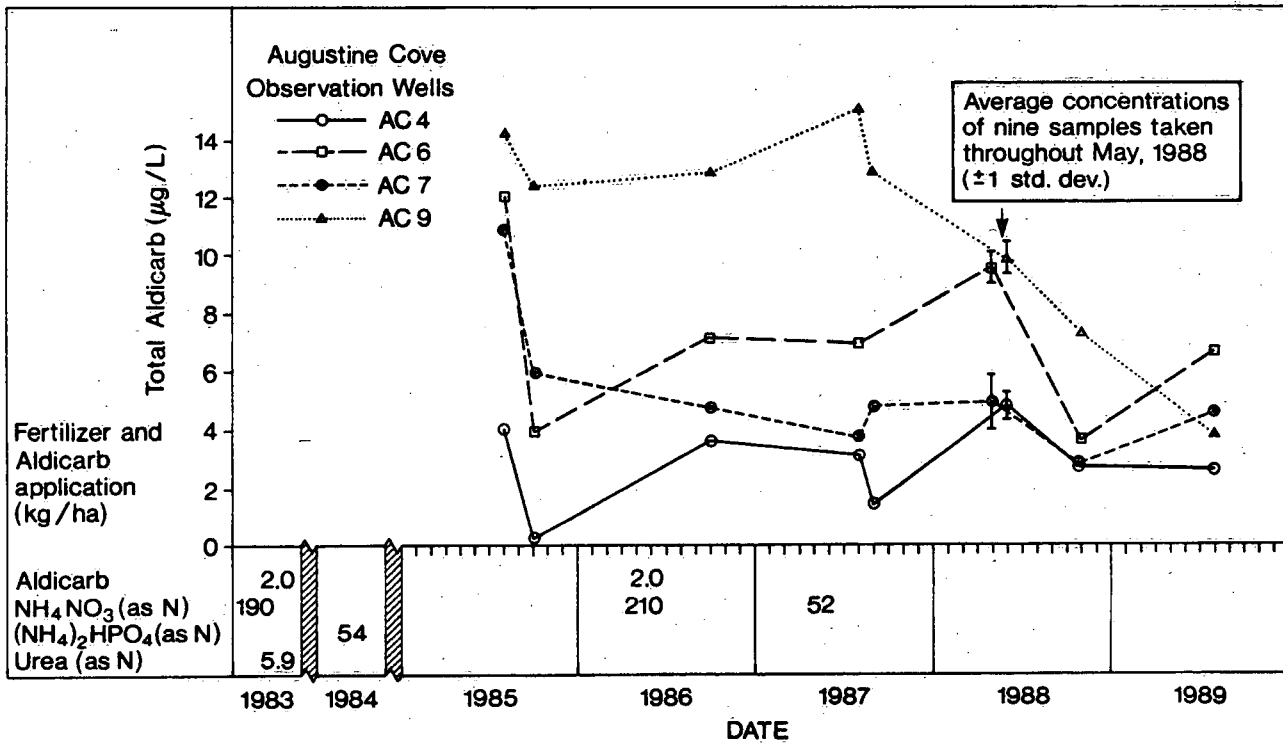
Figure 12. Total aldicarb concentrations for four observation wells at Augustine Cove (July 1985–July 1989). Pesticide and fertilizer applications are shown along the bottom of the figure.
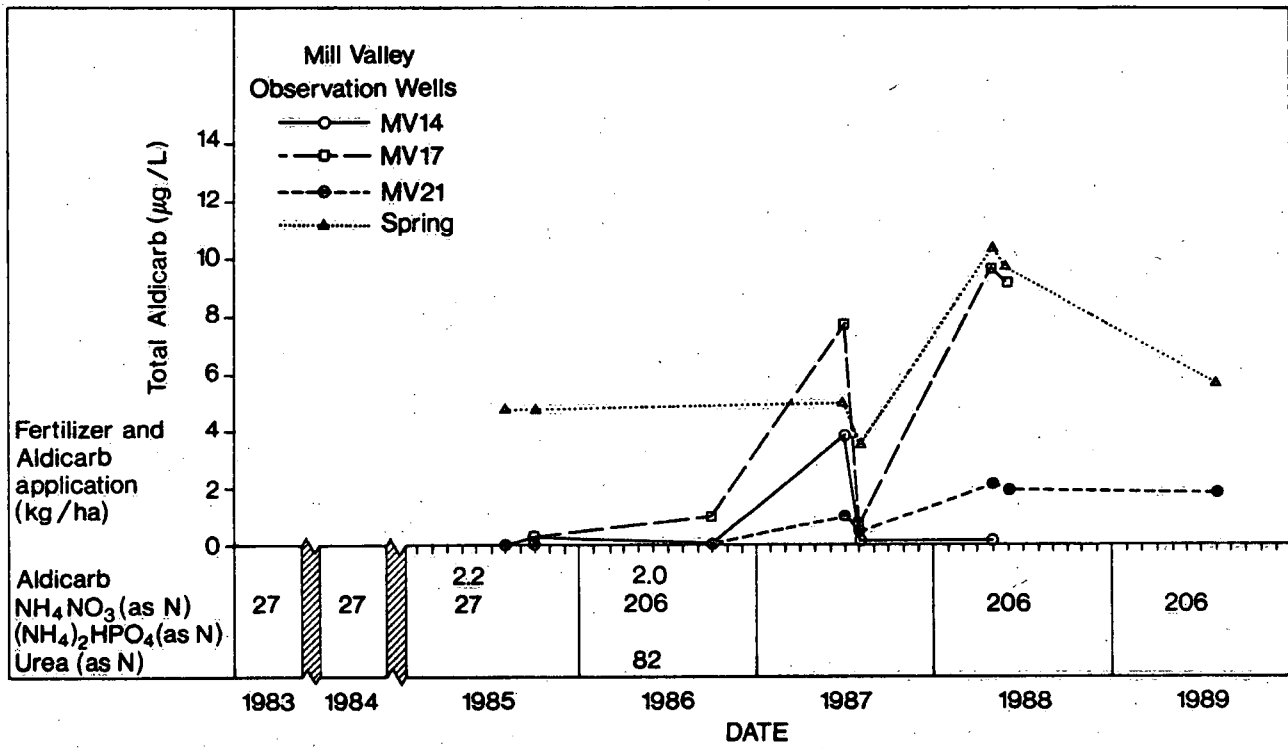
Figure 13. Total aldicarb concentrations for three observation wells and the spring at Mill Valley (July 1985–July 1989). Pesticide and fertilizer applications are shown along the bottom of the figure.

Figures 14 and 15 show a time series of the ASO_2/total aldicarb ratio for the Augustine Cove and Mill Valley sites. A remarkable consistency with respect to time is evident for the ASO_2/total aldicarb ratio at the two sites. Points for the early sampling periods are not plotted for some of the Mill Valley piezometers because aldicarb was not detected in the samples on these dates. The variation that does occur in the data for Mill Valley may be larger because of the difficulties in defining the ratio for very small concentrations of ASO and ASO_2.

ASO_2/total aldicarb ratios found on PEI are appreciably different from the average ratio of about 0.4 reported by Jones (1986) and 0.31 by Harkin et al. (1986) for studies conducted in the United States. The ASO_2/total aldicarb ratio at Augustine Cove covered the full range from 0.00 to 1.00, and the average was 0.73. At the Mill Valley site, the range was from 0.33 to 1.00, with an average of 0.59. The high ASO_2/total aldicarb ratios found in the PEI ground waters may be a result of the highly oxygenated conditions and relatively low pH levels found in these waters, which would inhibit the hydrolysis of the aldicarb residues. The abundance of oxygen may act to enhance the microbial catalyzed oxidation of ASO to ASO_2, driving the system towards ASO_2. As more ASO is oxidized to ASO_2, the ratio approaches 1.0.

Nitrate Concentrations

Nitrate concentrations (Figures 16 and 17) appear to follow the trends established by aldicarb. Nitrate is also considered to be a nonretarded chemical, yet it too shows a remarkable persistence and relatively constant concentration with respect to time. The pronounced drop in the concentration at the second sampling point at Augustine Cove is also similar to the drop experienced by aldicarb. Concentrations were generally lower at the Mill Valley site than at the Augustine Cove site, and within each field, concentrations were highest in the shallow piezometers located in the discharge areas.

Reasons for the similarities between aldicarb and nitrate may be physical and/or chemical. The mobility and nonretarded nature of both nitrate and the two aldicarb daughter products may simply produce similar leaching characteristics. However, the nitrification of ammonia-based fertilizers, which produces nitrate

ions (NO_3^-), also produces H^+, which lowers the pH of the water (see equation [11]). The decrease in pH brought about by the nitrification process will tend to inhibit the degradation of aldicarb if the pH is driven towards the range of 4 to 6, and may therefore establish a direct link between the presence of high concentrations of aldicarb residues and nitrate ions.

The data from the present monitoring program (Figure 18) demonstrate a relationship between high concentrations of total aldicarb and nitrate in the saturated zone (Priddle et al. 1988, 1989). Figure 18 is divided into four quadrants by lines drawn at the maximum acceptable concentration (MAC) for total aldicarb (9 μg/L) and for nitrate (10 mg/L NO_3^--N). Data points plotted in the upper right quadrant represent samples containing both total aldicarb and nitrate concentrations in excess of their maximum acceptable concentrations. Data points plotted in the lower right quadrant represent samples with unacceptable levels of aldicarb only. In 10 of the 11 samples containing unacceptable levels of aldicarb, nitrate levels were also in excess of its maximum acceptable concentration (10 mg/L NO_3^--N). It may be possible, therefore, to use nitrate as an indicator of domestic wells that are susceptible to aldicarb contamination. In a detailed sampling program on PEI, only those wells having excess nitrate levels would have to be analyzed for aldicarb.

Short-term Variation

Four piezometers at Augustine Cove were sampled frequently during May 1988 to observe the short-term, day-to-day fluctuations in the total aldicarb and nitrate concentrations and in the aldicarb speciation ratio. The results of the analyses are presented in Appendix C (Table C-8). The results for piezometer AC6 are plotted in Figure 19. The short-term variations observed were minor for all three parameters investigated. Relative standard deviations for total aldicarb ranged from 5.1% to 18.8% in the four piezometers tested, with an average of 9.6%. For comparison, a standard sample (10 μg/L of aldicarb sulfoxide and aldicarb sulfone) prepared in the laboratory was analyzed four times with a relative standard deviation of 3.8%. The relative standard deviations for the ASO_2/total aldicarb ratio in the four piezometers at Augustine Cove were lower, with a range of 1.4% to 3.1%, and an average of 1.9%.

Augustine Cove Observation Wells

Mole Ratio
$$\frac{ASO_2}{ASO + ASO_2}$$

AC 4
AC 6
AC 7
AC 9

Average ratio of nine samples taken throughout May, 1988

Ratio

1.0
0.8
0.6
0.4

Fertilizer and Aldicarb application (kg/ha)

0.2

0.0

	1983	1984	1985	1986	1987	1988	1989
Aldicarb	2.0			2.0			
NH_4NO_3 (as N)	190			210	52		
$(NH_4)_2HPO_4$ (as N)		54					
Urea (as N)	5.9						

DATE
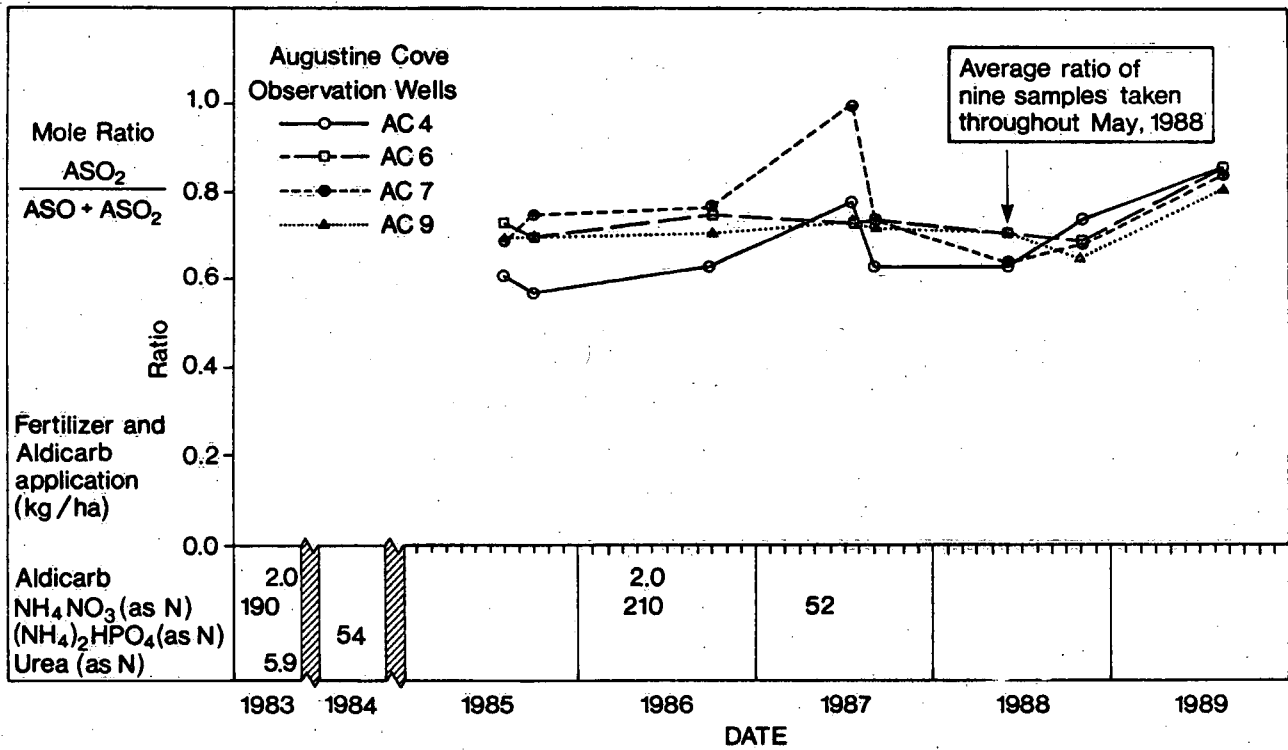
Figure 14. ASO_2/total aldicarb ratios for four observation wells at Augustine Cove (July 1985–July 1989). Pesticide and fertilizer applications are shown along the bottom of the figure.

Mill Valley Observation Wells

Mole Ratio
$$\frac{ASO_2}{ASO + ASO_2}$$

MV14
MV17
MV21
Spring

Ratio

1.0
0.8
0.6
0.4

Fertilizer and Aldicarb application (kg/ha)

0.2

0.0

	1983	1984	1985	1986	1987	1988	1989
Aldicarb			2.2	2.0			
NH_4NO_3 (as N)	27	27	27	206		206	206
$(NH_4)_2HPO_4$ (as N)							
Urea (as N)				82			

DATE
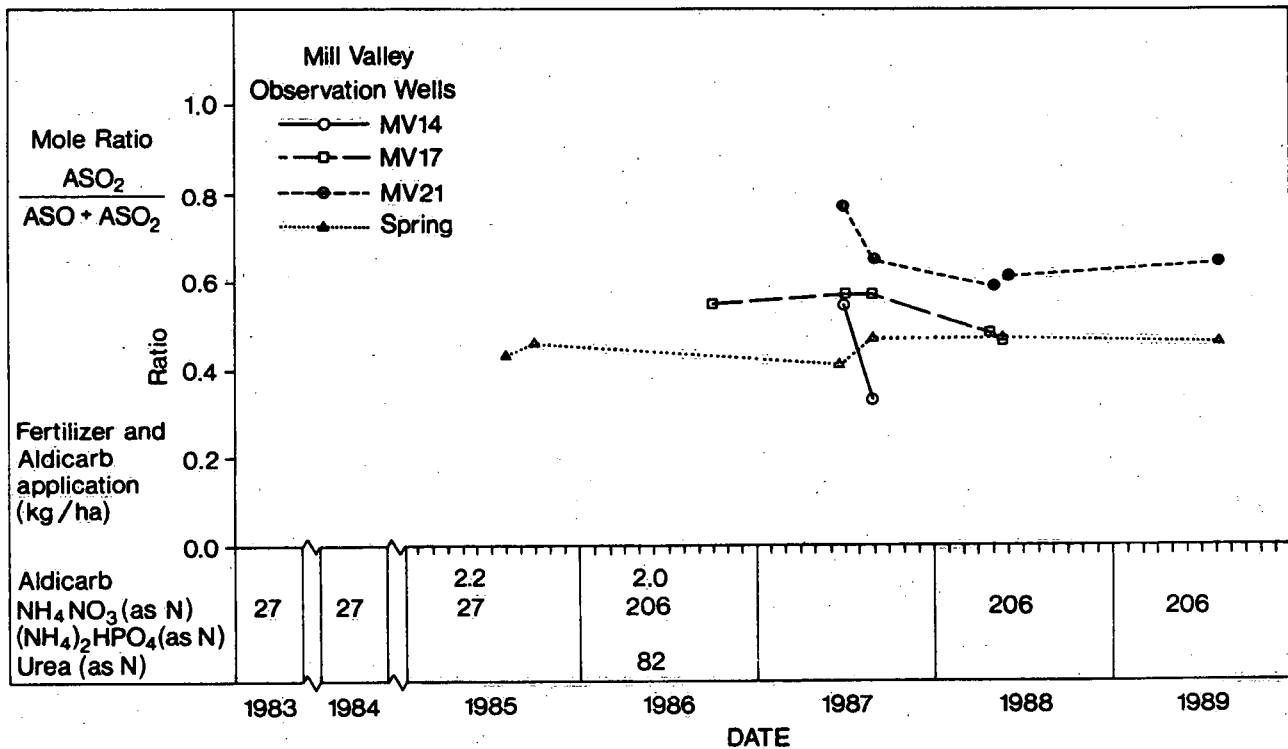
Figure 15. ASO_2/total aldicarb ratios for three observation wells and the spring at Mill Valley (July 1985–July 1989). Pesticide and fertilizer applications are shown along the bottom of the figure.
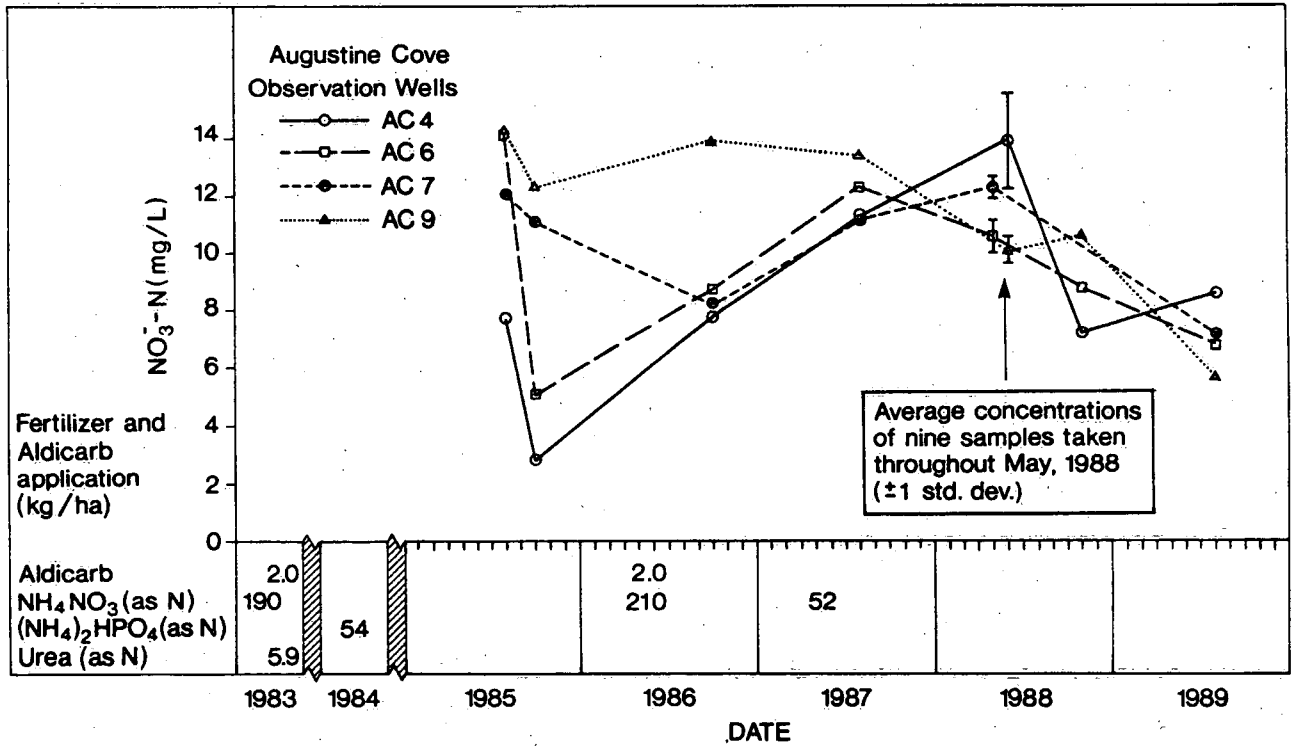
Figure 16. Nitrate (as N) concentrations for four observation wells at Augustine Cove (July 1985–July 1989). Pesticide and fertilizer applications are shown along the bottom of the figure.
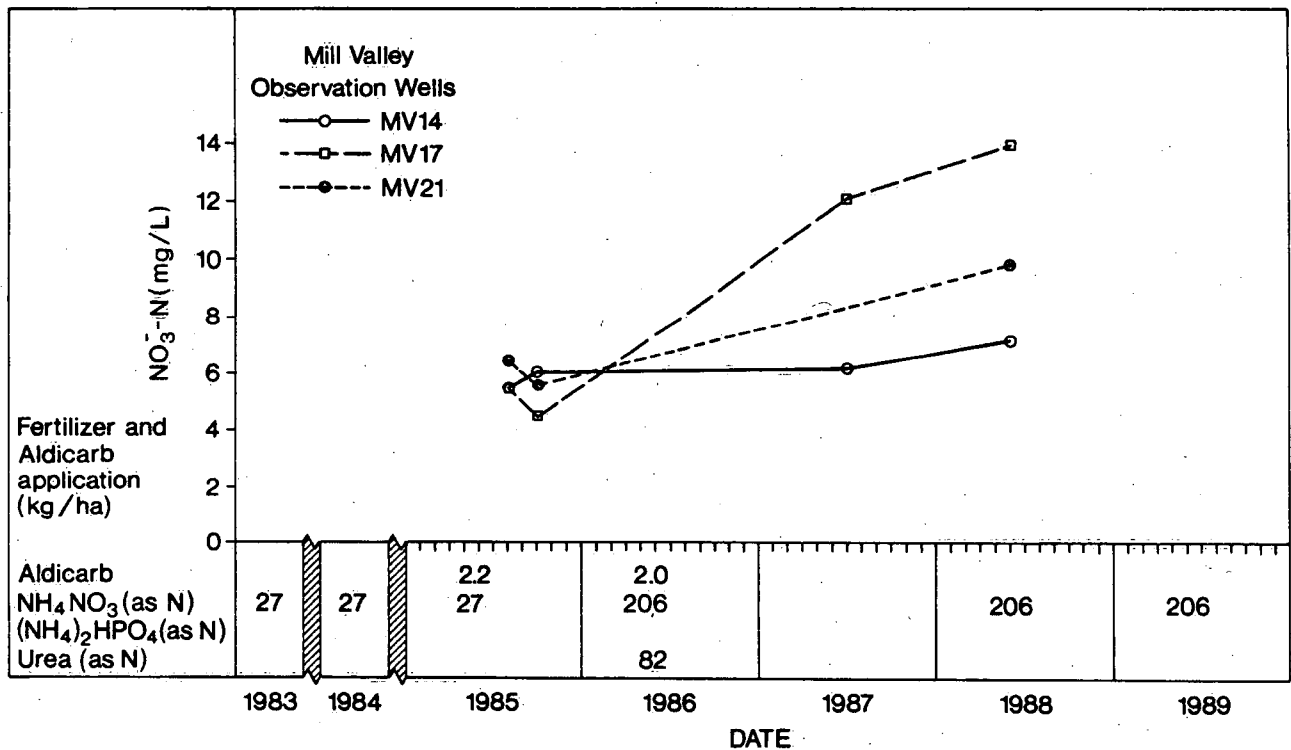
Figure 17. Nitrate (as N) concentrations for three observation wells at Mill Valley (July 1985–May 1988). Pesticide and fertilizer applications are shown along the bottom of the figure.
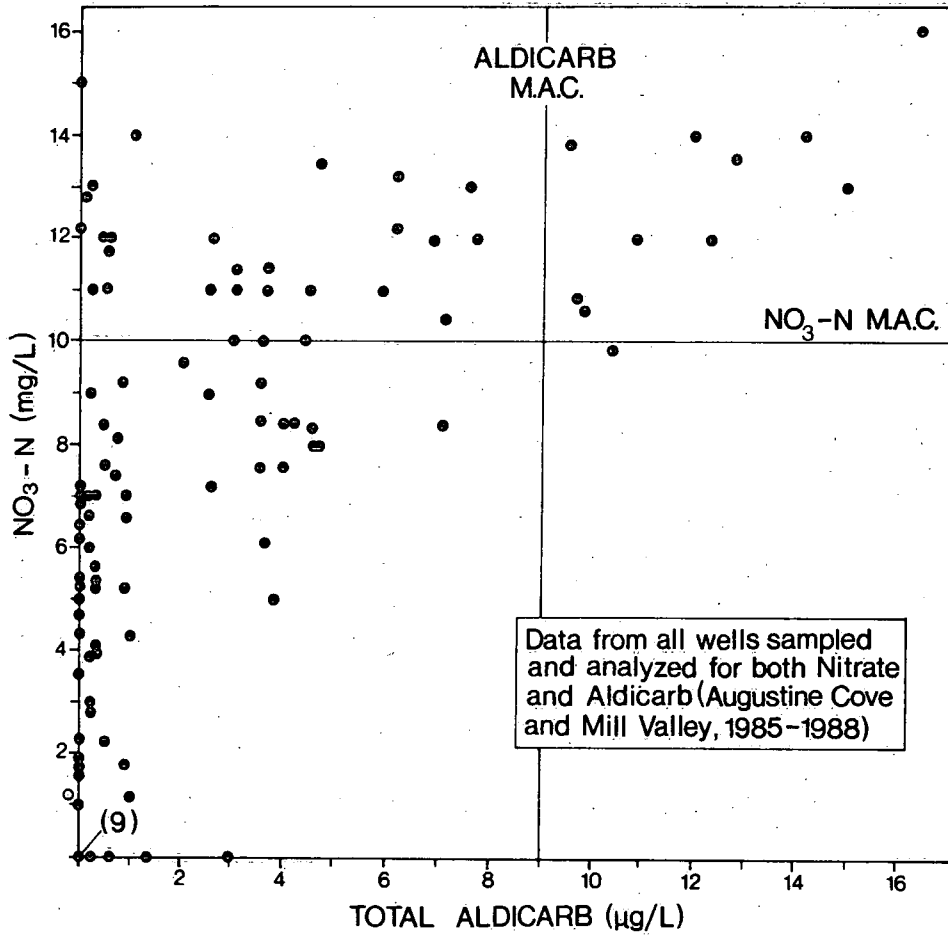
Figure 18. Nitrate (as N) versus total aldicarb concentrations for the observation wells at Augustine Cove and Mill Valley (1985–1988) (after Priddle et al. 1989).
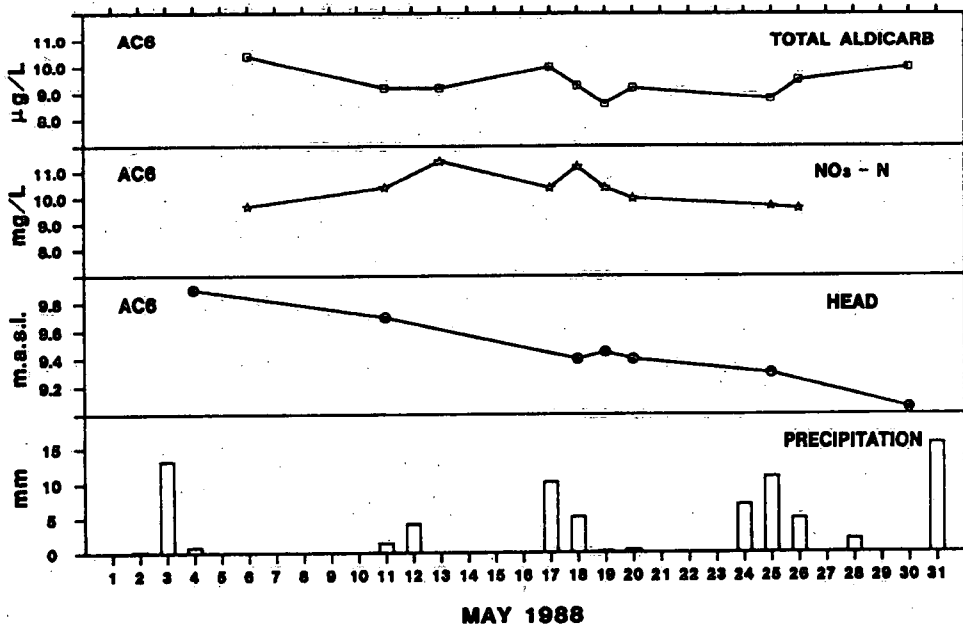
MAY 1988

Figure 19. Short-term variations in the total aldicarb and nitrate concentrations and hydraulic head in observation well AC6 at Augustine Cove (10 samples during May 1988) (after Priddle et al. 1989).

Model Simulations

Two numerical models were employed to simulate the processes that control the fate of aldicarb in the subsurface below the field sites on Prince Edward Island. The first model, PHREEQE (Parkhurst et al. 1980), a geochemical model, was used to investigate the influence of the oxidation of ammonium fertilizers on the half-life of aldicarb sulfoxide. The second model, LEACHMP (Wagenet and Hutson 1987), is a numerical solute transport code and was used to determine the primary factors controlling the fate and migration of aldicarb residues in the unsaturated zone. Only a very brief description of the PHREEQE model is provided with the results of the simulations. A more detailed description of LEACHMP accompanies the results from this model because it was the primary focus of the modelling effort.

GEOCHEMICAL SIMULATIONS WITH PHREEQE

A Brief Description of PHREEQE

PHREEQE (pH-REdox-EQuilibrium-Equations) is a geochemical reaction model based on an equilibrium approach. The model is useful in assessing the equilibrium conditions of chemical reactions in the solution phase. Mechanisms involved in the transport of the chemical species are not considered.

PHREEQE is capable of simulating the following:

1. speciation – determining the distribution of the dissolved mass between the possible species,

2. dissolution/precipitation – determining the saturation state of minerals and gases, and also the amount of mass transferred between the solid, aqueous, and gaseous phases as the process moves to an equilibrium state, and

3. reaction path processes – determining equilibrium conditions for the addition of reactants to a solution, the mixing of two solutions, temperature effects on a solution, and the titration of one solution with another.

The model is based on the principle of mass action and on mass, charge, and energy balance equations. A system of equations is produced by generating mass balance and mass action equations for each element and species present, with the exception of oxygen and hydrogen. The contribution of oxygen and hydrogen from the water molecule makes a mass balance on these two elements difficult for aqueous systems. The mass balance equations for oxygen and hydrogen are replaced with a mass action equation for water and a charge balance equation for the solution.

Simulations may be performed at a fixed pH, in which case, the charge of the solution is left unbalanced. It is also possible to achieve a charge balance by selecting a cation or anion that will be added to the solution in a sufficient quantity to balance the charge of the solution.

When simulating redox reactions, PHREEQE assigns an "operational valence" value (OPV) to each element that is capable of changing its oxidation state. Since electrons cannot be created or destroyed, an electron balance is achieved by adjusting the OPV of the elements involved in the redox reactions so that the net valence for the entire system remains constant. This eliminates the need for a mass balance equation on hydrogen and oxygen. As a result, the amount of these two elements available in the system is unlimited unless both the pH and pe of the solution are fixed.

PHREEQE Simulations

The PHREEQE model was used to investigate the influence of the oxidation of ammonium fertilizers on the persistence of aldicarb sulfoxide (ASO). The equilibrium pH was determined for a pure water sample at $10°C$, with an initial pH of 7.5, as incremental amounts of ammonium (NH_4^+) were oxidized to nitrogen (N_2). This reaction took place in the presence of varying amounts of calcite ($CaCO_3$), simulating that which naturally occurs in the sandstone units. The resulting pH of the solution, predicted by PHREEQE, was then related to the half-life of ASO through the hydrolytic half-life equations (equations [7]–[10]) developed by Lightfoot et al. (1987) to establish an indirect relationship between the amount of ammonium oxidation and the half-life of ASO.

The master species for the element, nitrogen, in the PHREEQE data base was converted from

the existing nitrate ion (NO_3^-) to ammonium (NH_4^+) and all pertinent species containing nitrogen were rewritten in terms of NH_4^+ rather than NO_3^-. Thermodynamic data for the new equations were taken from the CRC Handbook of Chemistry and Physics (Weast 1987).

$$2NH_4^+ = N_2 + 8H^+ + 6e^- \qquad (12)$$

$$NH_4^+ + 3H_2O = NO_3^- + 10H^+ + 8e^- \qquad (13)$$
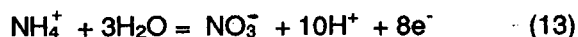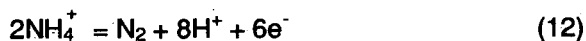
The oxidation reaction was allowed to proceed from NH_4^+ to N_2 (equation [12]) rather than from NH_4^+ to NO_3^- (equation [13]), even though the kinetics involved in the reactions often maintain a large amount of the nitrogen in groundwater as NO_3^-. The equation was allowed to proceed to N_2 as this was the thermodynamically stable product calculated by the model for the given conditions.

The half reaction given in equation (12) was coupled with the reduction of oxygen in the model. It was desired to fix the amount of oxygen available in the solution to a level of approximately 8 mg/L (the concentration observed in the field). However, only the change in the concentration of dissolved oxygen and hydrogen, and not the total mass, is monitored by PHREEQE. Therefore, the amount of oxygen consumed in the simulation could not be limited, and the oxidation of NH_4^+ was allowed to proceed to completion.

The acidity (H^+) produced by the oxidation of ammonium (NH_4^+) to nitrogen (N_2) will be less than the acidity produced had the oxidation reaction been allowed to proceed to nitrate (NO_3^-) (see equations [12] and [13]). The simplifying assumptions (i.e., unlimited supply of oxygen and the selection of the neutralizing capacity of the solution) necessary in the simulation prohibit a strict quantitative interpretation of the results. As a result, equation (12) should suffice in providing a qualitative understanding of the significance of the oxidation of ammonium-based fertilizers on the persistence of aldicarb in the groundwater under the field sites on Prince Edward Island.

A portion of the acidity produced during the oxidation of ammonium is neutralized by the dissolution of calcite according to the following equations:

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \qquad (14)$$

$$CO_3^{2-} + H^+ = HCO_3^- \qquad (15)$$
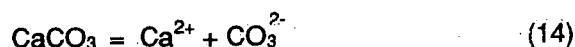
It was assumed in the simulations that the average calcium concentration (44 mg/L = 0.11×10^{-2} mol/L) found in the groundwater at the Augustine Cove site in 1987 was derived entirely from the dissolution of calcium carbonate $(CaCO_3)$. Although it is unclear as to whether this amount was contributed by the dissolution of calcite from the sandstone formation or by lime applied directly to the field, the source of the dissolved Ca^{2+} will not affect the results of the simulations. This concentration $(0.11 \times 10^{-2}$ mol/L) was taken as the base amount of calcite available to the solution.

The upper bound with respect to calcite in the PHREEQE simulations was obtained by performing a run with an unlimited amount of calcite available for dissolution. Additional runs were also performed with the base amount of calcite available to the solution being reduced by factors of 10, 100, and 1000.

Ammonium concentrations in the infiltrating water at the field sites have been estimated to be approximately 0.001 M after a fertilizer application (Priddle et al. 1988), and in the PHREEQE simulations, the range of ammonium oxidation varied from no ammonium oxidation to the oxidation of 0.1M NH_4^+.

A graphical representation of equations (7)–(10) is presented in Figure 20, and the results of the PHREEQE simulations are presented in Figures 21 and 22. The rate of degradation of ASO is dependent on the rate of both base- and acid-catalyzed hydrolysis reactions (equations [7] and [9], respectively). For a temperature of 10°C, the apex of the ASO curve in Figure 20 occurs at a pH of approximately 5.6. At this pH level, the resultant degradation rate of ASO via the acid- and base-catalyzed hydrolysis reactions is at a minimum, and this results in a maximum half-life for ASO. The horizontal line drawn in Figure 21 corresponds to the pH value where the degradation of ASO is at a minimum (maximum half-life for ASO). At higher pH values (above the horizontal line in Figure 21), the base-catalyzed reaction becomes increasingly dominant and causes the resultant degradation rate of ASO to increase, producing a shorter half-life for ASO. The same is true for lower pH values (below the horizontal line in Figure 21), except in this case, it is the acid-catalyzed reaction that becomes iincreasingly dominant. Figure 21 indicates that as the amount of ammonium oxidation increases, the equilibrium pH predicted by PHREEQE for all solutions, with the exception of the "UNLIMITED $CaCO_3$" line, falls below the pH value that will result in a maximum half-life for ASO. The
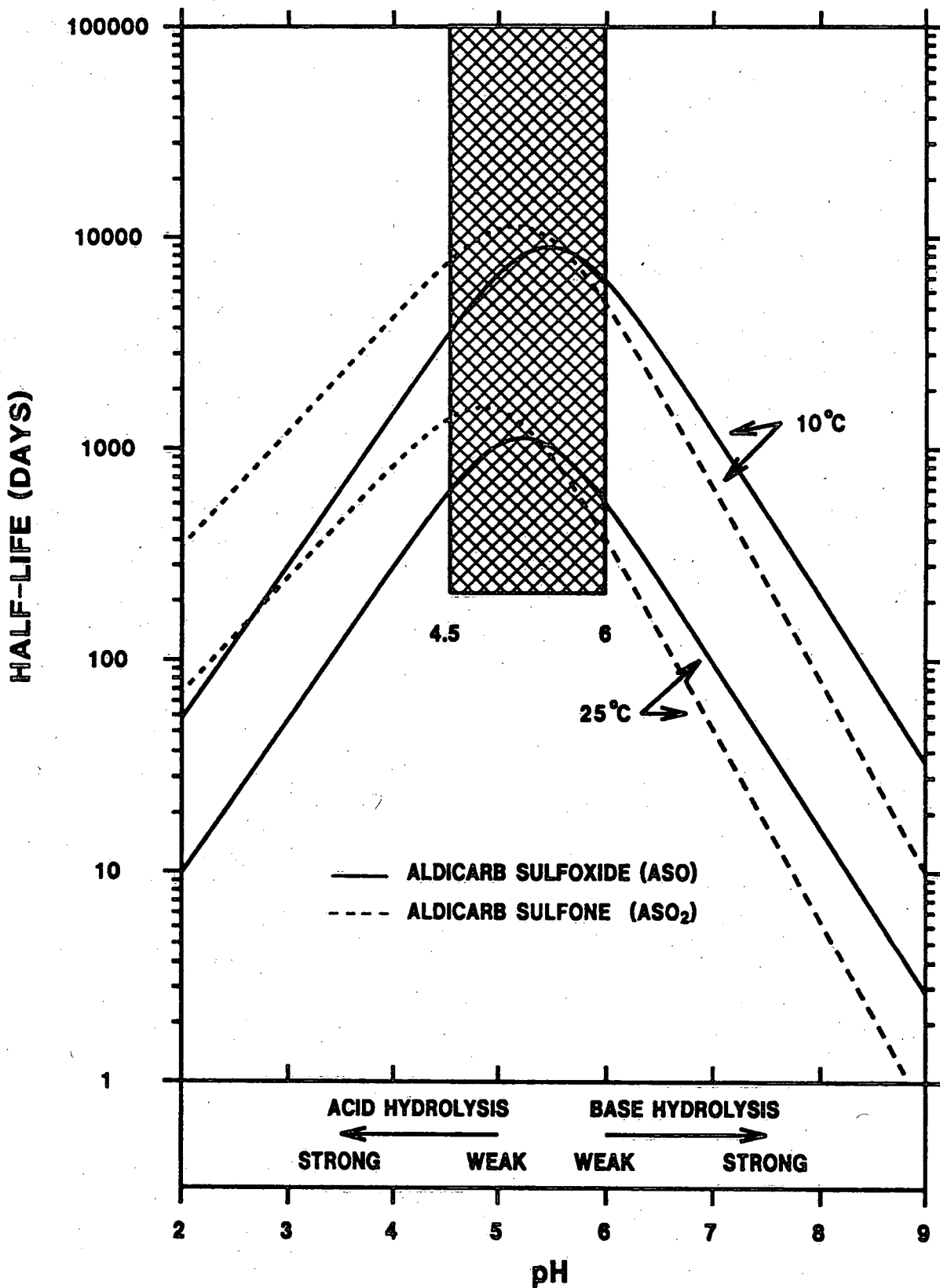
Figure 20. Effect of temperature and pH on the chemical hydrolysis of aldicarb sulfoxide and aldicarb sulfone (after Priddle *et al.* 1988).
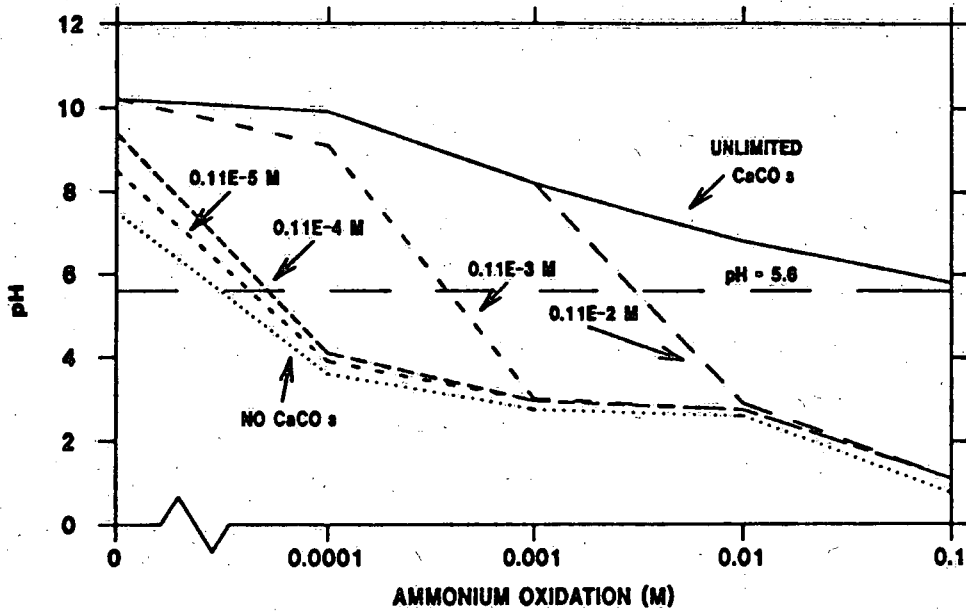
Figure 21. Effect of ammonium oxidation on the pH of solutions containing varying amounts of calcite.
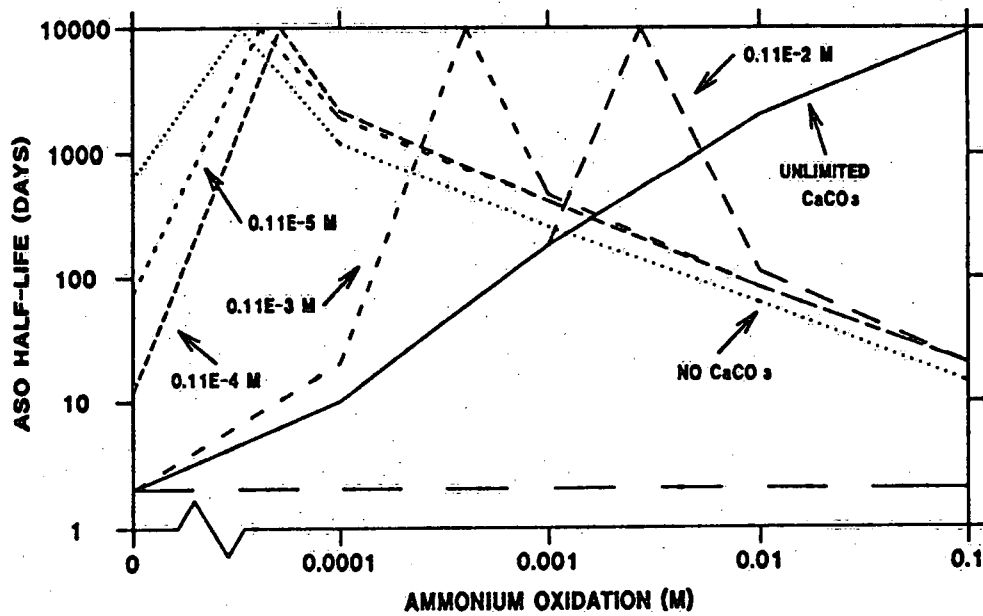
Figure 22. Effect of ammonium oxidation on the half-life of aldicarb sulfoxide in solutions containing varying amounts of calcite.

closer the resulting equilibrium pH is to the horizontal line, the greater the persistence of ASO.

Figure 22 couples the information presented in Figures 20 and 21. For a given amount of ammonium oxidation, the equilibrium pH predicted by PHREEQE (determined from Figure 21) was used to enter Figure 20. The resultant half-life for ASO was then determined by extending a vertical line from the pH value on the abscissa in Figure 20 to the line representing the degradation of ASO at 10°C. A horizontal line was then drawn to meet the ordinate, and the half-life for ASO was read. The results of this procedure are presented in Figure 22.

The influence of the oxidation of ammonium on the persistence of ASO can be illustrated with Figure 22 by drawing a horizontal line at the point of the initial half-life of ASO for a solution with no ammonium oxidation. If the line representing the solution rises above the horizontal line, it indicates that the oxidation of ammonium has a detrimental effect on the persistence of ASO. The resulting half-life of ASO is greater due to the oxidation of ammonium than the half-life of ASO had there been no ammonium oxidation.

The influence of ammonium oxidation on the persistence of ASO at the Augustine Cove site can be determined from Figure 22. The conditions most closely representing those in existence at Augustine Cove are 0.11×10^{-2} M of $CaCO_3$ available for dissolution and 0.001 M of ammonium available for oxidation. By drawing a horizontal line at the point of the initial half-life of ASO (representing no ammonium oxidation) for the solution containing 0.11×10^{-2} M of $CaCO_3$, it can be seen that the line representing 0.11×10^{-2} M of $CaCO_3$, available in solution rises above the horizontal line for all levels of ammonium oxidation shown in Figure 22. The horizontal line indicates that with no ammonium oxidation, the predicted half-life for ASO would be approximately two days. If the entire 0.001M ammonium assumed to be available in the ground water at Augustine Cove were oxidized, the predicted half-life for ASO would rise to approximately 460 days. Although several simplifying assumptions were necessary in order to perform the simulations, the results of the PHREEQE simulations qualitatively reveal that the oxidation of ammonium-based fertilizers has the potential to significantly increase the persistence of the aldicarb residues in the ground water under the field sites on Prince Edward Island.

LEACHMP SIMULATIONS

Classification of Solute Transport Models

Mathematical models are classified into one of three general categories: educational, management, or research models. The categories are distinguished from each other based on (Wagenet 1986) the following:

1. the extent to which they describe the basic processes involved,

2. the accuracy of the simulations, and

3. the amount of input characterization data required.

Educational models are the simplest of the three and are applicable to only a limited number of near ideal situations (e.g., steady state conditions, homogeneous soil profile). The governing processes are simply described, and the amount of input characterization data required by the models is restricted to only a few parameters. Results from the models provide only qualitative information.

Management models move a step beyond educational models because they describe the processes involved in more detail. They require larger (yet still not restrictive) amounts of input characterization data and provide semiquantitative results. These models are intended to provide management guidance and are designed so that the results are presented in a manner that allows for quick interpretation.

The third category is the research model. Research models attempt to describe the processes in as much detail as possible. As a result, they often require large amounts of input characterization data, some of which may not be readily available. Research models provide results that are more quantitatively accurate than the results from either management or educational models. However, their use is often more cumbersome (i.e., input data sets are more difficult to formulate, and longer execution times are required).

Two models, LEACHMP and PRZM, were considered for the solute transport simulations, and a comparison was made between the two (Mutch 1988). Based on the findings of this report, LEACHMP was chosen as the most appropriate model for the simulations to be performed.

Description of LEACHMP

LEACHMP (Leaching Estimation And CHemistry Model - Pesticides) is one of three solute transport modules incorporated in LEACHM (Wagenet and Hutson 1987). The three modules contained in LEACHM describe the transport of nitrogen (LEACHMN), inorganic salts (LEACHMS), and pesticides (LEACHMP) in the unsaturated zone of a soil profile. The modules run independently and are grouped together because many of the subroutines are common to all three modules. The following description refers to LEACHMP only.

LEACHMP is classified as a research/management model. The objective in formulating LEACHMP was to develop a model that would describe the natural processes in sufficient detail to provide useful and accurate results while restricting the amount and complexity of the input data required. It was also intended that the output would be organized in such a manner as to allow for a quick and simple interpretation, thereby providing managers with a tool that was easily used and understood.

LEACHMP is a one-dimensional, compartmentalized, finite difference, solute transport model for the unsaturated (vadose) zone. It can be visualized as a small column penetrating through the unsaturated zone and into the saturated zone if desired. The column is broken into a number of small compartments stacked one on top of the other. An additional compartment is added to both the top and bottom of the simulated column to allow the desired boundary conditions to be set for the simulation. Different parameters may be assigned to each compartment, giving the model the ability to simulate layered soils.

The development of the model is structured around the basic principles of water and solute movement in a porous medium. The flow of water within the model is based on Richards equation (Darcy's law and the continuity equation) with water flow being controlled by the characteristic curves of the soil. These curves relate the retentivity and conductivity of the soil to its matric potential.

Pesticide transport is coupled to the water flow portion of the model through an advective–dispersive equation. The primary transport mechanism of the pesticide is advection of the pesticide with the bulk flow of water. Secondary dispersive and diffusive transport mechanisms are also included. Pesticide attenuation is represented in the model with equations describing equilibrium sorption (linear and reversible),

chemical and/or biological degradation (first-order), and volatilization of the pesticide.

The finite difference equations in the model are solved with an implicit (Crank-Nicolson) solution technique, and the one-dimensional nature of the model is conducive to the formation of tridiagonal matrices that are rapidly solved by Gaussian elimination. The time step in LEACHMP is variable, and the model is able to handle transient climatic data, multiple pesticide applications, and varying boundary conditions.

At the beginning of each day, LEACHMP simulates both plant root and canopy growth (GROWTH), and these results are used to calculate the amount of evapotranspiration (POTET and ETRANS) and water and pesticide uptake (WUPTAK and PSINK) within the system. The solution to the water flow equation (WATFLO) is calculated according to the surface and bottom boundary conditions specified by the modeller, and the water flux determined in the WATFLO subroutine is used to calculate the solute flux (SOLUTE). Pesticide degradation is accounted for in PSINK, and the results are sent to the output files. Cumulative totals for many of the model parameters are sent to the output files, and mass balance checks are performed by the model to ensure the accuracy of the simulation. A flow chart for LEACHMP is presented in Figure 23.

Input Characterization Data Set and Model Setup

LEACHMP requires data from four general areas: climatic conditions, soil parameters, chemical characteristics of the pesticide, and farm management practices. Data for the study of aldicarb on Prince Edward Island were derived from a number of different sources. Climatic data were obtained from the Summerside (precipitation) and Charlottetown (pan evaporation) weather stations for the period 1983–1988. Soil parameters for the model were taken from MacDougall et al. (1981) (see Table 1), and the farm managers at the field sites provided information on the farming practices employed. Chemical information on aldicarb was obtained from a number of sources, including Carsel et al. (1984), Enfield et al. (1982), and Zhong et al. (1986). Additional model parameters were chosen with the advice of Dr. John Hutson (1988, Department of Agronomy, Cornell University, pers. com.), one of the authors of LEACHM.

The model was set up to simulate a 4.4-m soil column profile with 44 compartments, each 100 mm thick. A water table was placed at a depth of 3.0 m to

READ DATA

INITIALIZE VARIABLES

PARTITION TOTAL SOLUTE BETWEEN
SOLUTION AND ADSORBED PHASES

CALL WATDAT — CALCULATE WATER RETENTIVITY AND HYDRAULIC CONDUCTIVITY DATA FOR THE SOIL HYDROLOGICAL CONSTANTS USED, AND PRINTS IN TABULAR FORM

1 > DAY | END OF LAST DAY → YES → END
A → DAY+1 > DAY
→ NO

CALL GROWTH — SIMULATES CANOPY GROWTH AND ROOT GROWTH AND DISTRIBUTION USING EMPIRICAL OR REGRESSION EQUATIONS

CALL POTET — CALCULATES DAILY POTENTIAL EVAPORATION AND TRANSPIRATION FROM PAN EVAPORATION DATA AND CROP COVER

PESTICIDE ADDITION — YES → ADD PESTICIDE AND PARTITION BETWEEN SOLUTION AND SOLID PHASES
NO

To > T
T + TIME > TIME | T=1 → YES → A
NO

CALL TSTEP — CALCULATES THE LENGTH OF THE TIME STEP AS THE MINIMUM OF i) A SPECIFIED MAXIMUM, USUALLY 0.05 DAY, ii) TIME REMAINING TO THE END OF A 0.1 DAY INTERVAL, iii) TIME FOR A SPECIFIED MAXIMUM WATER FLUX TO OCCUR

CALL ETRANS — POTENTIAL TRANSPIRATION AND EVAPORATION FOR THE TIME STEP ASSUMING A SINUSOIDAL CHANGE DURING THE DAY.

CALL WUPTAK — CALCULATES WATER UPTAKE BY PLANTS ON ROOT DISTRIBUTION, RESISTANCE AND SOIL WATER POTENTIAL

CALL WATFLO — FINITE DIFFERENCE SIMULATION OF SOIL WATER FLOW EQUATION WITH SPECIFIED SURFACE BOUNDARY FLUX AND CHOICE OF BOTTOM BOUNDARY CONDITION.

CALL TEMP — FINITE DIFFERENCE SIMULATION OF HEAT FLOW.

CALL RRATE — ADJUSTS TEMPERATURE DEPENDENT PESTICIDE TRANSFORMATION RATES.

CALL PSINK — GAINS AND LOSSES OF EACH PESTICIDE SPECIES BY TRANSFORMATION AND/OR PLANT UPTAKE.

CALL SOLUTE — FINITE DIFFERENCE SOLUTION OF SOLUTE TRANSPORT EQUATION USING WATER FLUX GENERATED IN WATFLO.

TIME TO PRINT? → YES → PRINT CUMULATIVE TOTALS, PROFILE DATA, PLANT GROWTH AND SOLUTE UPTAKE.
NO

CUMULATIVE TOTALS
MASS BALANCE CHECK

Figure 23. Flowchart for LEACHMP (after Wagenet and Hutson 1987).

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simulate conditions found in the discharge area of the Augustine Cove field site (see Figure 6a). It was assumed that the initial soil profile (January 1, 1983) was free from aldicarb residues. A constant crop was specified for the field, and the model allowed for the plant uptake of water only. Degradation of the pesticide occurred in both the dissolved and sorbed states.

CALIBRATION OF LEACHMP

Field data from the Augustine Cove field site (see Table C-4, Appendix C) were used to calibrate LEACHMP. Two criteria were established for the calibration of LEACHMP. The model should be able to produce both a total aldicarb concentration (ASO + ASO$_2$) and an ASO$_2$/total aldicarb ratio that are consistent with the values observed in the field during the monitoring program. An observation depth of 3.25 m was chosen for the calibration of the model. This depth occurs just below the water table (3.00 m), and the concentrations predicted for this depth should correspond to the field data obtained from the saturated zone at the field site.

Calibration for the Period 1983-1985

The initial simulation period for the model calibration attempt was set from January 1, 1983, to December 31, 1985, and simulations were designed to calibrate the model predictions to the field data obtained in July and September 1985. The initial values for the degradation rate constants listed below were taken from Zhong et al. (1986).

1. K_1^* - oxidation of AS to ASO.

2. K_2^* - oxidation of ASO to ASO$_2$.

3. K_1 - hydrolysis of AS to a less toxic degradation product.

4. K_2 - hydrolysis of ASO to a less toxic deradation product.

5. K_3 - hydrolysis of ASO$_2$ to a less toxic degradation product.

Values for the rate constants and dispersivity were adjusted to calibrate the model results to the field data. The results at a depth of 0.25 m below the water table are shown in Figures 24 and 25 and were obtained with a dispersivity value of 0.10 m. Based on data in Figure 26, it appears that this value of dispersivity is reasonable for the scale of the simulation

(4.4 m). The values for the rate constants are shown in Figure 25. A reasonable agreement was obtained between the predicted results and the mean of the field data for both the total pesticide concentration and the ASO$_2$/total aldicarb ratio.

Calibration for the Period 1983-1987

With the calibration of the model complete for the first set of field data, the simulation period was extended to include the years 1986 and 1987, covering a time span that included an additional three sets of field data. An additional pesticide application occurred during the extended simulation period (May 1986). The timing of this application is indicated in Figure 27.

The rate constants obtained from the first phase of the calibration procedure (1983-1985) discussed in the preceding section were used in the initial simulation for the extended time frame (1983-1987). However, the results of the simulation were not satisfactory, and a second round of calibration simulations was performed with different rate constants. The results of the second phase of the calibration procedure are shown in Figures 27 and 28.

Predicted results were all within the range of observed field data, with the exception of the ASO$_2$/ total aldicarb ratio for August 1987. However, the differences between the computed values and the mean of the observed values (indicated with an "x" in Figures 27 and 28) were large for the data points for 1987.

Figure 27 shows a large peak of pesticide moving past the selected observation depth of 3.25 m during the years 1984 and 1985. Predicted total aldicarb concentrations are close to the observed mean for the 1985 sampling data. However, the predicted concentrations underestimate the mean value observed in the field in 1986.

In order to increase the concentration of total aldicarb in 1986 (to obtain a better match with the observed mean), the rate constants for the entire soil profile were lowered to produce longer half-lives for the three aldicarb species. However, the longer half-lives produced predicted total aldicarb concentrations that were far in excess of the observed mean value for the 1987 sampling dates, and the results of these simulations are not presented. The predicted concentrations and ratios that are presented in Figures 27 and 28 represent the best match obtained for the 1986 field data while still maintaining the 1987 predicted values within the observed range of field data.

Figure 24. Predicted values of the total aldicarb concentration at a depth of 3.25 m with LEACHMP and the total aldicarb concentrations observed in the field (calibration for the period 1983–1985, with $\alpha = 0.10$ m).

Figure 25. Predicted ASO_2/total aldicarb ratios at a depth of 3.25 m with LEACHMP and the range of ratios observed in the field (calibration for the period 1983–1985, with a = 0.10 m).
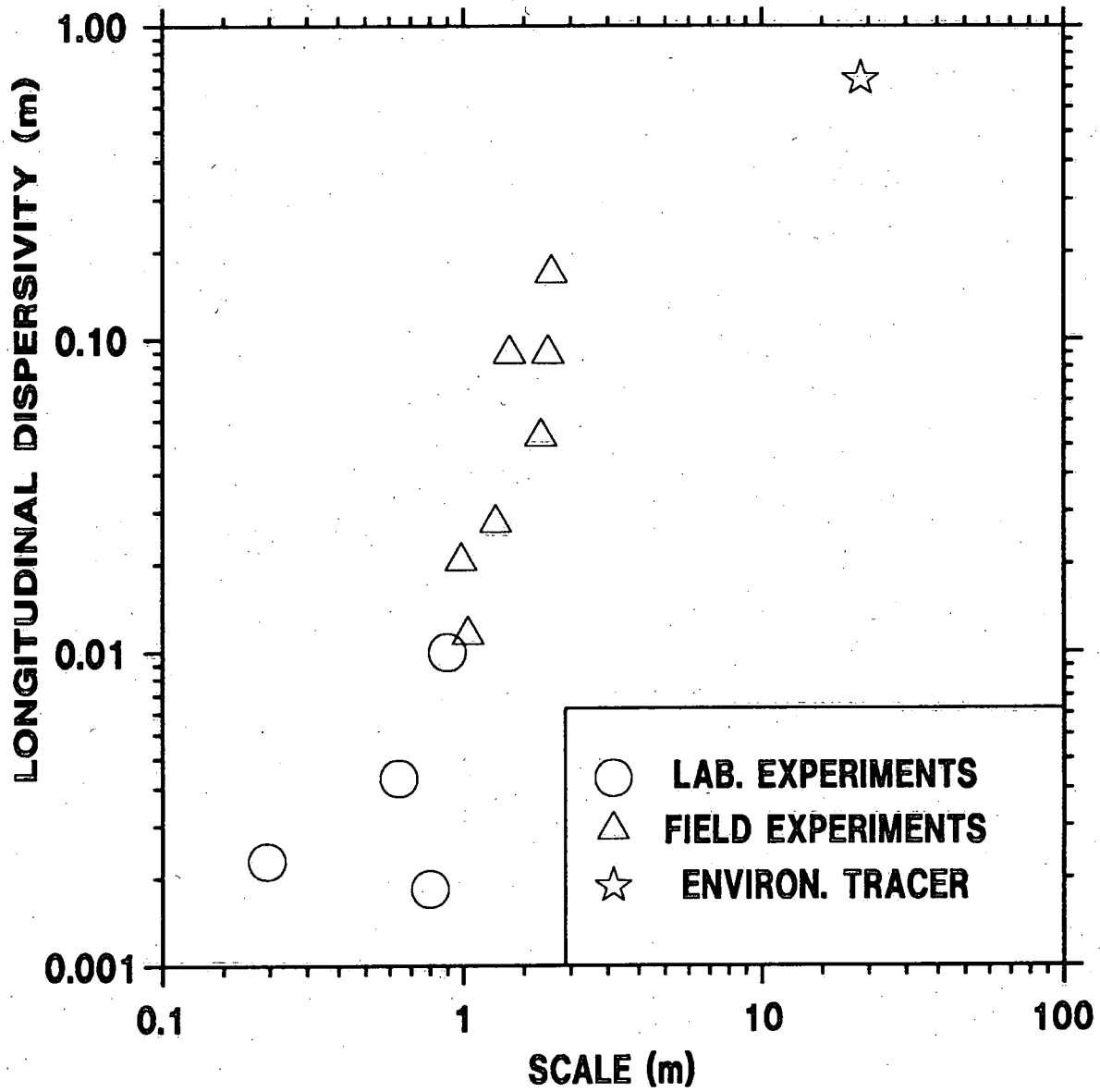
Figure 26. Plot of scale of observation versus longitudinal dispersivity for the unsaturated zone (after Tennessee Valley Authority 1985).
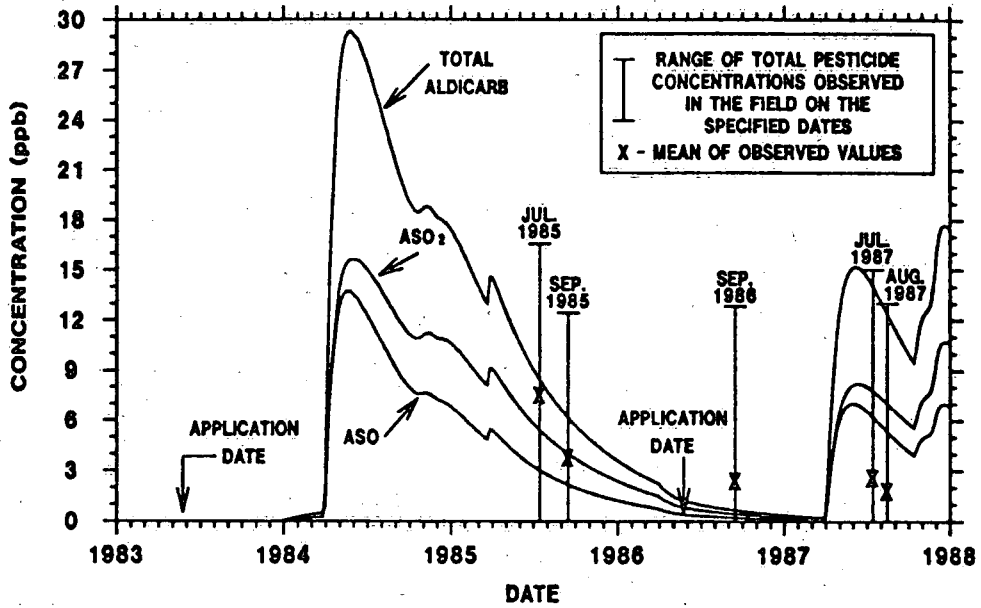
Figure 27. Predicted values of the total aldicarb concentration at a depth of 3.25 m with LEACHMP and the total aldicarb concentrations observed in the field (calibration for the period 1983–1987).
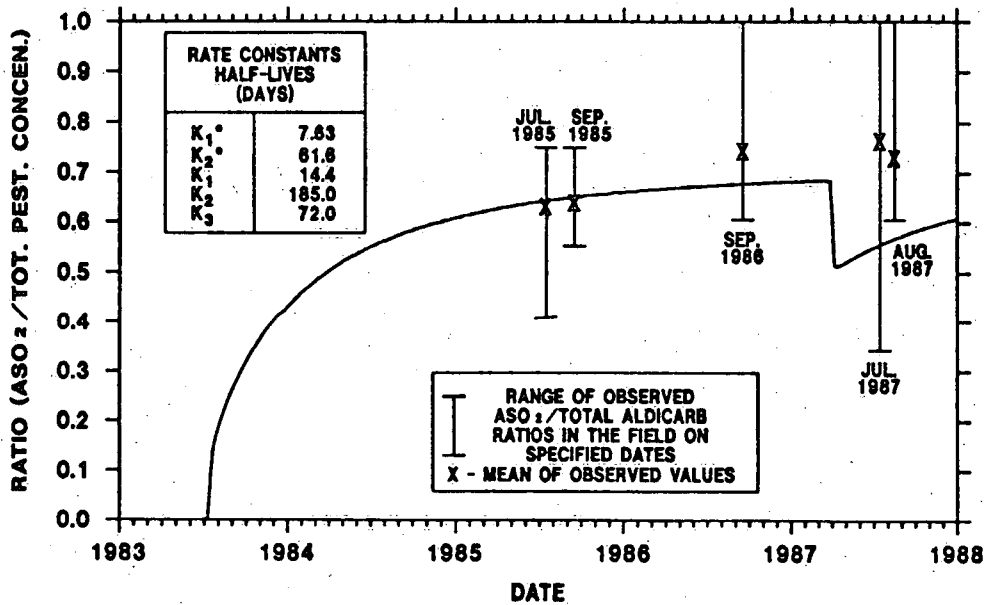
Figure 28. Predicted ASO₂/total aldicarb ratios at a depth of 3.25 m with LEACHMP and the range of ratios observed in the field (calibration for the period 1983–1987).
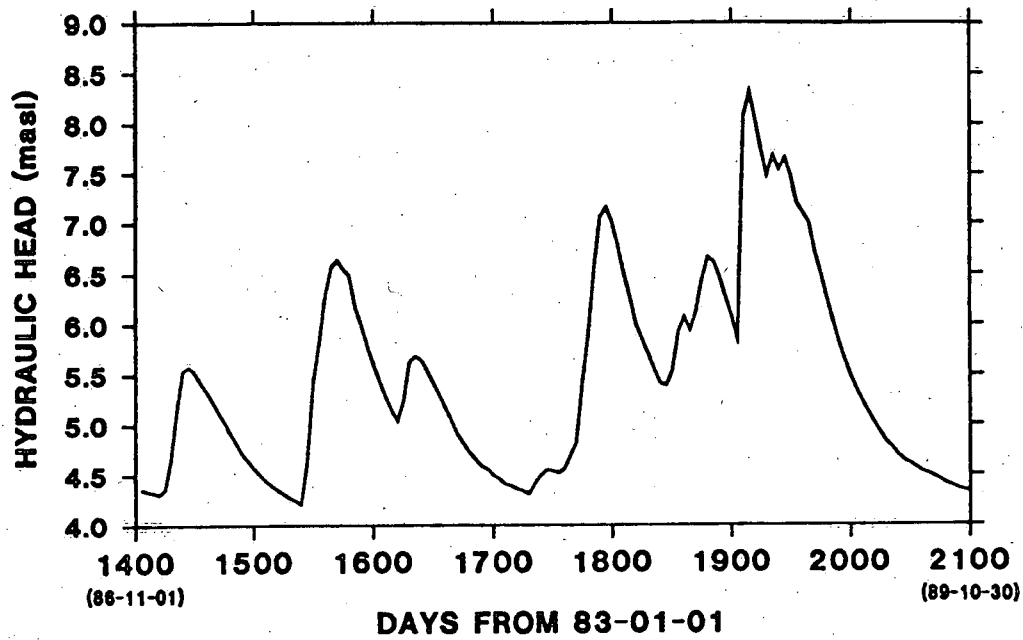
Figure 29. Hydrograph of continuous recording observation well at Augustine Cove (November 1986–June 1988).
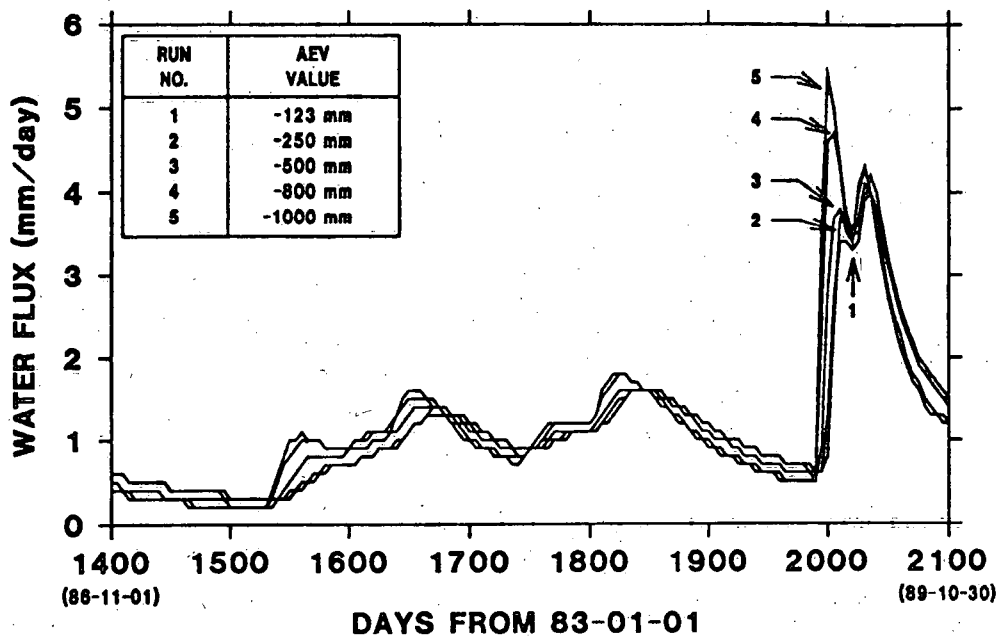
Figure 30. Predicted flux of water table at 3 m with LEACHMP.

The results for the ASO_2/total aldicarb ratio (Figure 28) were close to the mean observed values, however, the predicted results for the total aldicarb concentration were not. It was concluded that the simulation could not be considered as a successful calibration of the model.

Adjusting Air Entry Values and Rate Constants at Depth

Observed field concentrations for the individual wells (see Figure 12) show a relatively constant concentration over the entire sampling period, indicating that some sort of storage mechanism may exist for the pesticide. Model predictions, however, show large peaks in the pesticide concentrations followed by a decline to negligible levels during a later portion of the simulation period.

In an attempt to simulate the apparent storage properties of the real system, the air entry values (a parameter defining the retentivity curve of a soil) for the simulated soil were decreased to allow the soil to retain more water at a given matric suction. In addition, the rate constants at depth (>400 mm) were reduced from the values adopted for the surface layer, thus producing greater persistence at depth. It is a reasonable assumption to expect the rate constants to decline with depth because the oxidation of AS and ASO is microbially catalyzed. The rate of the oxidation reactions will normally experience a decrease as the microbial populations that catalyze the reactions also decrease with depth. Hydrolysis rate constants have also been observed to decline with depth (Ou *et al.* 1985a, 1988).

Initially, an attempt was made to calibrate the water flow portion of the model with the hydrograph (Figure 29) from the continuous recording observation well located at Augustine Cove. Five runs were performed, decreasing the air entry values (AEV) from -123 to -1000 mm. The results presented in Figure 30 indicate that although the magnitude of the water flux reaching the water table is relatively sensitive to the air entry value, the time of occurrence of the flux is not.

A weak but general agreement between the results shown in Figures 29 and 30 is evident, and this is all that can be expected considering the limitations imposed by the available data. Climatic data were taken from weather stations located approximately 30 km from the site, and the model was predicting the flux of water to a water table at a depth of 3.0 m, while the depth to

the water table in the observation well was approximately 10 m.

A series of simulations were conducted with air entry values ranging from -123 mm to -1000 mm, and the results for the predicted pesticide concentration and ASO_2/total aldicarb ratio are shown in Figures 31 and 32. They indicated that reducing the air entry value and the rate constants at depth did little to improve the calibration of LEACHMP. Total aldicarb concentrations for the 1986 sampling date were underestimated, while those for the 1987 date were overestimated. The ASO_2/total aldicarb ratio was also overestimated in 1985.

Rate Constants Determined in Column Studies

Column experiments with soil samples collected from the Augustine Cove field site were performed in the laboratory at the National Water Research Institute in Burlington, Ontario. The oxidation $(K_1{}^*)$ and hydrolysis (K_1) rate constants for the parent aldicarb were determined in these experiments. Although the pH produced during the tests was high (pH = 8.3), yielding aldicarb half-lives that may be low compared to those for the in situ conditions on PEI, the values of the rate constants were used as the starting point for another calibration series, independent from those described previously.

The predicted results for the independent calibration series, shown in Figures 33 and 34, are similar to those found in the previous calibration attempts. The total aldicarb concentrations were underestimated in 1986 and overestimated in 1987. It was recognized that further attempts to calibrate the model for the period from 1983 to 1987 would not produce significant improvements in the calibration. Adjusting the rate constants to increase the concentration in 1986 would only worsen the situation in 1987.

Calibration for the Period 1986–1988

In the final calibration series, an attempt was made to calibrate the model results to data from the second pesticide application period (1986–1988) only. The soil-pesticide concentration profile determined for the last day (December 31, 1985) of the simulation, which had been successfully calibrated for the first pesticide application period (1983–1985) (see Figure 24), was used as the initial soil-pesticide concentration profile (January 1, 1986) for this calibration series.
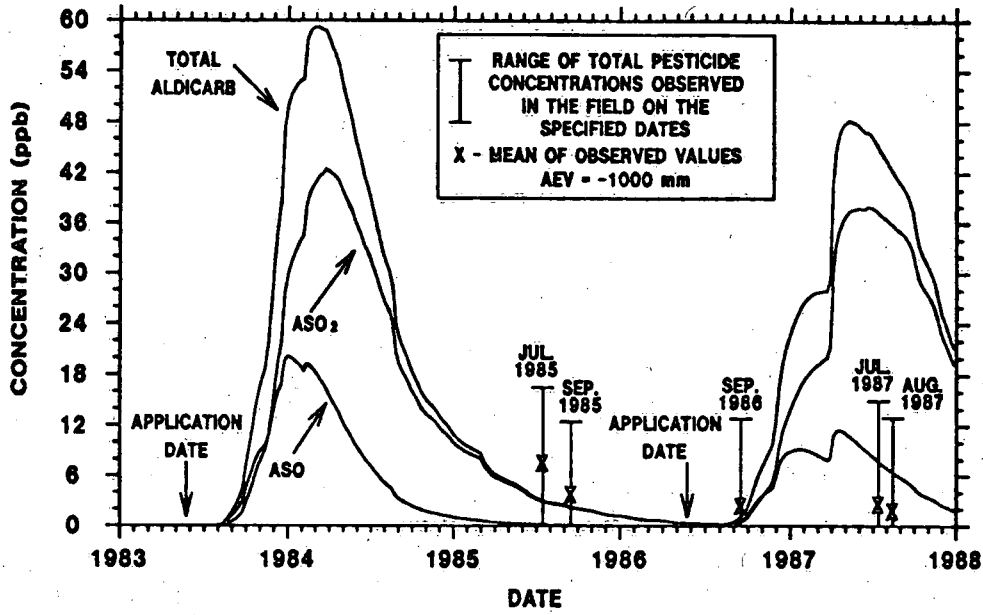
Figure 31. Predicted values of the total aldicarb concentration at a depth of 3.25 m with LEACHMP and the total aldicarb concentrations observed in the field (calibration for the period 1983–1987, adjusting air entry values and decreasing rate constants with depth).
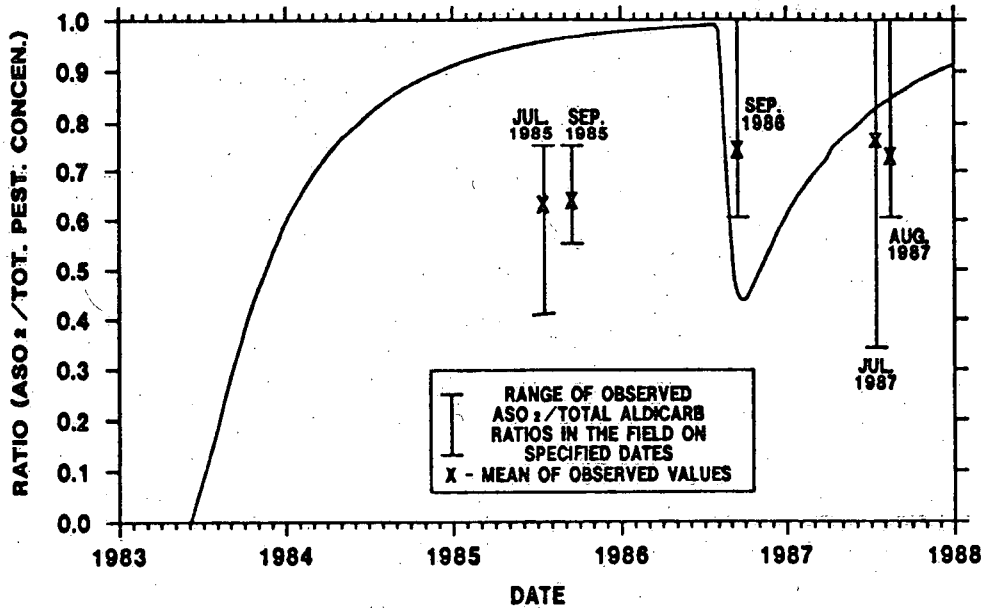
Figure 32. Predicted ASO$_2$/total aldicarb ratios at a depth of 3.25 m with LEACHMP and the range of ratios observed in the field (calibration for the period 1983–1987, air entry values and decreasing rate constants with depth).
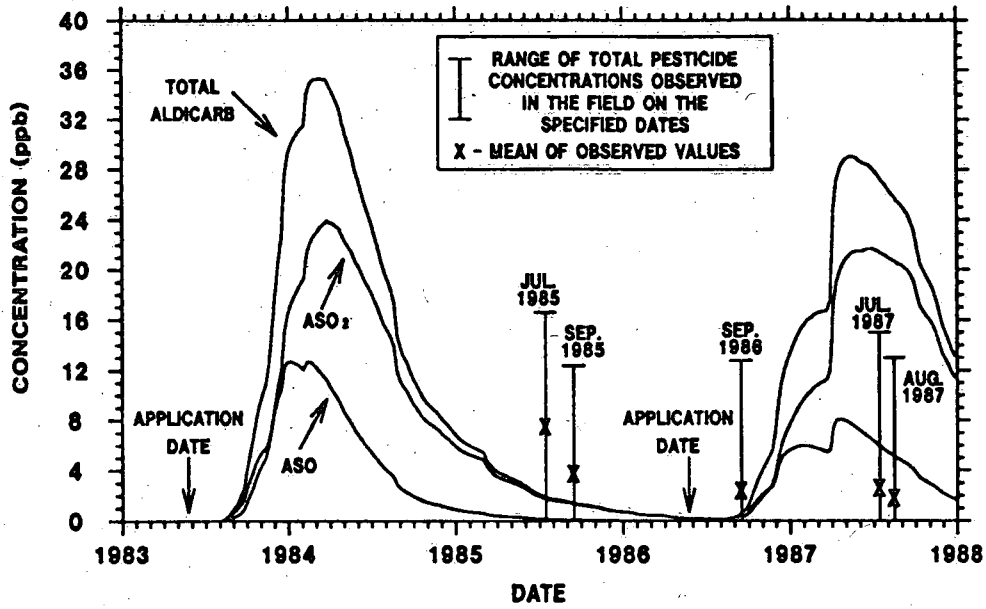
Figure 33. Predicted values of the total aldicarb concentration at a depth of 3.25 m with LEACHMP and the total aldicarb concentrations observed in the field (calibration for the period 1983–1987, starting with rate constants determined from columns experiments).
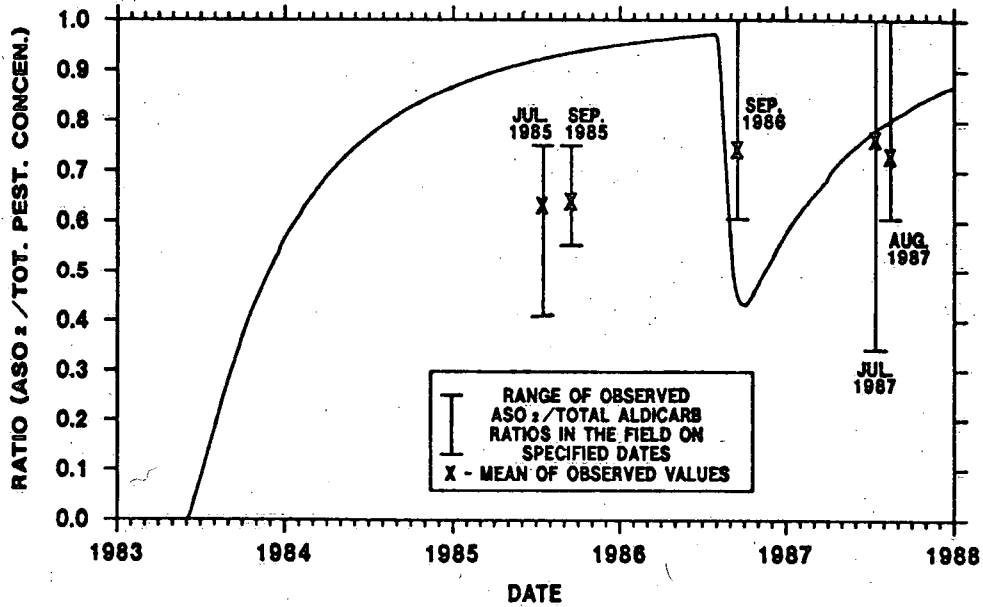
Figure 34. Predicted ASO_2/total aldicarb ratios at a depth of 3.25 m with LEACHMP and the range of ratios observed in the field (calibration for the period 1983–1987, starting with rate constants determined from column experiments).
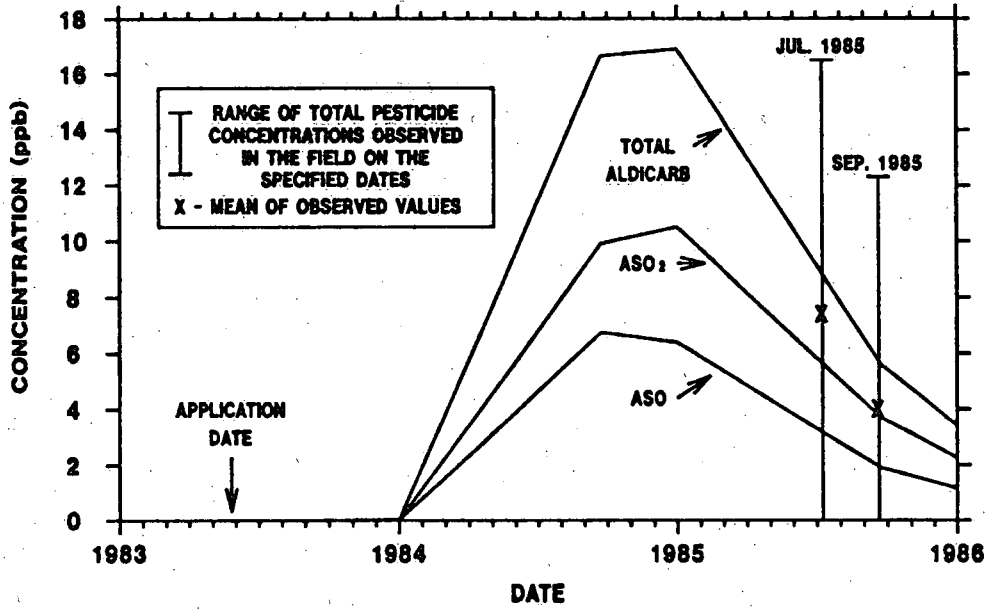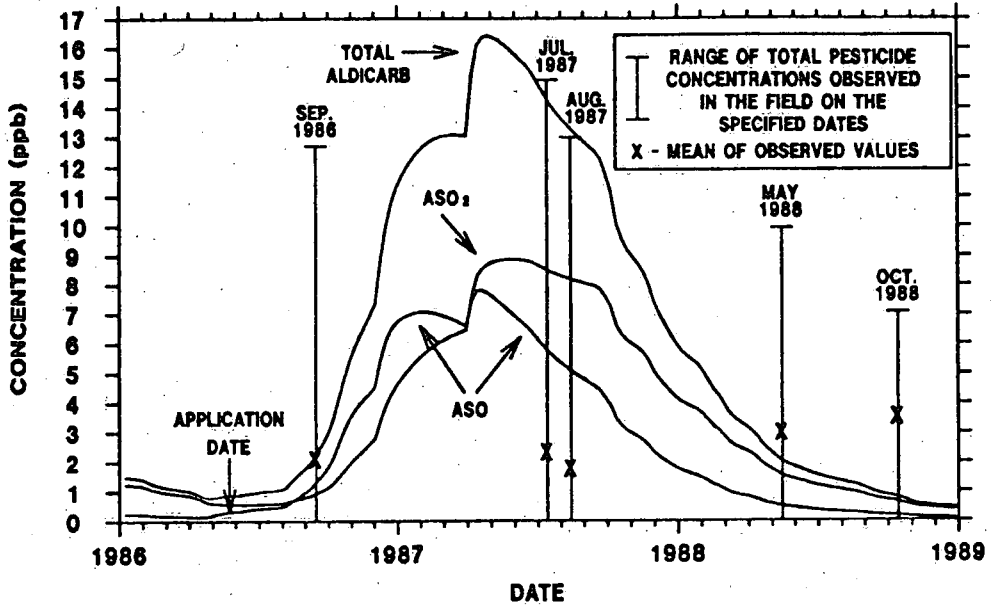
Figure 35. Predicted values of the total aldicarb concentrations at a depth of 3.25 m with LEACHMP and the and the total aldicrb concentrations observed in the field (calibration for the period 1986–1988).
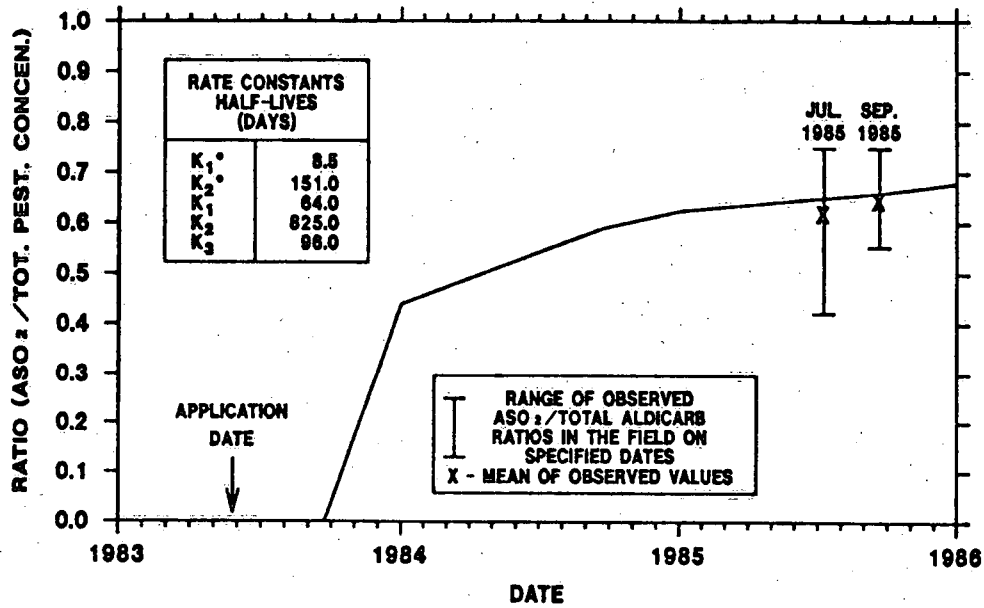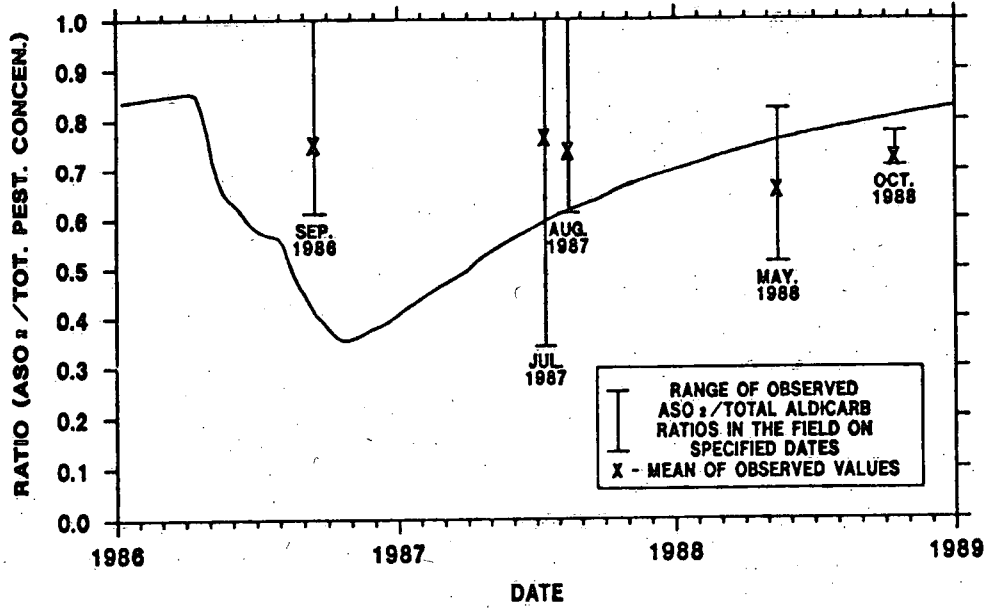

Figure 36. Predicted ASO₂/total aldicarb ratios at a depth of 3.25 m with LEACHMP and the range of ratios observed in the field (calibration for the period 1986–1988).

The final results for this calibration series are presented in Figures 35 and 36. The predicted total aldicarb concentrations were all within the observed range of the field data for the sampling dates. The concentrations for September 1986 and May 1988 were reasonably close to the observed mean values (within 1 ppb). However, the predicted concentrations for 1987 were again in excess of the mean values observed. The October 1988 mean value is based on a sampling of only four piezometers that generally had higher concentrations than the average concentration for the field. If all piezometers had been sampled in October 1988, the observed mean may have been closer to the predicted concentration. The ASO_2/total aldicarb ratios are outside the observed range for September 1986 and October 1988. Again, the October 1988 sampling consisted of only four piezometers, and the actual range of the ASO_2/total aldicarb ratio may have been larger if a more complete sampling had been undertaken. Based on the results presented in Figures 35 and 36, this calibration attempt cannot be considered as a successful calibration of the model.

LEACHMP SENSITIVITY STUDIES

Although it was not possible to adequately calibrate LEACHMP to the concentrations observed in the field, sensitivity studies were performed on the model parameters. These studies provide information on the processes that are most influential in controlling the fate of aldicarb in the unsaturated zone of a single, idealized, porous medium.

Model parameters evaluated through a sensitivity analysis include (1) the oxidation and hydrolysis rate constants, (2) the date and depth of the pesticide application, (3) pan evaporation values, and (4) the dispersivity value. The findings of these studies are summarized in the following subsections.

Sensitivity of the Total Aldicarb Concentration and Ratio to the Pesticide Degradation Rate Constants

Sensitivity studies were performed on the oxidation and hydrolysis rate constants of aldicarb and its daughter products. Initial values for the oxidation and hydrolysis rate constants were taken from the calibration simulations for the first set of field data discussed previously. These values were used as a base for the sensitivity studies, and the results of a simulation conducted with these rate constants were used as a reference against which all subsequent simulations could be compared. Six simulations were performed for each of the two oxidation and three hydrolysis rate constants.

The value of the selected rate constant was both increased and decreased by factors of 2, 5, and 10, while the remaining rate constants were held constant. The time series plots of the total aldicarb concentration and the ASO_2/total aldicarb ratios predicted in the simulations were then compared to the reference results.

Five plots are presented in Figure 37, one series of simulations for each of the oxidation and hydrolysis rate constants. The reference rate constants are shown in the upper right-hand corner of Figure 37.

For the case under study, the total aldicarb concentration (AS + ASO + ASO_2) was found to be most sensitive to the oxidation (K_1^*) and hydrolysis (K_1) rate constants of the parent aldicarb (see Figure 37). The predicted peak total aldicarb concentration ranged from approximately 20 to 110 ppb for a change of two orders of magnitude in the rate constants K_1^* and K_1.

The total aldicarb concentration was found to be least sensitive to the value of the rate constant for the oxidation of aldicarb sulfoxide (K_2^*). Predicted peak total aldicarb concentrations ranged from 55 to 85 ppb for a change of two orders of magnitude in the oxidation rate constant K_2^*.

Although neither of the two oxidation rate constants, K_1^* or K_2^*, leads to a direct reduction in the total aldicarb concentration (see Figure 1), the total aldicarb concentration is sensitive to one (K_1^*) and not to the other (K_2^*). The relative magnitude of the rate constants K_1^* and K_1 found in the best model calibration attempts are large in comparison to the values of the other rate constants. This indicates that the half-lives for K_1^* and K_1 are much smaller than those for the other reactions, and is consistent with the findings of Zhong et al. (1986).

If the oxidation rate constant K_1^* is small (a long half-life), a significant portion of the parent aldicarb will degrade via hydrolysis (K_1) before it can be oxidized to ASO and ASO_2. In this case, the total aldicarb concentration will decline more rapidly because the hydrolysis rate constants, K_2 and K_3, for ASO and ASO_2, respectively, are significantly smaller than the hydrolysis rate constant for AS (K_1) (the half-lives for ASO and ASO_2 are larger than the half-life of AS). Aldicarb is maintained as the parent pesticide, AS, for a longer period, where it degrades by the relatively rapid hydrolysis reaction (K_1).

A large oxidation rate constant (short half-life) for K_1^* will lead to the quick oxidation of AS to ASO, and
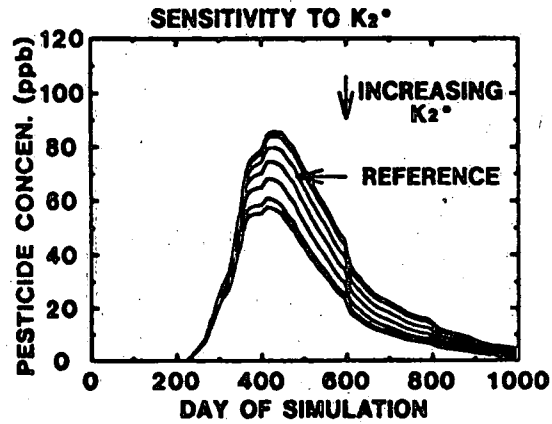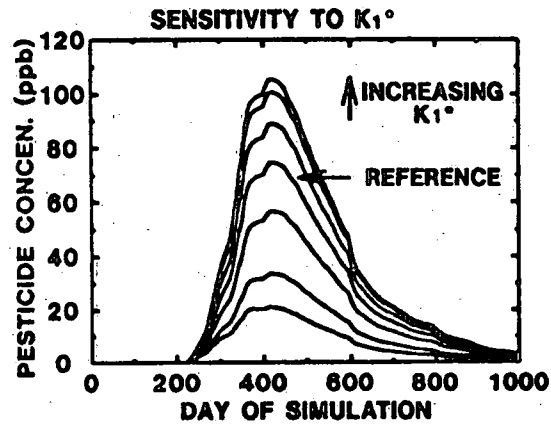
SENSITIVITY TO K₁°

SENSITIVITY TO K₂°

RATE CONSTANTS FOR REFERENCE SIMULATION		
	(0-0.4m)	(0.4-4.3m)
K_1^*	0.09082	0.01819
K_2^*	0.01125	0.00225
K_1	0.04812	0.00962
K_2	0.00374	0.00075
K_3	0.00962	0.00192

SENSITIVITY TO K₁

SENSITIVITY TO K₂
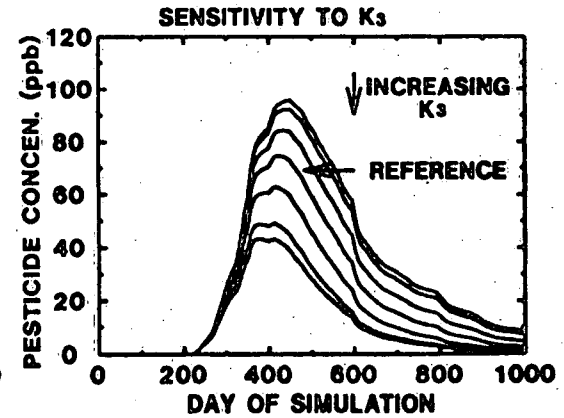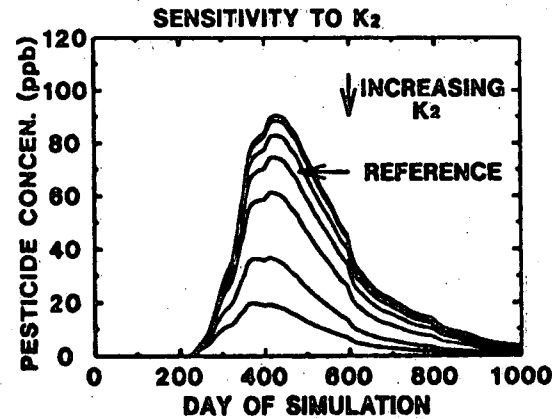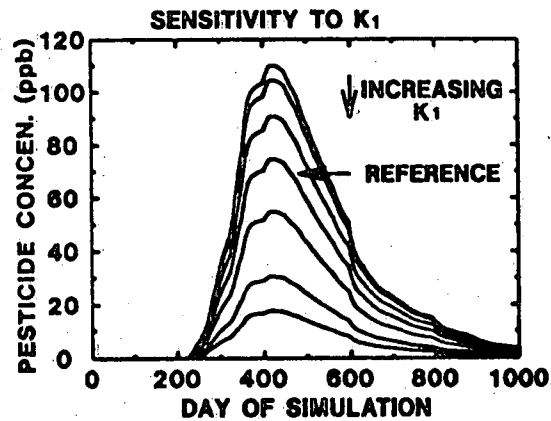
SENSITIVITY TO K₃

Figure 37. Sensitivity of the total aldicarb concentration at a depth of 3.25 m to the five degradation and transformation rate constants as predicted by LEACHMP. In each plot, the value of the selected rate constant is both increased and decreased by factors of 2, 5, and 10 from the reference value that is shown in the upper right-hand corner.

the total aldicarb concentration will persist at higher levels because the rate of the hydrolysis reaction of ASO is slower than that of AS.

In contrast to the total aldicarb concentration, the ASO_2/total aldicarb ratio (Figure 38) was not sensitive to the rate constants K_1^* and K_1, but was most sensitive to the value of the oxidation rate constant K_2^*. This rate constant is responsible for the partitioning of the pesticide between the two daughter products, ASO and ASO_2. The ASO_2/total aldicarb ratio is actually defined by

$$\frac{[ASO_2]}{[ASO] + [ASO] + [ASO_2]} \qquad (16)$$

but because the parent aldicarb, AS, disappears quickly and the ratio is effectively defined by

$$\frac{[ASO_2]}{[ASO] + [ASO_2]} \qquad (17)$$

it is therefore, essentially controlled by the rate constant K_2^* that describes the transformation from ASO to ASO_2. The ratio was also found to be sensitive to the rate constant K_3, and somewhat so to the rate constant K_2.

Sensitivity to Date and Depth of Pesticide Application

The total aldicarb concentration was also found to be sensitive to the date of application, but not to the depth of incorporation of the pesticide. Two factors were considered when determining the influence of the date of application on the total aldicarb concentration. The first factor considered was the change in the amount of infiltration that occurred as the date of application was extended from May 17 (application at planting) to June 21 (application at seedling emergence). Infiltration amounts are generally higher at the time of a mid-May application (because of a large spring recharge) than in mid-June (see Figure 10). Six simulations were performed to investigate the change in the total aldicarb concentration due solely to the change in the amount of infiltration as the application date was extended from May 17 to June 21. The simulations are representative of the period from 1983 to 1985, and the pesticide application that is simulated occurs on day 144 of the first year. The results of the simulations are presented in Figure 39.

For the period under study, the peak total aldicarb concentration declined as the application date was extended from day 137(a) (May 17) to day 158(a) (June 7). However, the decrease in the peak concen-

tration was small, declining from approximately 75 ppb (day 137[a]) to only 65 ppb (day 158[a]). Concentrations began to rise again as the application date was extended from day 158(a) to day 165(a) (June 14) and day 172(a) (June 21), and the peak concentration returns to approximately 75 ppb. The results indicate that the total aldicarb concentration reaching the water table does not change appreciably (<10 ppb) with a later pesticide application date when only the change in the amount of infiltration is considered.

The second factor that must be considered in a later application date is the temperature effect. The degradation of aldicarb is dependent on the temperature (see Figure 20), and the rate of degradation increases with increasing temperatures. The mean monthly soil temperature on Prince Edward Island (at a depth of 150 mm) increases by approximately 5°C between the months of May and June (MacDougall et al. 1981). Two additional simulations were performed with later pesticide application dates to investigate the influence that the change in temperature (due to a later application date) would have on the total aldicarb concentration. The simulations for the application dates, day 165(a) (June 14) and day 172(a) (June 21), were performed again, with the degradation rate constants in the top 400 mm of the soil adjusted to reflect a soil temperature of 15°C rather than 10°C, as was the case in the earlier simulations. The simulations are denoted as day 165(b) and day 172(b) in Figure 39. The temperature increase corresponds to the 5°C increase in the mean monthly soil temperature between May and June reported by MacDougall et al. (1981). The rate constants below 400 mm remained unchanged. The values for the rate constants K_1^* and K_1 in the top 400 mm were taken from laboratory experiments conducted by Lemley et al. (1988) at 15°C, while the remaining rate constants for the top 400 mm were taken from the results of experiments at 25°C (also conducted by Lemley et al. [1988]) and were adjusted to represent a temperature of 15°C.

The results presented in Figure 39 show an appreciable decline in the total aldicarb concentration when the temperature of the surface layers of the soil are increased. The peak concentrations fell from 75 ppb (day 172[a]) to 10 ppb (day 172[b]) for an application on the same day when the effect of temperature was considered.

The peak pesticide concentrations reaching the water table are virtually the same for the pesticide application dates of day 137(a) and day 172(a) in Figure 39. In these simulations, only the change in the amount of infiltration is considered as the appli-

SENSITIVITY OF RATIO TO K₁*

SENSITIVITY OF RATIO TO K₂*

	RATE CONSTANTS FOR REFERENCE SIMULATION	
	(0-0.4m)	(0.4-4.3m)
K_1^*	0.09082	0.01819
K_2^*	0.01125	0.00225
K_1	0.04812	0.00962
K_2	0.00374	0.00075
K_3	0.00962	0.00192

SENSITIVITY OF RATIO TO K₁

SENSITIVITY OF RATIO TO K₂

SENSITIVITY OF RATIO TO K₃
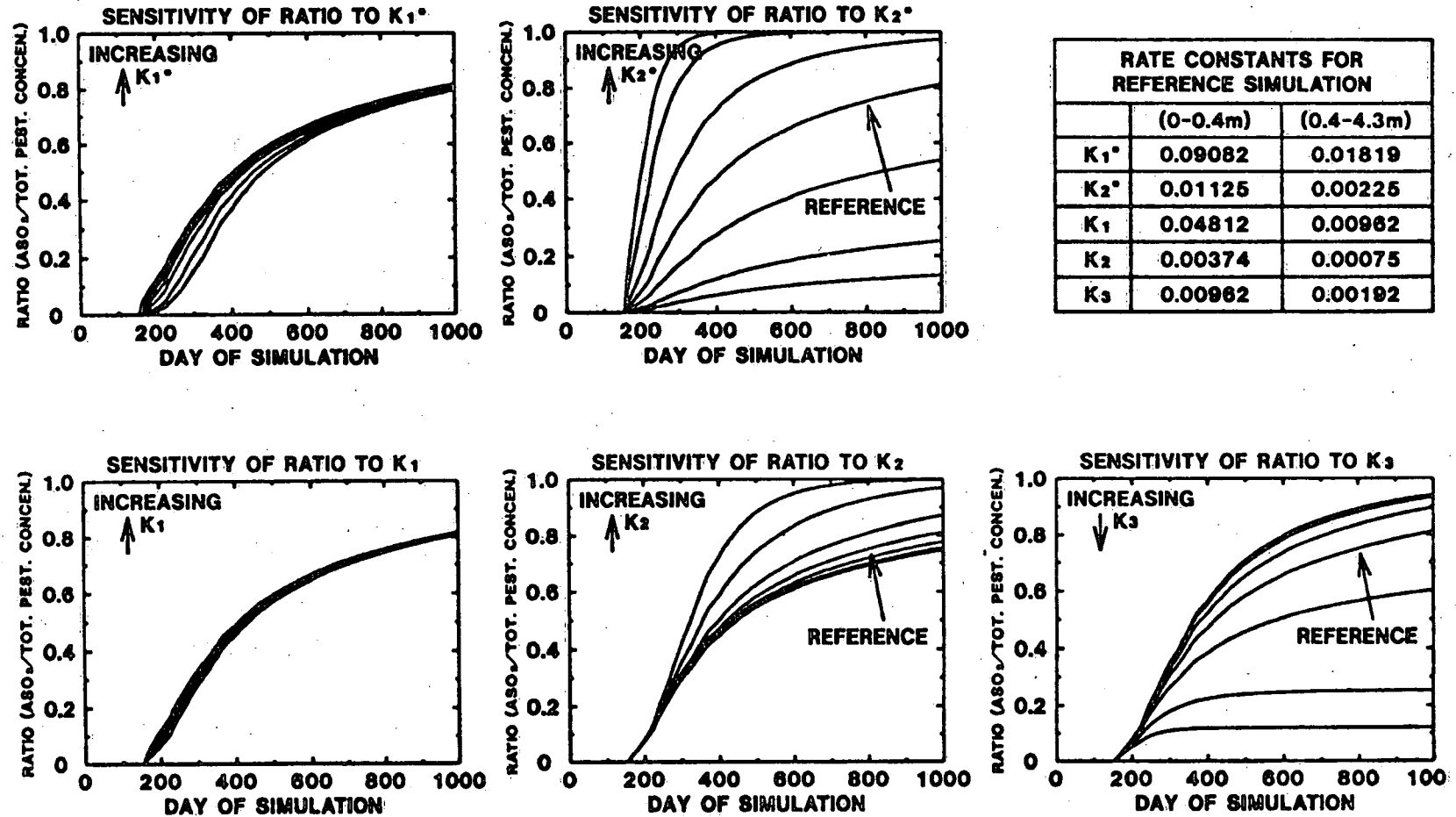
Figure 38. Sensitivity of the ratio (ASO_2/total aldicarb) at a depth of 3.25 m to the five degradation and transformation rate constants as predicted by LEACHMP. In each plot, the value of the selected rate constant is both increased and decreased by factors of 2, 5, and 10 from the reference value that is shown in the upper right-hand corner.
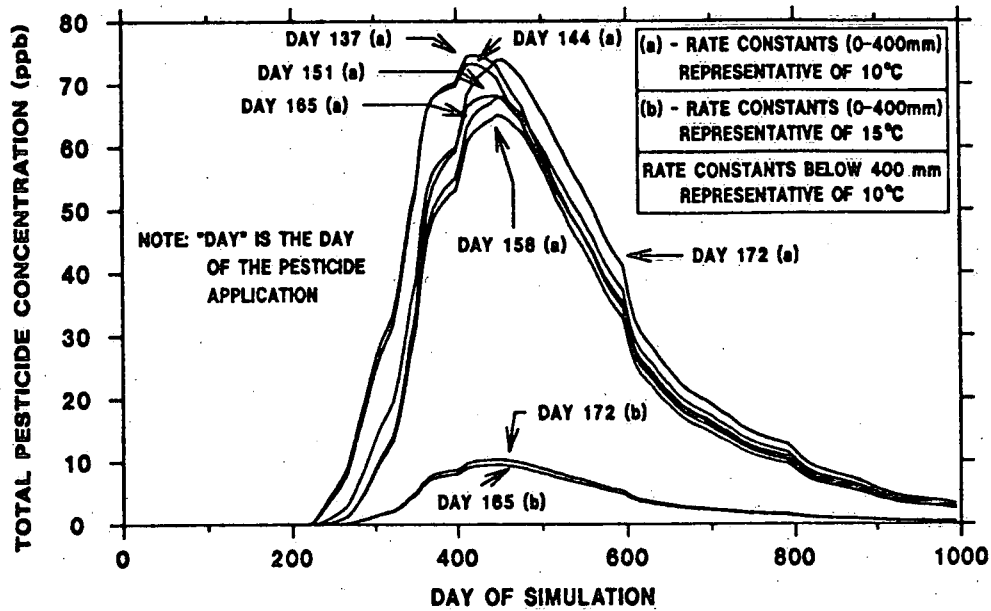
Figure 39. Sensitivity of the total aldicarb concentration at a depth of 3.25 m predicted by LEACHMP to the date of application of the pesticide.
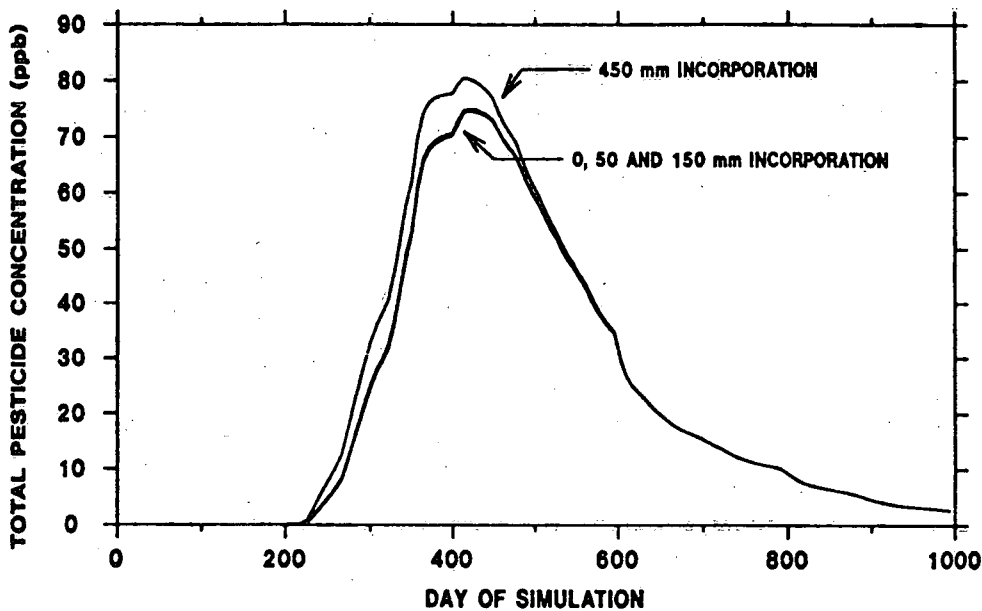
Figure 40. Sensitivity of the total aldicarb concentration at a depth of 3.25 m predicted by LEACHMP to the depth of incorportion of the pesticide.

cation date of the pesticide is delayed from day 137(a) to day 172(a). However, there is a significant decline in the peak pesticide concentration reaching the water table when the temperature effects of the delayed pesticide application are superimposed (day 165[b] and day 172[b] in Figure 39). This implies that the change in temperature, rather than the change in the amount of infiltration, is the most important factor in the reduction of the total aldicarb concentration at the water table as the pesticide application is delayed from planting (approximately day 137) to an application at seedling emergence (approximately day 172). Applications on days 165(a) and 172(a) without an adjustment in the rate constants for the temperature effect resulted in a reduction in the peak concentration by a factor of only approximately 1.2 from those produced with an application on day 137(a). When the temperature effect was considered (day 165[b] and day 172[b]), the peak concentration was reduced by a factor of more than 5.

It must be recognized that these simulations were conducted with a constant soil temperature throughout the year (10°C for days 137[a] to 172[a] and 15°C in the second set of simulations performed for days 165[b] and 172[b]) and that the simulations do not accurately represent the temperature fluctuations (mean monthly soil temperatures of -1.3°C in February and 17.3°C in August) occurring in the field during the course of a year (MacDougall et al. 1981). However, the significant reduction predicted in the total aldicarb concentration with an emergence application suggests that applications made in mid-June (with warmer soil temperatures) should significantly reduce the amount of pesticide leaching to the groundwater table.

The total aldicarb concentration was found to be insensitive to the depth of application (Figure 40) for a reasonable range of incorporation depths. The small variation observed with the 450-mm depth of incorporation results from the pesticide being incorporated to a depth beneath the active root layer where degradation rates decline sharply, representing a worst-case scenario.

Sensitivity to Pan Evaporation Values

Observed pan evaporation values are often multiplied by a pan evaporation coefficient when estimating evaporation from reservoirs or lakes. A typical value for the pan evaporation coefficient is often taken as 0.7 (Linsley et al. 1982). Pan evaporation values in the LEACHMP code are not reduced by this pan evaporation coefficient, so an additional simulation was performed to test the influence that a pan evaporation coefficient would have on the total pesticide concentration reaching the water table. The total pesticide concentrations predicted by LEACHMP using the reported pan evaporation values were compared to the predicted concentrations for a run where the pan evaporation values in the input data set were reduced to 70% of the reported values (equivalent to a pan evaporation coefficient of 0.7). The results in Figure 41 indicate that the model is relatively insensitive to a pan evaporation coefficient of 0.7.

The depth at which the total pesticide concentration is observed may have influenced the amount of variation seen. The effects of water loss from evapotranspiration may be dampened by the time the water infiltrates to a depth of 3.25 m. Variations in the total aldicarb concentration due to the pan evaporation coefficient may be more evident if the total aldicarb concentrations were observed at a shallower depth where the effects of evapotranspiration may be more pronounced.

Sensitivity to the Value of Dispersivity

The influence of the dispersivity value on the total aldicarb concentration was investigated by performing a number of simulations with different values of dispersivity selected from an appropriate range indicated in Figure 26. The total aldicarb concentration was found to be sensitive to the value of dispersivity. The predicted peak concentration in Figure 42 ranged from approximately 60 to 135 ppb, and the timing of the peak concentration at a depth of 3.25 m varied from 120 to 300 days after the date of the pesticide application.

A dispersivity value of 10 cm selected from Figure 26 was used in the majority of the attempted calibration simulations. At this value of dispersivity, a compromise was reached between the magnitude (75 ppb) of the peak total aldicarb concentration and the time of occurrence of the peak (275 days after application) at or just below the water table. This more closely approximates the relatively constant and persistent nature of the pesticide observed in the field. Smaller dispersivity values (e.g., 1.0 cm) result in a very high peak concentration, while larger values (e.g., 100 cm) reduce the peak concentration significantly, but cause the peak to move through the profile much more rapidly.

PAN COEFFICIENT = 0.7

PAN COEFFICIENT = 1.0

TOTAL PESTICIDE CONCENTRATION (ppb)

DAY OF SIMULATION
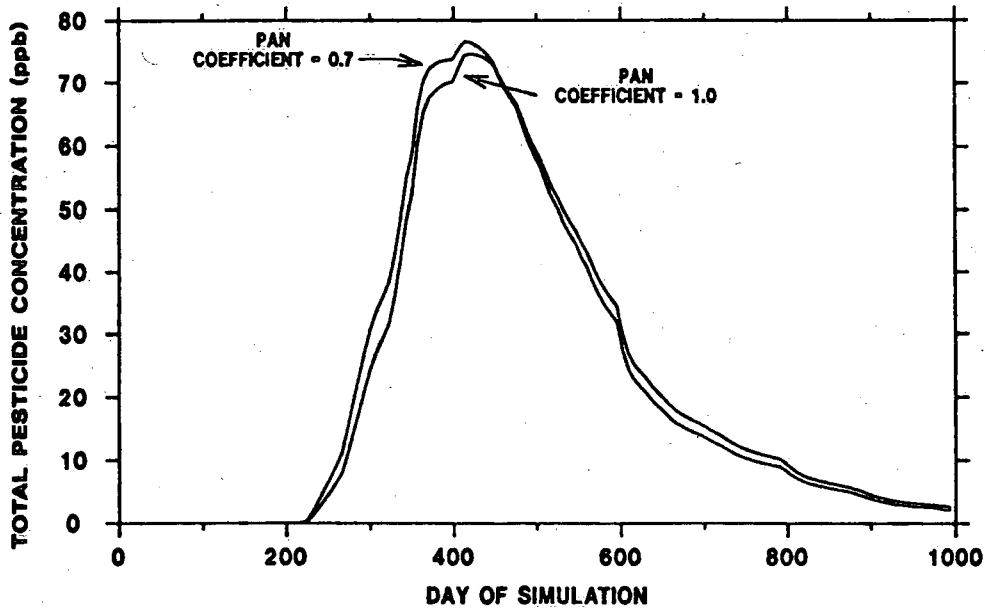
Figure 41. Sensitivity of the total aldicarb concentration at a depth of 3.25 m predicted by LEACHMP to the value of the pan evaporation coefficient.

RATE CONSTANTS (HALF-LIVES IN DAYS)		
	(0–0.4m)	(0.4–4.3m)
K °	7.6	38.1
K °	61.6	308.0
K	14.4	72.0
K	185.0	926.0
K	72.0	360.0

10 mm

50 mm

100 mm

200 mm

500 mm

1000 mm

TOTAL PESTICIDE CONCENTRATION (ppb)
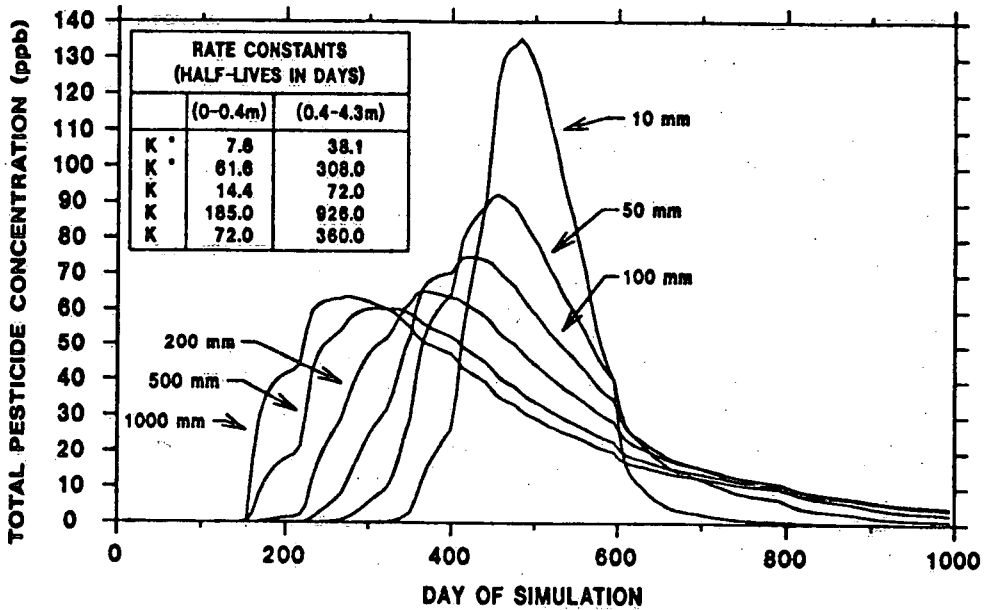
DAY OF SIMULATION

Figure 42. Sensitivity of the total aldicarb concentration at a depth of 3.25 m predicted by LEACHMP to the value of dispersivity.

DISCUSSION OF SIMULATION RESULTS

It appears from the numerous attempts (over 100 simulations) that have been made, that the model cannot be adequately calibrated to the data collected from the field sites on Prince Edward Island. Although the concentrations and ratios in most instances fall within the range of the observed field data, the data from individual wells at the two field sites indicate that total aldicarb concentrations and ratios were much more stable over the period of the monitoring program than was predicted by LEACHMP.

The inability of the model to reproduce the concentrations observed in the field lends support to the theory that other mechanisms not accounted for in LEACHMP are involved in the fate and migration of aldicarb in the sandstone aquifer of Prince Edward Island. The long half-lives predicted for the oxidation and hydrolysis reactions by the model in the best calibration attempt suggest that there are processes at work that may inhibit the degradation of aldicarb in the unsaturated zone. The persistence of high and relatively consistent concentrations observed in the field over the five-year monitoring program also suggests that there may be some sort of in situ storage mechanism acting to retain the aldicarb species, slowly releasing the pesticide residues over time. There are several possible mechanisms that may be involved:

1. pH and temperature conditions that lead to the inhibition of aldicarb degradation,

2. adsorption of the pesticide with a much slower desorption,

3. downslope migration of aldicarb within the flow system,

4. slow infiltration through the unsaturated till, and

5. matrix diffusion in the sandstone unit.

The likelihood of each of these mechanisms accounting for the differences between the concentrations observed in the field and the predicted concentrations with LEACHMP is discussed below.

Inhibition of Aldicarb Degradation

There are a number of natural and anthropogenic conditions existing at the field sites that may lead to the inhibition of the degradation of the aldicarb residues. As discussed earlier, the rate of the detoxifying hydrolysis reaction is highly dependent on both the pH and temperature. The rate of the hydrolysis reaction is slowest in the pH range of 5 to 6 (see Figure 20) because neither acid- nor base-catalyzed hydrolysis reactions are dominant in this pH range. Therefore, the persistence of aldicarb residues is greatest in this range. The rate of degradation at a given pH also decreases with decreasing temperatures.

The soils at the three field sites (see Table 1), the ground water in the lowland discharge areas (see Tables C-1 to C-3), and the spring rain and snowmelt on PEI are all acidic (in the range of pH = 4 to 7) and will all contribute to a decrease in the rate of the hydrolysis reactions of the aldicarb residues by moving the pH towards the zone of greatest persistence (pH = 5 to 6 in Figure 20).

In addition, anthropogenic conditions may also lead to the inhibition of the degradation of the pesticide residues. The pesticide is applied at planting in mid-May, when the mean soil temperature at a depth of 150 mm is about 7.0°C (MacDougall et al. 1981). The degradation of aldicarb will be much slower than if the application were delayed until mid-June (plant emergence), when the mean soil temperature at 150 mm rises to approximately 13.4°C (MacDougall et al. 1981). Aldicarb, being a systemic pesticide, is extracted from the soil by the plant root system. However, with an application of the pesticide at planting, there is no root system developed to extract the pesticide from the soil, and much of the pesticide may be leached away before the root system is developed to a sufficient extent to extract an appreciable amount of the pesticide. An application of the pesticide at plant emergence would allow more aldicarb to be extracted by the developing root system of the plant.

Ammonium-based fertilizers are also added to the fields at the time of planting. The PHREEQE simulations conducted to investigate the effect of ammonium oxidation on the half-life of ASO, while not being quantitatively accurate for the conditions at the field sites, do provide qualitative information that indicates that the oxidation of ammonium can lead to significantly longer half-lives for the aldicarb residues. In the simulations that were performed with PHREEQE, the half-life of ASO rose from 2 days to 460 days with the oxidation of 0.001 M of ammonium.

Sorption of Aldicarb with a Subsequent Slow Release

It is unlikely that significant amounts of aldicarb are being adsorbed at the three field sites. Sorption is

generally inversely proportional to the solubility of the chemical (Moye and Miles 1988), and aldicarb and its two daughter products all have relatively high water solubilities (≥ 6000 mg/L) (Carsel et al. 1985).

Studies have also found little evidence of significant sorption of the three aldicarb species in soil that does not have a significant organic matter content, which is the case at the field sites on PEI (Richey et al. 1977; Miles and Delfino 1985; Lemley et al. 1988). Aldicarb was essentially nonretarded in sandy (Palmyra) soils on Long Island, N.Y., with f_{oc} values less than 2% (Zhong et al. 1986), and Moye and Miles (1988) conclude that significant sorption of aldicarb should occur only in highly organic soils. Information presented in Table 1 and Table A-1 (Appendix A) indicates that the soils at the field sites cannot be considered highly organic because f_{oc} values are generally less than 2% in the upper 300 mm and decline to approximately 0.1% below this depth.

Finally, laboratory column tests performed on samples collected from the field sites produced retardation factors of 1.25 and 1.26 for aldicarb and aldicarb sulfoxide, respectively. This indicates that the aldicarb residues move with an average velocity equal to 80% of that of the groundwater (Jackson et al. 1989), and that the movement of aldicarb should, therefore, be controlled largely by the bulk movement of ground water in the PEI sandstone.

For the reasons outlined above, the adsorption of aldicarb, with a slow subsequent desorption of the pesticide, could not solely account for the persistence of aldicarb observed at the field sites.

Downslope Migration of Aldicarb

Generally, total aldicarb concentrations observed in the piezometers in the upland recharge areas (i.e., AC4 in Figure 12 for Augustine Cove) were significantly lower than the concentrations found in wells farther along the flow path (i.e., AC6, AC7, and AC9 in Figure 12). Evidence of this observation at the Mill Valley site is found in Figure 13.

In addition, the pH levels in the upland recharge areas tend to be greater than or equal to 7.0 (see Tables C-1 and C-2), suggesting that the degradation rate of the aldicarb residues would be relatively rapid at these pH levels (see Figure 20). Therefore, any contribution of aldicarb residues supplied from the upland areas to the downslope wells would be significantly lower than the original concentrations observed in the wells in the upland areas. The con-

centrations observed in the upland areas prior to any migration of the pesticide towards the discharge area are lower than those found in the discharge areas. Therefore, the process of downslope migration could not solely account for the high and relatively consistent concentrations observed in the field over the five-year monitoring program.

Slow Infiltration through the Unsaturated Till

A relatively high, continuous flux of pesticide percolating through the vadose zone in the direct vicinity of the downslope wells would have to accompany the processes discussed above if the concentrations observed in the field are to be explained.

In the past, it was believed that vertical infiltration of water in the unsaturated zone was primarily controlled by fractures and macropores in the unsaturated zone. However, Foster (1975), Beven and Germann (1981), and others have proposed alternative recharge mechanisms for infiltration in the unsaturated zone. It is now recognized that the infiltration of water and solutes in the unsaturated zone is affected to a significant degree by the matrix porosity, as well as by the fractures and/or macropores. Fractured materials with significant matrix porosity have been termed fissured porous media or dual porosity media and include sandstones, limestones, and chalks. The recharge processes that are occurring in the PEI sandstone may be similar to those proposed for the British Chalk that underlies a large portion of Britain (Foster 1975).

In studies of the tritium profiles in the British Chalk, it has been concluded that 85% of the total flow in the vadose (unsaturated) zone occurred by intergranular seepage at a rate of less than a metre per year. Foster (1975), in reviewing this work, presented a new model for the recharge mechanisms in the unsaturated zone in the British Chalk. Reeves (1979) provides a good description of the infiltration model and mechanisms proposed by Foster (1975). The Chalk is divided into two components:

1. an intergranular (micro) pore space, which is almost fully saturated with static soil water, and

2. fissures, fractures, and macropores, with varying levels of saturation, which are responsible for water transmission and for free-draining water storage (2%–3% of total porosity).

The second group is further subdivided into two classes. For the sake of brevity, the term fissure is

used to describe the three components (fissures, fractures, and macropores) of the second grouping.

2.a microfissures – profuse, small, effective openings responsible for slow but persistent water transmission in the unsaturated zone, and

2.b macrofissures – rare, effective openings $\approx$ 1 mm responsible for rapid transmission of water in the unsaturated zone during high intensity rainfall events and for transmission of water in the saturated zone.

In the proposed unsaturated model, infiltrating water from irrigation or rainfall is first used to make up any water deficit in the intergranular pores resulting from evapotranspiration from the root zone. Next, the small microfissures are filled, replacing any water lost by evapotranspiration and/or gravity drainage. Infiltration in excess of this replacement volume begins to progressively fill larger and larger pores, thereby activating flow in the macrofissures. Initiation of flow in the macrofissures significantly increases the hydraulic conductivity of the unsaturated zone, raising the hydraulic conductivity of the soil until it either reaches the saturated hydraulic conductivity of the soil or is equal to the infiltration rate of the rainfall or irrigation event (Reeves 1979).

The amount and intensity of rainfall required to produce macrofissure flow is highly dependent on the antecedent moisture conditions. The establishment of flow in these large pores will result in the rapid transmission of water and solutes (up to several metres per hour) and, depending on the continuity of the pores, may account for the rapid response of the water table to infiltration events (Reeves 1979). It is unlikely that solutes being carried in the macrofissures would have sufficient time to diffuse into the intergranular matrix to any great extent.

Infiltration intensities producing macropore flow may not be that common. Based on tritium concentrations in the saturated zone in the British Chalk, Reeves (1979) estimated that only 10%–20% of the infiltration during a year occurred by rapid transmission through the macropores, with the remaining portion occurring via the slow microfissure/intergranular flow.

The slow infiltration of the recharge water has significant implications for the transport of solutes in the unsaturated zone. If a large portion of the infiltration takes place as slow microfissure flow (approximately 70 mm/day in the case of the British Chalk)

(Oakes 1979), then there may be sufficient time for lateral molecular diffusion of the solutes from the microfissure water into the porous matrix. The time available for the diffusion process, the fissure aperture, and the matrix porosity are all important factors in determining the extent of solute diffusion (Foster and Smith-Carington 1980).

The flow of water in the microfissures increases the amount of solute diffusion into the matrix by increasing both the time and area of contact between the infiltrating solution and the matrix (Oakes 1979). The diffusion process is considered to be reversible, with solutes diffusing into the matrix when solute concentrations are higher in the microfissure flow than in the matrix pore water, and diffusing back into the fissure water from the matrix when the chemical gradient is reversed. During periods with no infiltration, the solutes in the matrix pore water, will diffuse within the pore water and equilibrate the concentration in the pores (Foster 1975). Foster (1975) and Oakes (1979) have proposed that these mechanisms may account for the observed velocity difference between water (250 m/yr) and tritium (1 m/yr) in the British Chalk, accounting for the persistence of high concentrations of tritium in the upper vadose zone. Reeves (1979) quotes the work of Young et al. and Mercer and Hill, who found that nitrate and chloride ions behave in a manner similar to that of tritium in the Chalk, and Foster (1975) concludes that the proposed diffusion process has a considerable capacity for solute storage.

If a similar recharge process is occurring on Prince Edward Island, it is possible that a reservoir of aldicarb residues may have accumulated in the vadose zone by the diffusion process, and that the stored aldicarb residues are then slowly released and leached to the water table. Support for this hypothesis comes from a study conducted on Long Island, New York. Pacenka et al. (1987) observed large amounts of aldicarb being stored in the vadose zone even though the material in the vadose zone was a coarse-grained material and was very permeable. Aldicarb residues were still being leached to the water table five years after the last application of the pesticide on Long Island. It is therefore possible that the slow infiltration of the pesticide residues may be responsible, in part, for the persistent nature of the aldicarb residues in the sandstones of Prince Edward Island.

Matrix Diffusion in the Saturated Sandstone

Matrix diffusion processes in the saturated zone may also be partially responsible for the persistence

of aldicarb in the PEI sandstone. Grisak and Pickens (1981) have shown that relatively high concentrations of solutes can diffuse from the mobile fracture water into the relatively immobile matrix water of the saturated bedrock, allowing large amounts of solute to be stored over time. As conditions change and water with a lower solute concentration passes through the fractures, the chemical gradient will be reversed and reverse diffusion will occur, increasing the level of contamination in the mobile fracture water.

Francis and Gale (1988) report intergranular (matrix) porosities averaging 16% in the fractured sandstones on Prince Edward Island, indicating that the matrix diffusion mechanism could provide a large amount of storage for aldicarb residues and could partially account for the persistence of aldicarb observed in the field.

LEACHMP is a one-dimensional model for simulating the transport of a solute in a single porous medium. It has no mechanism to account for the temporary storage of aldicarb in a dual porosity system such as the fractured sandstones on Prince Edward Island. Therefore, it cannot be expected to reproduce the results observed in the field at the three sites on PEI if the mechanisms discussed here are acting to retain the aldicarb residues, slowly releasing them to the water table over time.

Summary and Conclusions

Prince Edward Island is dependent on ground water for essentially all of its water needs. Its economy is also dependent on the agriculture industry and its use of pesticides. To ensure that the use of pesticides does not adversely affect the quality of the groundwater supplies, an understanding of the fate of pesticides in the subsurface must be attained. The following summary and conclusions were derived from the study of the fate of aldicarb in the sandstones and overlying till of Prince Edward Island.

1. Results from the five-year groundwater quality monitoring program (1985–1989) reveal that aldicarb residues were maintained at relatively high concentrations at the three field sites on Prince Edward Island. For example, concentrations of total aldicarb as high as 6.6 ppb and 5.6 ppb were found at the Augustine Cove and Mill Valley field sites, respectively, for groundwater samples taken more than two years after the last pesticide application. Total aldicarb concentrations were relatively consistent over the duration of the monitoring program, and little short-term variation was observed during a period of frequent sampling in May 1988.

Total aldicarb concentrations were, in general, lower at the sites with a greater unsaturated zone thickness. The greater unsaturated zone thickness produced more alkaline conditions and resulted in ground water with a higher pH, which would in turn result in the faster degradation of the aldicarb residues.

2. The ASO_2/total aldicarb ratios were also relatively consistent over the five-year sampling period. Ratio values were higher than those reported for studies conducted in the United States. This is most likely due to the highly oxygenated conditions found in the groundwater at the field sites on PEI, which may be enhancing the oxidation of aldicarb sulfoxide to aldicarb sulfone and thereby raising the value of the ASO_2/total aldicarb ratio. The pH and temperature effects that inhibit the degradation of aldicarb on PEI may also be partially responsible for the high ratio values observed. By inhibiting the degradation of the aldicarb residues, more time is available for the system to proceed to ASO_2 via transformation, thereby increasing the ratio values.

3. Nitrate concentrations also demonstrated a remarkable persistence, with relatively constant concentrations over the five-year monitoring period. The field data collected demonstrates that a relationship may exist between high concentrations of aldicarb residues and high levels of nitrate. The acidity produced by the nitrification of ammonium fertilizers may lower the pH to a point where the degradation of aldicarb is inhibited, leading to the persistence of high concentrations of aldicarb residues. Simulations conducted with the PHREEQE model also demonstrate that the oxidation of ammonium may be inhibiting the degradation of the aldicarb residues.

4. The field sites on Prince Edward Island were hydraulically tested. Slug tests conducted in the shallow piezometers resulted in a range of hydraulic conductivities from 1.5×10^{-7} m/s to 1.0×10^{-3} m/s, with a geometric mean of 2.9×10^{-5} m/s. Hydraulic conductivities varied from a geometric mean of 1.7×10^{-6} m/s to 3.2×10^{-5} m/s in the open hole slug tests performed in the inclined boreholes at the Augustine Cove field site. Three short-term pumping tests conducted at the Augustine Cove site provided a transmissivity range of 1.0×10^{-4} m²/s to 3.1×10^{-4} m²/s and a storativity range of 1.2×10^{-2} to 2.7×10^{-4}.

5. It was not possible to calibrate the results of LEACHMP to the data obtained from the field sites on Prince Edward Island. The inability of the model to reproduce the concentrations observed in the field suggests that there may be a storage mechanism acting to retain the pesticide in a nondegraded form, allowing a slow release of aldicarb residues to the water table over time. The long-term persistence of the aldicarb residues, coupled with the long half-lives predicted in the best model simulations, indicate that the degradation of the aldicarb residues is being inhibited.

The acidity of the soil and recharge water on Prince Edward Island, the low temperatures associated with "at planting" applications of aldicarb, and the oxidation of ammonium-based fertilizers all appear to lead to the inhibition of the degradation of the aldicarb residues.

A matrix diffusion process appears to be the most likely mechanism for the slow infiltration of the pesticide through the unsaturated zone and for the

storage of aldicarb residues in the saturated zone of the PEI sandstones.

6. Sensitivity studies were performed with LEACHMP. The model simulates solute transport in a single porous medium, and, as such, the findings of the sensitivity study may not be strictly applicable to the situation on Prince Edward Island. However, the sensitivity studies were useful in determining which parameters could be used to adjust the model predictions in the calibration attempts. The results indicate that the total aldicarb concentration predicted by LEACHMP is most sensitive to the value of the oxidation and hydrolysis rate constants. It is also sensitive to the value of dispersivity and to the date of the pesticide application. The total aldicarb concentration at the water table was found to be relatively insensitive to the depth of incorporation of the pesticide and to the value of the pan evaporation coefficient.

Conclusions drawn from the study suggest that if applications of aldicarb are to continue, the application of the pesticide should occur at plant emergence rather than at the time of planting to take advantage of the higher soil temperatures and the existence of a plant root system, which is responsible for the uptake of the pesticide. Pesticide application at plant emergence may also be beneficial in that it will separate the application of the pesticide from the application of ammonium-based fertilizers that currently occurs with the planting of the seed potatoes. If the two applications are separated, the acidity produced by the oxidation of the ammonium-based fertilizers may be partially neutralized prior to the application of the pesticide. This may lessen the detrimental effects of the oxidation of the ammonium-based fertilizers on aldicarb degradation.

Results from the monitoring program suggest that a relationship may exist between excess concentrations of aldicarb and nitrate. It may therefore be possible to use nitrate analysis of domestic water supplies as a screening process to determine which wells should be analyzed for aldicarb residues.

The simulations with LEACHMP demonstrate that an extension to the model is required if it is to be able to simulate the conditions existing on Prince Edward Island. The extension to the model should provide a mechanism to account for the matrix diffusion storage of the pesticide in the unsaturated and saturated zones.

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Appendix A
Fractional Organic Carbon Content in Soil Samples from Augustine Cove and Mill Valley

Table A-1. Fractional Organic Carbon Content in Soil Samples from Augustine Cove and Mill Valley

Site	Sample number	Depth below grade (mm)	f_{oc} value (%)	Standard deviation	Number of replicates
Augustine Cove	AC1	150	1.069	0.039	2
	AC2	150	1.002	0.058	2
	AC3	300	0.122	0.011	2
	AC4	300	0.127	0.017	2
	AC5	500	0.053	0.002	2
	AC6	500	0.058	0.004	2
	AC7	8 m (cuttings)	<0.004		2
	#2 silica	Packing sand	<0.004		3
Mill Valley	MV1	150	1.460	0.107	2
	MV2	150	1.351	0.240	2
	MV3	300	3.832	0.177	2
	MV4	300	0.327	0.203	2
	MV5	500	0.301	0.011	2
	MV6	500	0.279	0.008	2
	MV7	1000	0.054	0.001	2
	MV8	1000	0.060	0.002	2

**Appendix B
Hydrogeological Results from Field
Sites**

Piez. no.	Depth to mid-screen (m)	Top of pipe elev. (m)	Hydraulic heads (m)							
			June 5, 1987	June 29, 1987	July 31, 1987	Aug. 24, 1987	Oct. 14, 1987	Feb. 26, 1988	May 4, 1988	May 11, 1988
AC1	18.80	19.48	8.43	9.07	8.20	7.85	7.80	10.01	11.32	11.18
AC2	12.70	19.37	8.28	8.94	8.06	7.72	7.66	9.88	11.22	11.09
AC25	8.51	19.53	Dry	Dry	Dry	Dry	Dry	Dry	11.63	11.61
AC3	16.70	17.28	7.54	7.99	7.26	6.89	6.90	8.93	9.97	9.76
AC4	12.70	17.73	7.47	7.97	7.23	6.85	6.86	8.93	9.97	9.76
AC34	10.20	17.32	7.47	7.97	7.23	6.86	6.86	8.93	9.97	9.76
AC5	9.60	12.36	7.47	7.95	7.26	6.91	6.92	8.83	9.83	9.62
AC6	6.60	12.10	7.45	7.95	7.21	6.81	6.81	8.89	9.89	9.69
AC35	3.50	12.53	Dry	Dry	Dry	Dry	Dry	Dry	9.90	9.68
AC7	6.60	10.94	7.43	7.94	7.19	6.79	6.79	8.82	9.79	9.62
AC8	3.60	11.15	7.44	7.94	7.19	6.80	Dry	8.88	9.83	9.65
AC36	2.90	11.25	Dry	Dry	Dry	Dry	Dry	Dry	9.70	9.61
AC9	5.10	10.12	NR	NR	8.92	8.61	7.18	8.92	NR	9.67
AC10	3.60	11.39	7.65	8.10	7.44	7.14	7.21	8.97	10.20	9.74
AC30	10.50	11.23	7.69	8.11	7.48	7.19	7.25	8.91	9.84	9.61
AC22	16.90	20.02	8.86	9.59	8.90	8.39	8.22	10.09	11.02	11.03
AC23	9.10	19.96	Dry	Dry	Dry	Dry	Dry	Dry	11.37	11.32
AC24	5.60	19.93	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry
AC26	10.00	17.52	7.67	8.18	7.43	7.09	7.10	9.12	10.31	10.03
AC27	9.50	10.14	7.39	7.82	7.20	6.89	6.90	8.62	9.56	9.33
AC28	6.60	10.42	7.42	7.85	7.22	6.90	6.82	8.69	9.54	9.34
AC29	2.20	9.63	7.72	8.05	7.32	6.99	7.75	NR	8.96	8.80
AC31	10.60	11.26	7.81	8.21	7.61	7.33	7.42	8.95	9.75	9.62
AC32	6.50	11.37	8.09	8.48	7.75	7.47	7.67	9.16	9.97	9.77
AC33	2.30	11.13	Dry	Dry	Dry	Dry	Dry	Dry	9.97	9.65

Stream elevation: June 11, 1987 = 8.06 m (cross section ABCD in Figure 6b).

NR = no recording.

Piez. no.	May 18, 1988	May 19, 1988	May 20, 1988	May 25, 1988	June 1, 1988	June 19, 1988	July 4, 1988	July 10, 1988	Dec. 30, 1988	Mar. 4, 1989
					Hydraulic Heads (m)					
AC1	10.54	10.50	10.49	10.38	9.95	9.06	8.60	8.45	8.99	8.04
AC2	10.42	10.38	10.37	10.26	9.81	8.91	8.44	8.29	8.92	7.89
AC25	10.83	10.77	10.76	10.65	10.23	10.19	10.18	10.17	10.17	10.16
AC3	9.42	9.45	9.44	9.32	9.02	8.20	7.74	7.60	8.15	7.13
AC4	9.40	9.45	9.44	9.32	9.02	8.19	7.72	7.57	8.13	7.05
AC34	9.42	9.45	9.44	9.32	9.02	8.19	7.72	7.58	8.14	7.09
AC5	9.29	9.33	9.31	9.17	8.88	8.13	7.71	7.58	8.09	7.10
AC6	9.40	9.41	9.40	9.28	8.98	8.15	7.68	7.54	8.10	7.04
AC35	9.39	9.41	9.40	9.28	8.98	8.47	Dry	Dry	8.37	Dry
AC7	9.32	9.34	9.31	9.21	8.91	8.10	7.63	7.47	8.02	6.94
AC8	9.41	9.39	9.26	9.27	8.97	8.14	7.67	7.53	8.08	7.00
AC36	9.50	9.40	9.36	9.28	9.07	8.17	Dry	Dry	8.12	Dry
AC9	9.53	9.53	9.46	9.23	8.98	8.24	7.84	7.72	NR	5.62
AC10	9.66	9.60	9.52	9.28	9.04	8.29	7.88	7.75	8.27	7.31
AC30	9.35	9.36	9.33	9.15	8.92	8.26	7.91	7.79	8.25	7.42
AC22	10.42	10.39	10.40	10.29	9.96	9.39	9.10	9.02	9.36	8.68
AC23	10.62	10.58	10.59	10.48	10.12	9.69	9.61	9.68	9.68	9.60
AC24	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry
AC26	9.64	9.68	9.67	9.54	9.21	8.38	7.90	7.75	8.34	7.30
AC27	9.00	9.02	8.98	8.84	8.59	7.94	7.60	7.49	7.97	7.09
AC28	9.06	9.08	9.05	8.89	8.69	8.00	8.15	7.52	8.03	7.11
AC29	9.00	8.71	8.64	8.58	8.78	8.08	8.47	7.87	8.61	8.55
AC31	9.32	9.33	9.31	9.17	8.95	8.35	8.03	7.92	8.28	7.60
AC32	9.51	9.53	9.51	9.36	9.16	8.53	8.20	8.10	8.53	7.82
AC33	9.96	9.87	9.81	9.59	9.85	9.36	9.52	9.20	Dry	Dry

Table B-2. Hydraulic Heads—Mill Valley (1987–1989)

Piez. no.	Depth to mid-screen (m)	Top of pipe elev. (m)	Hydraulic heads (m)				
			June 5, 1987	June 29, 1987	July 31, 1987	Aug. 24, 1987	Oct. 17, 1987
MV12	18.80	24.14	12.68	12.65	12.41	12.31	12.17
MV13	12.70	24.14	12.79	12.74	Brk	Brk	Brk
MV38	9.90	24.06	Dry	Dry	Dry	Dry	Dry
MV14	18.80	20.37	10.37	10.36	10.20	10.15	10.07
MV15N	12.28	20.36	NR	NR	NR	NR	NR
MV37N	9.92	19.60	NR	NR	NR	NR	NR
MV16	9.60	12.10	9.01	9.04	8.93	8.90	8.88
MV17	5.60	11.74	8.99	9.02	8.92	8.89	8.87
MV18N	4.45	11.67	NR	NR	NR	NR	8.88
MV19	9.60	12.05	9.04	9.07	8.97	8.88	8.92
MV20	9.60	13.02	9.41	9.46	9.32	9.28	9.25
MV21	5.00	12.66	9.41	9.45	9.31	9.28	9.25
MV39	13.20	25.00	15.29	15.26	14.96	14.82	14.54
MV40	12.91	21.00	NR	NR	NR	NR	10.76
MV41	6.07	13.15	NR	NR	NR	NR	8.85

Stream elevation: June 17, 1987 = 8.83 m (cross section JLM in Figure 8b).
NR = no recording.
Brk = broken piezometer.

Table B-2. Continued

Piez. no.	Hydraulic heads (m)						
	Feb. 26, 1988	May 4, 1988	May 11, 1988	May 12, 1988	May 19, 1988	May 25, 1988	June 1, 1988
MV12	13.39	14.43	14.20	14.15	13.85	13.68	13.55
MV13	12.50	Brk	Brk	Brk	Brk	Brk	Brk
MV38	Dry	14.96	14.69	14.64	14.25	14.07	Dry
MV14	10.84	11.77	11.51	11.45	11.20	11.05	10.92
MV15N	NR	11.91	11.64	11.57	11.29	11.11	10.95
MV37N	NR	12.02	11.77	11.72	11.41	11.22	11.05
MV16	9.34	10.10	9.81	9.77	9.57	9.45	9.35
MV17	NR	10.11	9.82	9.78	9.58	9.46	9.35
MV18N	9.28	9.82	9.56	9.52	9.37	9.28	9.22
MV19	9.36	10.02	9.73	9.70	9.52	9.41	9.33
MV20	9.80	10.53	10.25	10.20	10.00	9.87	9.78
MV21	9.80	10.53	10.26	10.21	10.01	9.88	9.78
MV39	NR	13.88	16.62	16.58	16.31	16.19	16.05
MV40	NR	12.87	12.72	12.68	12.40	12.22	12.06
MV41	9.37	10.44	10.13	10.07	9.82	9.66	9.54

Piez. no.	Hydraulic heads (m)				
	June 19, 1988	July 4, 1988	July 10, 1988	Dec. 30, 1988	Mar. 4, 1989
MV12	13.15	12.96	12.94	12.87	12.70
MV13	Brk	Brk	Brk	Brk	Brk
MV38	Dry	Dry	Dry	Dry	Dry
MV14	10.62	10.43	10.47	10.40	10.27
MV15N	10.58	10.48	10.39	10.31	10.19
MV37N	10.66	10.49	10.46	10.37	10.23
MV16	9.16	9.07	9.06	9.06	8.98
MV17	9.14	9.06	9.04	NR	NR
MV18N	9.07	9.00	8.99	9.03	8.96
MV19	9.16	9.09	9.08	9.09	9.02
MV20	9.57	9.47	9.45	9.45	9.37
MV21	9.56	9.47	9.44	9.45	9.37
MV39	15.67	15.50	15.49	NR	NR
MV40	11.72	11.56	11.53	11.37	NR
MV41	9.27	9.16	9.13	8.70	7.30

Table B-3. Hydraulic Heads—New Annan (1987–1989)

Piez. no.	Depth to mid-screen (m)	Top of pipe elev. (m)	Hydraulic heads (m)				
			June 5, 1987	June 30, 1987	July 30, 1987	Aug. 24, 1987	May 11, 1988
NA1A	10.97	29.74	18.97	18.95	18.84	18.78	21.09
NA1B	12.15	29.73	18.62	18.60	18.49	18.43	20.76
NA2C	13.10	27.34	14.91	14.97	14.51	14.59	16.67
NA3	12.20	21.66	10.32	10.70	9.86	10.30	NR
NA4A	9.14	19.59	10.89	11.11	10.47	10.75	NR
NA4B	12.20	19.63	10.35	10.73	9.92	10.23	NR
NA5A	8.53	18.56	11.19	11.21	10.78	10.99	NR
NA5B	13.11	18.61	10.87	11.13	10.45	10.63	NR

NR = no recording

Table B-3. Continued

Piez. no.	Hydraulic heads (m)					
	May 19, 1988	May 25, 1988	June 1, 1988	June 19, 1988	July 4, 1988	July 10, 1988
NA1A	20.60	20.34	20.08	19.31	19.08	19.05
NA1B	20.28	20.02	19.75	18.97	18.74	18.70
NA2C	16.34	14.63	15.22	15.44	15.19	15.11
NA3	11.66	11.00	10.80	10.78	10.20	10.54
NA4A	12.23	11.76	11.51	11.26	10.94	11.03
NA4B	11.77	11.16	11.00	10.93	10.40	10.69
NA5A	12.34	11.97	11.67	11.29	11.20	11.07
NA5B	12.16	11.61	11.39	11.21	10.86	10.99

Table B-4. Hydraulic Conductivities (m/s) Determined by Shallow Piezometer Slug Tests—Augustine Cove

Piez. no.	Hvorslev (1951)					Cooper et al. (1967)
	Test 1	Test 2	Test 3	Test 4	Geometric mean	
AC1	3.3E-6[1]	3.3E-6	-	-	3.3E-6	9.8E-6[1]
AC2	5.2E-5[1]	3.2E-5	-	-	4.1E-5	8.9E-5[1]
AC25	-	-	-	-	-	-
AC3	5.3E-6[1]	4.7E-6	5.7E-6	-	5.2E-6	1.5E-5[1]
AC4	2.8E-5[1]	2.8E-4	4.4E-5	-	7.0E-5	2.2E-5[1]
AC34	-	-	-	-	-	-
AC5	9.3E-5[1]	8.9E-5	7.6E-5	8.5E-5	8.6E-5	8.0E-5[1]
AC6	-	-	-	-	-	-
AC35	-	-	-	-	-	-
AC7	6.0E-4	3.6E-4	-	-	4.6E-4	-
AC8	-	-	-	-	-	-
AC36	-	-	-	-	-	-
AC9	3.0E-5	-	-	-	3.0E-5	-
AC10	-	-	-	-	-	-
AC30	2.4E-6	-	-	-	2.4E-6	6.4E-6
AC22	1.2E-5	-	-	-	1.2E-5	-
AC23	-	-	-	-	-	-
AC24	-	-	-	-	-	-
AC26	-	-	-	-	-	-
AC27	1.4E-4[1]	1.1E-4	1.4E-4	-	1.3E-4	3.2E-4[1]
AC28	1.9E-4[1]	2.4E-4	2.8E-4	-	2.3E-4	-
AC29	-	-	-	-	-	-
AC31	3.3E-5	-	-	-	3.3E-5	-
AC32	7.0E-6	-	-	-	7.0E-6	-
AC33	-	-	-	-	-	-
				Geometric mean	2.9E-5	3.3E-5

[1]Data from 1986 (Priddle et al. 1987).

Table B-5. Hydraulic Conductivities (m/s) Determined by Shallow Piezometer Slug Tests—Mill Valley

Piez no.	Test 1	Test 2	Test 3	Test 4	Test 5	Geometric mean
			Method of analysis: Hvorslev (1951)			
MV12	4.5E-5	6.3E-5	-	-	-	5.3E-5
MV13	-	-	-	-	-	-
MV38	-	-	-	-	-	-
MV14	5.2E-5	1.5E-4	6.1E-5	8.0E-5	-	7.8E-5
MV15N	-	-	-	-	-	-
MV37N	-	-	-	-	-	-
MV16	1.1E-4	2.3E-4	2.0E-4	3.0E-4	2.0E-4	2.0E-4
MV17	1.0E-3	-	-	-	-	1.0E-3
MV18N	-	-	-	-	-	-
MV19	3.3E-4	-	-	-	-	3.3E-4
MV20	3.0E-4	-	-	-	-	3.0E-4
MV21	3.3E-4	-	-	-	-	3.3E-4
MV39	2.4E-4	2.6E-4	2.6E-4	2.6E-4	2.3E-4	2.5E-4
					Geometric mean	2.2E-4

Table B-6. Hydraulic Conductivities (m/s) Determined by Shallow Piezometer Slug Tests—New Annan

Piezometer number	Hydraulic conductivity[*]
NA1A	3.1E-5
NA1B	4.5E-6
NA2A	8.7E-6
NA3	2.3E-6
NA4A	2.1E-6
NA4B	3.1E-7
NA5A	1.2E-5
NA5B	1.5E-7
Geometric mean	2.8E-6

*Method of analysis: Hvorslev (1951).

**Appendix C
Geochemical Results from Field
Sites**

Table C-1. Geochemical Results—Augustine Cove

Piez. no.	Depth to mid-screen (m)	July 1985				Sept. 1985	
		pH	E_H (mV)	DO (mg/L)	NO_3^--N (mg/L)	NO_3^--N (mg/L)	HCO_3^- (mg/L)
AC1	18.80	8.0	660	8.0	9.2	22.0	<1.0
AC2	12.70	7.2	690	9.8	9.2	14.0	18.0
AC3	16.70	7.9	470	8.9	4.3	15.0	36.0
AC4	12.70	7.5	470	9.0	7.6	2.8	104.0
AC5	9.60	6.8	200	0.3	<0.2	<0.2	122.0
AC6	6.60	6.3	540	2.8	14.0	5.0	31.0
AC7	6.60	6.4	490	9.0	12.0	11.0	91.0
AC8	3.60	5.9	500	9.0	13.0	NR	NR
AC9	5.10	NR	NR	NR	14.0	12.0	109.0
AC10	3.60	NR	NR	NR	16.0	NR	NR

NR = no recording.
ND = non-detectable.

Table C-1. Continued

Geochemical results (in situ)

Piez. no.	Depth to mid-screen (m)	Sept. 1986					
		pH	E_H (mV)	SC (µS)	DO (mg/L)	NH_3 (mg/L)	HCO_3^- (mg/L)
AC1	18.80	7.6	430	320	8.7	0.3	104
AC2	12.70	7.0	490	256	9.2	0.2	70
AC25	8.51	NR	NR	NR	NR	NR	NR
AC3	16.70	8.2	390	250	7.8	0.2	109
AC4	12.70	7.0	430	284	8.7	0.1	101
AC34	10.20	7.0	430	330	8.1	0.1	101
AC5	9.60	6.9	140	240	0.2	ND	120
AC6	6.60	6.4	420	310	5.7	0.1	49
AC35	3.50	NR	NR	NR	NR	NR	NR
AC7	6.60	5.6	480	280	NR	ND	50
AC8	3.60	NR	NR	NR	NR	NR	NR
AC36	2.90	NR	NR	NR	NR	NR	NR
AC9	5.10	6.6	480	45	NR	NR	94
AC10	3.60	NR	NR	NR	NR	NR	NR
AC30	10.50	NR	NR	NR	NR	NR	NR
AC22	16.90	7.3	380	NR	NR	NR	NR
AC23	9.10	NR	NR	NR	NR	NR	NR
AC24	5.60	NR	NR	NR	NR	NR	NR
AC26	10.00	7.0	440	420	NR	NR	NR
AC27	9.50	6.8	130	410	0.3	0.2	207
AC28	6.60	6.3	330	382	0.4	NR	124
AC29	2.20	NR	NR	NR	NR	NR	NR
AC31	10.60	NR	NR	NR	NR	NR	NR
AC32	6.50	NR	NR	NR	NR	NR	NR
AC33	2.30	NR	NR	NR	NR	NR	NR

Table C-1. Continued

Geochemical results (lab analysis)

Sept. 1986

Piez. no.	NO_3^--N (mg/L)	DOC (mg/L)	Fe^{2+} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	SiO_2 (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)
AC1	8.4	1.1	NR	37.0	5.6	16.9	0.96	NR	13.8	14.3
AC2	8.1	0.5	NR	36.0	3.7	6.9	0.84	NR	12.3	14.2
AC25	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC3	1.9	1.1	NR	28.0	9.1	5.8	0.87	NR	7.0	10.4
AC4	7.6	0.8	NR	43.0	4.9	7.6	0.79	NR	15.3	14.2
AC34	8.4	1.0	NR	45.0	4.1	7.6	0.81	NR	16.4	14.6
AC5	0.05	8.7	NR	36.0	3.7	5.9	0.36	NR	0.6	10.6
AC6	8.4	1.0	NR	35.0	4.5	9.8	0.93	NR	20.0	17.7
AC35	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC7	8.0	0.6	NR	36.0	3.5	0.5	0.98	NR	17.2	17.1
AC8	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC36	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC9	13.6	0.9	NR	66.0	4.3	9.4	1.10	NR	25.2	24.6
AC10	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC30	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC22	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC23	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC24	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC26	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC27	0.04	8.0	NR	61.0	7.9	8.0	0.44	NR	3.0	15.1
AC28	1.2	1.9	NR	52.0	5.6	14.2	0.65	NR	35.8	28.5
AC29	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC31	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC32	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC33	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR

Table C-1. Continued

Geochemical results (in situ)

June/July 1987

Piez. no.	pH	E_H (mV)	SC (μS)	Temp. (°C)	DO (mg/L)	NH$_3$ (mg/L)	HCO$_3^-$ (mg/L)
AC1	8.0	380	300	7	NR	ND	107
AC2	6.9	690	250	7	10.0	ND	60
AC25	NR	NR	NR	NR	NR	NR	NR
AC3	8.2	510	230	13	8.0	0.1	117
AC4	7.1	550	280	7	10.0	0.4	96
AC34	7.3	540	380	10	10.0	0.2	143
AC5	6.9	150	240	8	0.5	0.6	123
AC6	6.3	560	280	11	9.0	0.5	45
AC35	NR	NR	NR	NR	NR	NR	NR
AC7	6.6	510	310	14	8.0	0.1	76
AC8	NR	NR	NR	NR	NR	NR	NR
AC36	NR	NR	NR	NR	NR	NR	NR
AC9	7.5	470	490	14	6.0	0.3	151
AC10	NR	NR	NR	NR	NR	NR	NR
AC30	6.8	160	450	12	0.4		265
AC22	7.2	470	290	12	10.0	ND	95
AC23	NR	NR	NR	NR	NR	NR	NR
AC24	NR	NR	NR	NR	NR	NR	NR
AC26	6.7	530	350	12	NR	ND	NR
AC27	6.8	150	450	15	0.4	NR	242
AC28	6.4	320	400	13	0.6	NR	124
AC29	NR	NR	NR	NR	NR	NR	NR
AC31	7.2	120	370	16	0.6	NR	192
AC32	6.1	340	250	15	0.8	0.4	90
AC33	NR	NR	NR	NR	NR	NR	NR

Table C-1. Continued

	Geochemical results (lab analysis)										
	June/July 1987										May 1988
Piez. no.	NO_3^--N (mg/L)	DOC (mg/L)	Fe^{2+} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	SiO_2 (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NO_3^--N (mg/L)
AC1	11.0	0.0	0.0	38.5	5.3	12.8	0.99	9.8	11.5	16.6	11.8
AC2	11.0	0.0	0.0	33.5	3.7	6.9	0.84	9.8	11.4	17.4	12.0
AC25	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC3	1.7	0.0	0.0	27.5	9.1	6.1	0.89	14.0	6.6	10.7	4.0
AC4	10.0	0.0	0.0	41.0	4.0	7.8	0.73	10.3	14.7	16.6	13.4
AC34	11.0	0.0	0.0	57.0	3.2	10.1	0.69	10.7	19.0	14.8	12.2
AC5	0.0	8.8	7.6	35.9	3.7	6.1	0.34	14.1	0.0	10.5	0.2
AC6	12.0	0.0	0.0	29.7	4.9	10.0	1.10	11.8	21.8	18.1	9.8
AC35	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC7	10.0	0.0	0.0	38.9	3.9	8.1	0.86	11.1	17.2	17.0	11.4
AC8	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	11.4
AC36	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC9	13.0	0.0	0.0	68.7	4.7	9.0	0.94	14.6	22.8	23.1	10.6
AC10	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	9.8
AC30	0.0	11.0	11.0	60.0	8.4	10.9	0.67	18.2	0.0	12.0	<0.2
AC22	9.0	0.0	0.0	45.0	2.5	9.2	0.62	10.7	14.3	17.0	12.8
AC23	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC24	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC26	10.0	0.0	0.0	43.0	3.0	6.9	0.68	8.6	16.3	15.5	9.0
AC27	0.0	6.3	9.9	61.0	7.7	8.1	0.44	16.3	3.1	15.8	1.6
AC28	1.8	1.7	1.2	54.0	5.4	11.5	0.48	13.3	29.0	24.4	2.2
AC29	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
AC31	0.0	5.3	6.3	46.0	5.8	8.5	0.50	16.3	1.5	10.2	0.1
AC32	0.0	6.2	1.0	26.3	2.7	11.4	1.10	16.1	18.4	12.0	1.0
AC33	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	2.2

Table C-2. Geochemical Results—Mill Valley

Piez. no.	Depth to mid-screen (m)	July 1985			Sept. 1985	
		pH	E_H (mV)	DO (mg/L)	NO_3^--N (mg/L)	HCO_3^- (mg/L)
MV12	18.80	NR	NR	3.5	4.3	65
MV13	12.70	7.8	470	7.6	7.0	113
MV14	18.80	NR	NR	5.4	6.0	77
MV15	12.28	NR	NR	5.2	3.9	82
MV16	9.60	8.1	470	5.2	5.4	76
MV17	5.60	7.9	470	5.4	4.3	75
MV18	4.45	NR	NR	NR	<0.2	490
MV19	9.60	NR	NR	7.0	7.0	88
MV20	9.60	8.1	470	1.6	2.3	84
MV21	5.00	7.9	570	6.4	NR	NR
Spring	-	NR	NR	NR	8.0	70

NR = no recording.

Table C-2. Continued

Piez. no.	Depth to mid-screen (m)	June 1987						May 1988
		pH	E_H (mV)	SC (µS)	DO (mg/L)	NO_3^--N (mg/L)	HCO_3^- (mg/L)	NO_3^--N (mg/L)
MV12	18.80	7.8	490	280	10.0	4.7	90	5.0
MV13	12.70	7.6	460	410	10.0	7.0	151	NR
MV38	9.90	NR	NR	NR	NR	NR	NR	NR
MV14	18.80	8.0	490	280	10.0	6.1	NR	7.0
MV15N	12.30	NR	NR	NR	NR	NR	NR	7.4
MV37N	9.90	NR	NR	NR	NR	NR	NR	NR
MV16	9.60	8.0	500	280	10.0	5.6	NR	NR
MV17	5.60	7.3	520	250	9.0	12.0	NR	13.8
MV18N	4.50	NR	NR	NR	NR	NR	NR	13.2
MV19	3.60	7.8	550	290	9.0	6.9	112	12.1
MV20	9.60	8.0	490	230	9.0	2.9	112	5.2
MV21	5.00	7.5	560	280	10.0	6.6	115	9.6
MV39	13.20	7.8	530	310	10.0	6.6	123	NR
Spring	-	7.2	540	270	NR	NR	NR	NR

Table C-3. Geochemical Results—New Annan

Piez. no.	Sept. 1986 NO$_3^-$-N (mg/L)	July 1987					May 1988 NO$_3^-$-N (mg/L)
		pH	E$_H$ (mV)	SC (µS)	DO (mg/L)	HCO$_3^-$ (mg/L)	
NA1A	15.0	7.7	470	500	8.0	121	30.0
NA1B	13.0	7.9	480	430	9.0	116	17.5
NA2A	16.0	7.8	400	320	0.5	161	0.4
NA2B	NR	7.9	480	340	9.0	118	13.8
NA2C	NR	7.8	490	410	9.0	118	29.0
NA3	4.4	7.5	510	900	7.0	283	5.4
NA4A	6.8	NR	NR	NR	NR	NR	13.6
NA4B	7.4	7.3	510	650	6.0	268	14.4
NA4C	NR	7.8	490	330	8.0	133	NR
NA5A	14.0	6.8	530	730	5.0	322	23.5
NA5B	14.0	7.4	510	520	7.0	201	22.5

NR = not recorded.

Table C-4. Total Aldicarb Concentrations and ASO$_2$/Total Aldicarb Ratios—Augustine Cove

Piez. no.	Depth to mid-screen (m)	July 1985		Sept. 1985	
		Total aldicarb (µg/L)	Sulfone/total aldicarb ratio	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
AC1	18.80	0.8	0.60	0.9	0.60
AC2	12.70	3.6	0.42	1.0	0.60
AC3	16.70	1.0	0.70	ND	-
AC4	12.70	4.0	0.60	0.2	0.50
AC5	9.60	3.0	0.47	ND	-
AC6	6.60	12.0	0.73	3.9	0.69
AC7	6.60	10.8	0.69	5.9	0.75
AC8	3.60	7.6	0.70	12.3	0.70
AC9	5.10	14.2	0.68	NS	NS
AC10	3.60	16.4	0.70	NS	NS

ND = non-detectable.
NS = not sampled.

Table C-4. Continued

Piez. no.	Depth to mid-screen (m)	Sept 1986			
		Aldicarb sulfoxide (µg/L)	Aldicarb sulfone (µg/L)	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
AC1	18.80	0.1	0.3	0.4	0.80
AC2	12.70	0.3	0.4	0.7	0.60
AC25	8.51	NS	NS	NS	NS
AC3	16.70	ND	ND	ND	-
AC4	12.70	1.1	2.5	3.6	0.69
AC34	10.20	1.3	2.9	4.2	0.69
AC5	9.60	ND	ND	ND	-
AC6	6.60	1.6	5.5	7.1	0.77
AC35	3.50	NS	NS	NS	NS
AC7	6.60	1.0	3.7	4.7	0.79
AC8	3.60	NS	NS	NS	NS
AC36	2.90	NS	NS	NS	NS
AC9	5.10	3.4	9.4	12.8	0.73
AC10	3.60	NS	NS	NS	NS
AC30	10.50	ND	0.1	0.1	1.00
AC22	16.90	ND	0.1	0.1	1.00
AC23	9.10	NS	NS	NS	NS
AC24	5.60	NS	NS	NS	NS
AC26	10.00	1.2	3.1	4.3	0.72
AC27	9.50	ND	ND	ND	-
AC28	6.60	ND	1.0	1.0	1.00
AC29	2.20	NS	NS	NS	NS
AC31	10.60	ND	ND	ND	-
AC32	6.50	ND	ND	ND	-
AC33	2.30	ND	ND	ND	-

Table C-4. Continued

Piez. no.	Depth to mid-screen (m)	June/July 1987		Aug. 1987	
		Total aldicarb (µg/L)	Sulfone/total aldicarb ratio	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
AC1	18.80	0.4	0.75	0.4	0.80
AC2	12.70	0.5	0.60	0.4	0.80
AC25	8.51	NS	NS	NS	NS
AC3	16.70	0.1	1.00	0.1	1.00
AC4	12.70	3.1	0.81	1.4	0.64
AC34	10.20	2.6	0.69	1.7	0.59
AC5	9.60	ND	-	0.3	1.00
AC6	6.60	6.9	0.75	7.1	0.76
AC35	3.50	NS	NS	NS	NS
AC7	6.60	3.7	1.00	4.8	0.75
AC8	3.60	NS	NS	NS	NS
AC36	2.90	NS	NS	NS	NS
AC9	5.10	5.0	0.72	12.8	0.71
AC10	3.60	NS	NS	NS	NS
AC30	10.50	1.3	1.00	ND	-
AC22	16.90	0.2	1.0	ND	-
AC23	9.10	NS	NS	NS	NS
AC24	5.60	NS	NS	NS	NS
AC26	10.00	4.5	0.80	NS	NS
AC27	9.50	0.6	0.33	0.4	1.00
AC28	6.60	0.9	1.00	0.5	1.00
AC29	2.20	NS	NS	NS	NS
AC31	10.60	0.2	1.00	ND	-
AC32	6.50	ND	-	ND	-
AC33	2.30	NS	NS	NS	NS

Table C-4. Continued

Piez. no.	Depth to mid-screen (m)	May 5, 1988		May 30, 1988	
		Total aldicarb (µg/L)	Sulfone/total aldicarb ratio	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
AC1	18.80	0.6	1.00	NS	NS
AC2	12.70	0.9	0.20	NS	NS
AC25	8.51	ND	-	NS	NS
AC3	16.70	0.3	0.70	ND	-
AC4	12.70	4.8	0.69	4.3	0.65
AC34	10.20	6.3	0.68	5.4	0.66
AC5	9.60	ND	-	ND	-
AC6	6.60	10.4	0.76	10.2	0.74
AC35	3.50	10.1	0.73	NS	NS
AC7	6.60	3.7	0.67	6.2	0.69
AC8	3.60	3.2	0.69	5.6	0.62
AC36	2.90	2.5	0.68	NS	NS
AC9	5.10	9.8	0.76	9.5	0.72
AC10	3.60	9.7	0.74	9.2	0.69
AC30	10.50	ND	-	ND	-
AC22	16.90	0.1	1.0	NS	NS
AC23	9.10	ND	-	NS	NS
AC24	5.60	NS	NS	NS	NS
AC26	10.00	2.6	0.69	NS	NS
AC27	9.50	ND	-	NS	NS
AC28	6.60	0.5	0.80	NS	NS
AC29	2.20	0.1	0.00	ND	-
AC31	10.60	ND	-	NS	NS
AC32	6.50	ND	-	NS	NS
AC33	2.30	ND	-	ND	-

Table C-4. Continued

Piez. no.[*]	Depth to mid-screen (mbgs)	May 1988			
		Aldicarb sulfoxide (µg/L)	Aldicarb sulfone (µg/L)	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
DAC1-1	33.42	NS	NS	NS	NS
DAC1-2	28.54	NS	NS	NS	NS
DAC1-3	26.07	ND	ND	ND	-
DAC1-4	21.70	ND	ND	ND	-
DAC1-5	15.64	0.6	1.0	1.6	0.60
DAC2-1	25.43	ND	ND	ND	-
DAC2-2	22.23	0.1	0.2	0.3	0.70
DAC2-3	16.82	0.4	0.8	1.2	0.70
DAC2-4	13.14	0.3	0.9	1.2	0.80
DAC3-1	26.19	ND	ND	ND	-
DAC3-2	22.99	ND	ND	ND	-
DAC3-3	18.90	ND	ND	ND	-
DAC3-4	9.22	ND	ND	ND	-

[*]Multilevel priezometers

mbgs - metres below ground surface

Piez. no.	Depth to mid-screen (m)	July 1989			
		Aldicarb sulfoxide (µg/L)	Aldicarb sulfone (µg/L)	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
AC1	18.80	ND	ND	ND	-
AC2	12.70	ND	0.2	0.2	1.00
AC25	8.51	NS	NS	NS	NS
AC3	16.70	ND	ND	ND	-
AC4	12.70	0.4	2.2	2.6	0.84
AC34	10.20	0.8	2.0	2.8	0.71
AC5	9.60	ND	2.6	2.6	1.00
AC6	6.60	1.6	5.6	6.6	0.84
AC35	3.50	NS	NS	NS	NS
AC7	6.60	0.7	3.8	4.5	0.83
AC8	3.60	0.2	2.8	3.0	0.91
AC36	2.90	NS	NS	NS	NS
AC9	5.10	0.7	3.1	3.8	0.81
AC10	3.60	ND	2.4	2.4	1.00
AC30	10.50	NS	NS	NS	NS
AC22	16.90	NS	NS	NS	NS
AC23	9.10	NS	NS	NS	NS
AC24	5.60	NS	NS	NS	NS
AC26	10.00	NS	NS	NS	NS
AC27	9.50	NS	NS	ND	-
AC28	6.60	ND	2.6	2.6	1.00
AC29	2.20	NS	NS	NS	NS
AC31	10.60	NS	NS	NS	NS
AC32	6.50	ND	ND	ND	-
AC33	2.30	NS	NS	NS	NS

Table C-5. Total Aldicarb Concentrations and ASO₂/Total Aldicarb Ratios—Mill Valley

Piez. no.	Depth to mid-screen (m)	July 1985		Sept. 1985	
		Total aldicarb (µg/L)	Sulfone/total aldicarb ratio	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
MV12	18.80	ND	-	ND	-
MV13	12.70	0.5	0.40	0.3	0.30
MV14	18.80	ND	-	0.8	1.00
MV15	12.30	0.3	1.00	0.3	0.30
MV16	9.60	ND	-	ND	-
MV17	5.60	ND	-	NS	NS
MV18	4.50	NS	NS	NS	NS
MV19	9.60	ND	-	ND	ND
MV20	9.60	ND	-	ND	-
MV21	5.00	ND	-	ND	-
Spring		4.7	0.40	4.6	0.43

ND = non-detectable.
NS = not sampled.

Table C-5. Continued

Piez. no.	Depth to mid-screen (m)	Sept. 1986			
		Aldicarb sulfoxide (µg/L)	Aldicarb sulfone (µg/L)	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
MV12	18.80	ND	ND	ND	-
MV13	12.70	ND	0.1	0.1	1.00
MV38	9.90	NS	NS	NS	NS
MV14	18.80	ND	ND	ND	-
MV15N	12.30	NS	NS	NS	NS
MV37N	9.90	NS	NS	NS	NS
MV16	9.60	ND	0.1	0.1	1.00
MV17	5.60	0.5	0.6	1.1	0.60
MV18N	4.50	ND	0.2	0.2	1.00
MV19	9.60	0.4	0.5	0.9	0.60
MV20	9.60	ND	ND	ND	-
MV21	5.00	ND	0.1	0.1	1.00
MV39	13.20	ND	ND	ND	-

Table C-5. Continued

Piez. no.	Depth to mid-screen (m)	June/July 1987		Aug. 1987	
		Total aldicarb (µg/L)	Sulfone/total aldicarb ratio	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
MV12	18.80	ND	-	ND	-
MV13	12.70	0.9	0.00	NS	NS
MV38	9.90	NS	NS	NS	NS
MV14	18.80	3.7	0.54	0.3	0.30
MV15N	12.30	NS	NS	NS	NS
MV37N	9.90	NS	NS	NS	NS
MV16	9.60	0.3	0.70	0.2	0.50
MV17	5.60	7.7	0.57	0.7	0.60
MV18N	4.50	NS	NS	NS	NS
MV19	9.60	ND	-	ND	-
MV20	9.60	0.2	1.00	ND	-
MV21	5.00	0.9	0.80	0.3	0.70
MV39	13.20	0.2	0.50	0.4	0.50
Spring	-	4.8	0.48	3.4	0.41

Table C-5. Continued

Piez. no.	Depth to mid-screen (m)	May 5, 1988		May 30, 1988	
		Total aldicarb (µg/L)	Sulfone/total aldicarb ratio	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
MV12	18.80	ND	-	NS	NS
MV13	12.70	NS	NS	NS	NS
MV38	9.90	NS	NS	NS	NS
MV14	18.80	0.1	1.00	NS	NS
MV15N	12.30	0.7	0.60	0.7	0.70
MV37N	9.90	1.8	0.60	1.9	0.60
MV16	9.60	8.0	0.47	6.8	0.50
MV17	5.60	9.6	0.48	9.0	0.46
MV18N	4.50	6.1	0.56	4.2	0.53
MV19	9.60	ND	-	ND	-
MV20	9.60	0.9	0.70	0.6	0.70
MV21	5.00	2.1	0.60	1.9	0.60
MV39	13.20	2.0	0.50	NS	NS
MV40	12.90	1.7	0.50	NS	NS
MV41	6.10	8.0	0.46	9.4	0.46
Spring	-	10.2	0.47	9.4	0.47

Table C-5. Continued

Piez. no.	Depth to mid-screen (m)	July 1989			
		Aldicarb sulfoxide (µg/L)	Aldicarb sulfone (µg/L)	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
MV12	18.80	ND	ND	ND	-
MV13	12.70	NS	NS	NS	NS
MV38	9.90	NS	NS	NS	NS
MV14	18.80	NS	NS	NS	NS
MV15N	12.30	0.4	0.7	1.1	0.63
MV37N	9.90	0.4	0.5	0.9	0.54
MV16	9.60	0.7	0.8	1.5	0.51
MV17	5.60	NS	NS	NS	NS
MV18N	4.50	1.0	1.3	2.3	0.55
MV19	9.60	1.0	1.2	2.2	0.52
MV20	9.60	0.2	0.4	0.6	0.66
MV21	5.00	0.6	1.1	1.8	0.64
MV39	13.20	NS	NS	NS	NS
MV40	12.90	1.0	1.9	2.9	0.63
MV41	6.10	2.4	2.4	4.8	0.50
Spring	13.20	2.9	2.7	5.6	0.46

Table C-6. Total Aldicarb Concentrations and ASO$_2$/Total Aldicarb Ratios—New Annan

Piez. no.	Sept. 1986		July 1987		May 1988	
	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
NA1A	0.6	0.32	1.5	0.45	2.5	0.54
NA1B	0.5	0.40	0.7	0.13	0.6	0.16
NA2A	2.0	0.43	ND	-	ND	-
NA2B	0.7	0.27	1.1	0.44	1.4	0.55
NA2C	0.4	0.50	1.4	0.63	3.1	0.60
NA3	ND	-	0.1	1.00	0.4	0.50
NA4A	0.5	0.60	NS	NS	1.7	0.51
NA4B	1.3	0.62	1.5	0.45	1.9	0.51
NA4C	ND	-	ND	-	NS	NS
NA5A	3.7	0.55	5.9	0.54	4.3	0.59
NA5B	1.5	0.51	3.7	0.55	3.0	0.58

ND = non-detectable.
NS = not sampled.

Table C-7. Aldicarb Extractions from Soil Samples Taken from the Augustine Cove Site (Sept.–Oct. 1988)

Sample number	Depth below grade (m)	Total aldicarb (µg/kg)	Sulfone/total aldicarb ratio
DRY1-1	0.0 - 1.0	ND	-
DRY1-2	1.0 - 2.0	ND	-
DRY1-3	2.0 - 3.0	ND	-
DRY1-4	4.5	1.0	0.80
DRY1-5	8.0	1.0	0.70
DRY2-1	0.0 - 1.0	0.5	1.00
DRY2-2	1.0 - 2.0	ND	-
DRY2-3	2.0 - 3.0	ND	-
DRY3-1	0.0 - 1.0	ND	-

ND = non-detectable.
Analysis Procedure:
- soils kept cool until analysis.
- 25 g of soil mixed with 20 mL of distilled water in a 40-mL vial.
- samples shaken for 20 hours.
- samples centrifuged at 1500 rpm for 20 minutes.
- supernatant withdrawn by syringe and filtered (0.45 µm).
- samples analyzed by HPLC with on-line precolumn concentration.

Table C-8. Short-term Variation in Total Aldicarb Concentrations and in the ASO_2/Total Aldicarb Ratio
(Augustine Cove, May 1988)

Piezometer: AC4				Piezometer: AC6		
Date	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio		Date	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
May 5	4.8	0.67		May 6	10.4	0.75
May 11	5.1	0.65		May 11	9.2	0.71
May 17	5.1	0.65		May 13	9.3	0.72
May 18	4.2	0.63		May 17	10.2	0.72
May 19	4.1	0.64		May 18	9.4	0.72
May 20	4.2	0.60		May 19	8.7	0.72
May 25	3.9	0.62		May 20	9.3	0.71
May 26	4.1	0.64		May 25	8.9	0.70
May 30	4.3	0.63		May 26	9.6	0.70
				May 30	10.2	0.72
Mean	4.4	0.64		Mean	9.5	0.72
Standard deviation	0.4	0.02		Standard deviation	0.5	0.01
Relative standard deviation	9.1%	3.1%		Relative standard deviation	5.3%	1.4%

Piezometer: AC7				Piezometer: AC9		
Date	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio		Date	Total aldicarb (µg/L)	Sulfone/total aldicarb ratio
May 6	3.7	0.66		May 9	9.8	0.74
May 11	3.7	0.63		May 11	11.0	0.71
May 13	4.3	0.63		May 13	9.8	0.72
May 17	5.3	0.66		May 17	10.3	0.71
May 18	5.4	0.65		May 18	9.7	0.72
May 19	3.8	0.64		May 19	9.5	0.71
May 20	5.2	0.64		May 20	9.0	0.71
May 25	5.8	0.64		May 25	10.1	0.72
May 30	6.2	0.68		May 26	9.2	0.70
				May 30	9.5	0.72
Mean	4.8	0.65		Mean	9.8	0.72
Standard deviation	0.9	0.01		Standard deviation	0.5	0.01
Relative standard deviation	18.8%	1.5%		Relative standard deviation	5.1%	1.4%