

This manuscript has been prepared for the
National Water Well Association
Agricultural Impacts on Ground Water
Conference Proceedings

This copy is to provide information
prior to publication.

ALDICARB AND NITROGEN RESIDUES
IN A SANDSTONE AQUIFER

by

M.W. Priddle¹, R.E. Jackson¹,
A.S. Crowe¹ and J.P. Mutch²

¹Rivers Research Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, L7R 4A6

²Ground Water Studies Group
University of New Brunswick
Fredericton, N.B., Canada

January 1988
NWRI Contribution #88-02

NITROGEN AND ALDICARB RESIDUES IN A SANDSTONE AQUIFER

M.W. Priddle, R.E. Jackson and A.S. Crowe
National Water Research Institute, Burlington, Ontario L7R 4A6

J.P. Mutch
Ground Water Studies Group
University of New Brunswick
Fredericton, NB

Executive Summary

The research presented in this paper was conducted in cooperation with IWD, Atlantic Region and the PEI Government. A 1983-84 study revealed that the potato pesticide, Temik (active ingredient - aldicarb) was present in a number of drinking water wells on PEI. This posed a health threat to these residents because of the extreme toxicity of aldicarb. It was felt that an investigation into the migration and fate of aldicarb in the groundwaters of PEI was necessary. Reasons for the persistence of aldicarb in the aquifer of PEI are presented in this paper. Furthermore, changes to agricultural practices that would lessen its persistence in the groundwater are proposed.

RÉSIDUS D'AZOTE ET D'ALDICARBE DANS UN AQUIFÈRE GRÉSEUX

M.W. Priddle, R.E. Jackson and A.S. Crowe

National Water Research Institute, Environment Canada

Burlington, Ontario, Canada L7R 4A6

J.P. Mutch

Ground Water Studies Group

University of New Brunswick

Fredericton, N.B., Canada

RÉSUMÉ

Le présent article décrit une étude réalisée en coopération avec la DGEI, région de l'Atlantique et le gouvernement de l'Île-du-Prince-Edouard. Une étude réalisée en 1983-1984 a montré qu'on retrouvait dans un certain nombre de puits d'eau potable de l'Île-du-Prince-Edouard le pesticide pour les pommes de terre Temik (dont l'ingrédient actif est l'aldicarbe). Cela pose un danger pour la santé vu l'extrême toxicité de l'aldicarbe. Il semblait nécessaire d'étudier la migration de l'aldicarbe et son devenir dans les eaux souterraines de l'Île-du-Prince-Edouard. Les raisons de la persistance de l'aldicarbe dans les aquifères de l'Île-du-Prince-Edouard sont présentées ici. De plus, des modifications des pratiques agricoles qui en diminueraient la persistance dans les eaux souterraines sont proposées.

ALDICARB AND NITROGEN RESIDUES IN A SANDSTONE AQUIFER

M.W. Priddle, R.E. Jackson and A.S. Crowe
National Water Research Institute, Environment Canada
Burlington, Ontario, Canada L7R 4A6

J.P. Mutch
Ground Water Studies Group
University of New Brunswick
Fredericton, N.B., Canada

ABSTRACT

The factors contributing to aldicarb persistence have been clearly demonstrated by numerous workers in the last few years. Temperature and pH are the two most important factors affecting the degradation of aldicarb. Low pH (5-6) and low temperature inhibit the hydrolysis of the toxic aldicarb species to non-toxic transformation products.

During the past three years, the ground water chemistry has been monitored in the sandstone aquifer beneath two potato fields to which aldicarb has been applied. These sites are located on Prince Edward Island (PEI) in eastern Canada. Persistence of the toxic species - aldicarb sulfoxide and aldicarb sulfone - has been noted in areas of low pH (5-7) and high nitrate. At one site the correlation between high nitrate and high aldicarb has been very good for 3 years of sampling. It seems that high aldicarb values ($>5 \mu\text{g/L}$) rarely ever appear without elevated nitrate concentrations ($>10 \text{ mg/L}$) and that there may be chemical as well as physical reasons for this correlation.

The possibility of a link between ammonia fertilizer degradation and aldicarb persistence is investigated. Nitrification (oxidation of ammonia) is a source of nitrate and protons, therefore lowering pH. The ground waters of the sandstone aquifer are highly oxygenated (5-10 mg/L) suggesting ideal nitrification conditions in the unsaturated zone. Finally ground water temperatures on PEI are usually less than 10°C throughout the year. These low temperatures accompanied with the decrease in pH due to nitrification present ideal conditions for aldicarb persistence. This combination of factors is examined in order to evaluate the relationship between aldicarb and nitrogen residues to ground water contamination on Prince Edward Island.

RÉSIDUS D'AZOTE ET D'ALDICARBE DANS UN AQUIFÈRE GRÉSEUX

M.W. Priddle, R.E. Jackson and A.S. Crowe

National Water Research Institute, Environment Canada

Burlington, Ontario, Canada L7R 4A6

J.P. Mutch

Ground Water Studies Group

University of New Brunswick

Fredericton, N.B., Canada

RÉSUMÉ

De nombreux chercheurs ont, ces dernières années, clairement démontré les facteurs qui contribuent à la persistance de l'aldicarbe. La température et le pH sont les deux facteurs les plus importants à jouer un rôle dans la dégradation de l'aldicarbe. Un faible pH (5-6) et de basses températures empêchent la transformation par hydrolyse de l'espèce toxique aldicarbe en produit non toxique.

La chimie des eaux souterraines d'un aquifère gréseux situé sous deux champs de pommes de terre traités à l'aldicarbe a été surveillée durant les trois dernières années. Ces cultures sont situées à l'Île-du-Prince-Edouard dans l'est canadien. On a noté la persistance d'espèces toxiques: l'érivés sulfoxyde et sulfone de l'aldicarbe, là où le pH était faible (5-7) et la teneur en nitrate élevée. À l'un des sites, la corrélation entre teneur élevée en nitrate et teneur élevée en aldicarbe a été très bonne durant les trois années d'échantillonnage.

Il semble que des teneurs élevées en aldicarbe (supérieures à 5 µg/L) apparaissent rarement sans qu'il y ait aussi des teneurs élevées en nitrate (supérieures à 10 mg/L), et que cela pourrait bien s'expliquer par des raisons autant chimiques que physiques.

On étudie la possibilité d'un lien entre dégradation d'un fertilisant ammoniacal et persistance de l'aldicarbe. La nitrification (oxydation de l'ammoniac) est une source de nitrate et de protons, ce qui fait donc baisser le pH. Les eaux souterraines de l'aquifère gréseux sont très oxygénées (5-10 mg/L) ce qui indiquerait des conditions idéales de nitrification dans la zone non saturée. Finalement, à l'île-du-Prince-Edouard, les températures des eaux souterraines sont généralement inférieures à 10°C durant toute l'année. Ces faibles températures, associées à une diminution du pH par suite de la nitrification représentent des conditions idéales à la persistance de l'aldicarbe. On examine cette combinaison de facteurs afin d'évaluer les rapports entre les résidus d'aldicarbe et d'azote et la contamination des eaux souterraines à l'île-du-Prince-Edouard.

INTRODUCTION

Pesticide contamination of ground water is an environmental and public health concern throughout Canada, particularly in the Maritime provinces (see Fig. 1) where ground water is a major source of water for all uses, e.g. food processing, drinking, etc. Surveys of farm wells on Prince Edward Island (PEI) in 1983/84 indicated that low levels (1-6 $\mu\text{g/L}$) of the toxic insecticide aldicarb were present in 18% of high-risk wells around potato fields (Matheson et al., 1987). Aldicarb residues have also been found in drinking water wells as a result of application to potatoes in the Northeastern United States (especially Long Island, N.Y.) and Wisconsin (Jones, 1986b).

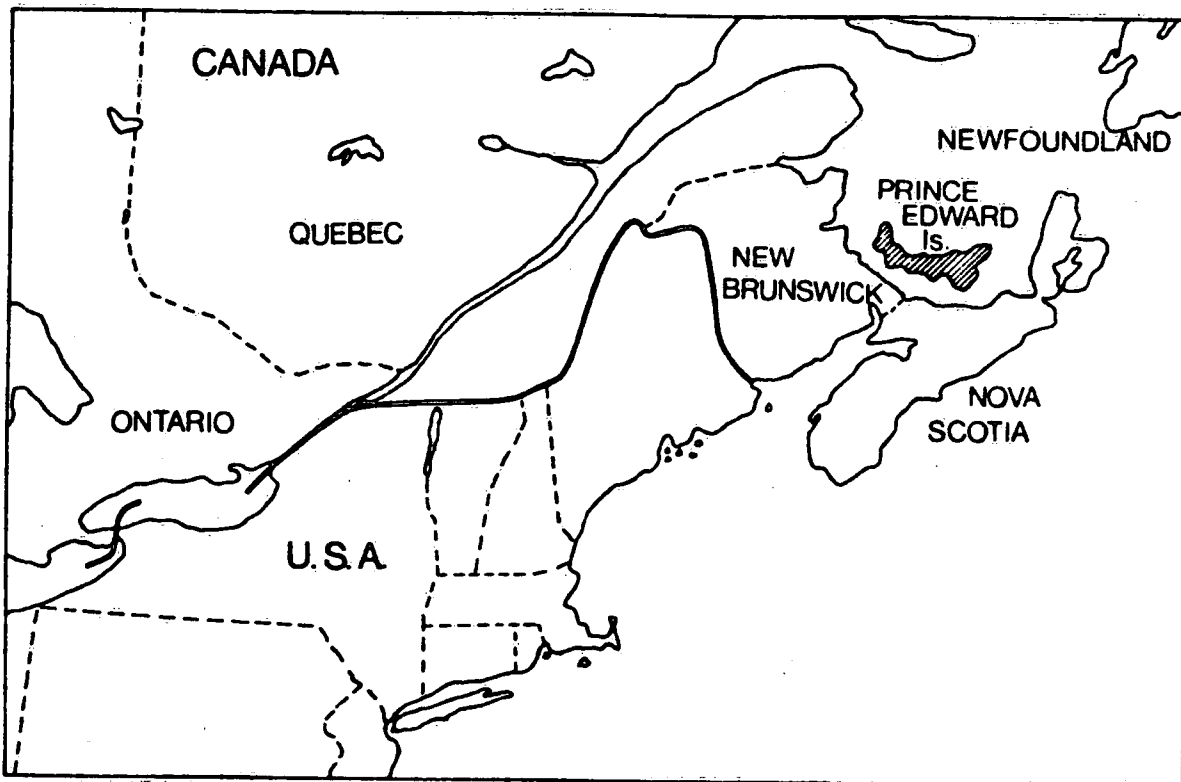


Fig. 1. Location of PEI in eastern North America

Aldicarb is an extremely toxic carbamate insecticide (Oral LD_{50} (rats) = 0.9 mg/kg) with a solubility of 0.6% and a hydrolysis half-life ranging from a few weeks to years (Lightfoot et al., 1987). Because of its toxicity, aldicarb is applied in granular form (as Temik - 10% aldicarb) during spring planting of potatoes, along with urea or ammonium nitrate fertilizer. The granules dissolve and the insecticide undergoes rapid microbially-catalyzed oxidation to the sulfoxide, which may undergo either hydrolysis to relatively non-toxic oximes and nitriles or further oxidation to the sulfone and then similar hydrolytic degradation. Health and Welfare Canada has issued an interim guideline value for total aldicarb (aldicarb, aldicarb sulfoxide and aldicarb sulfone) in drinking water of 9 $\mu\text{g/L}$ (Toft, 1986).

The migration and fate of aldicarb in ground water has been extensively studied at various sites under a wide variety of conditions

(e.g., Jones, 1986b; Harkin et al., 1986). The objective of this study is to gain an understanding of the transport and transformations of aldicarb under the particular conditions of the fractured sandstone aquifer of Prince Edward Island and the overlying till, which is the sole source supply of water for the Island (Francis, 1981). From this study information will be gained in order to refine guidelines on the use of Temik in Canada.

A detailed examination of the ground water and aquifer conditions beneath two fields on PEI is being undertaken. In this paper, chemical conditions are described and the factors leading to aldicarb persistence in the subsurface are discussed.

FIELD SITES

Two sites on PEI (see Fig. 1) were chosen to conduct field assessments of aldicarb persistence. These sites were selected because there had been accurate documentation of pesticide and fertilizer use over the last few years and evidence of aldicarb residues in nearby farm wells (at one site). Both of these fields are located in the main potato growing area of eastern Prince County, PEI (see Fig. 2). The hydrostratigraphy consists of 2-3 m of till underlain by fractured fine-grained sandstone rebeds of Permo-Carboniferous age (van de Poll, 1983). The sandstone aquifer is basically unconfined and, due to the decreasing number of fractures and their decreasing aperture, the permeability decreases with depth. Therefore the most productive zones are also the most easily contaminated (Francis, 1981). Ground water flow and contaminant transport are controlled by the degree, orientation and continuity of fracturing.

Groundwater monitoring was conducted using 5.04 cm, schedule 40, PVC piezometers that were installed using an air-rotary drilling rig. Screens (#6 slot) were either 1 or 1.5 m long and a sand-pack (one to two metres of #2 silica sand) was used with a one metre bentonite seal placed above it. The hole was backfilled with native material produced during the drilling of the borehole (see Fig. 3).

In June of 1985, ten piezometers were installed in a 13 ha field near Augustine Cove. Five pairs (one deep, one shallow) were arranged in a pattern resembling a "T" which had its base at the topographic high point of the field. This arrangement will allow a tracer test to be conducted at a later date. In June of 1986, 15 more piezometers were installed at various locations throughout the field. Three nests of three piezometers were placed at the outer edges of the field. The other six were single water table wells placed alongside the nests installed the previous year. In 1987, three deep boreholes were drilled and hydraulically tested prior to installing a four or five port multilevel in each.

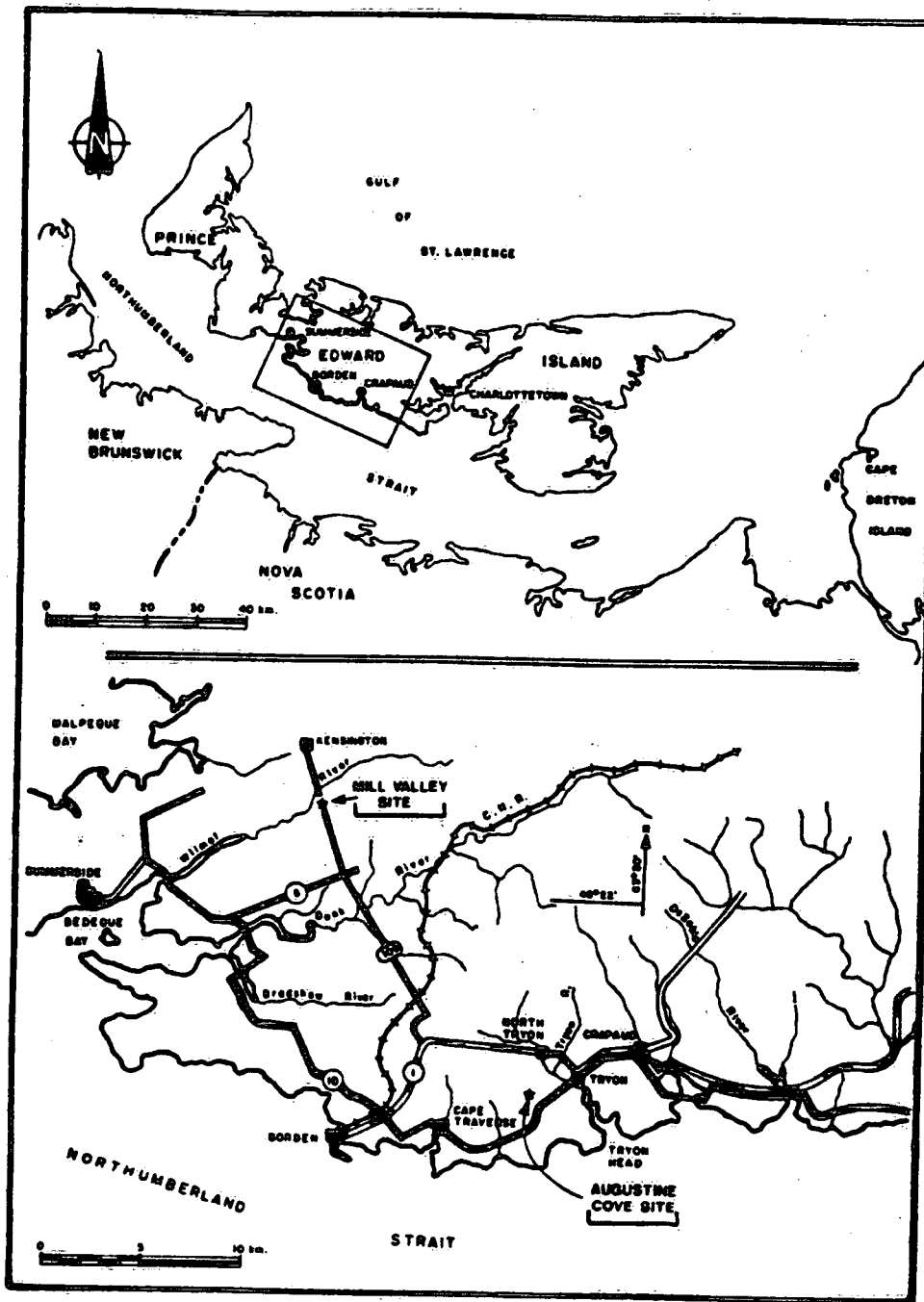


Figure 2 Location of field sites on Prince Edward Island

Figure 4 shows a plan view of the site with water table contours. Figure 5 is the cross section ABCD showing the stratigraphy and the lines of equal hydraulic head in the aquifer. In mapping the water table from the 1986 and 1987 data it seemed that water was recharging the aquifer from the stream and being discharged through a fracture zone (out of the plane of the paper in Fig. 5) in the vicinity of piezometers 5 and 6.

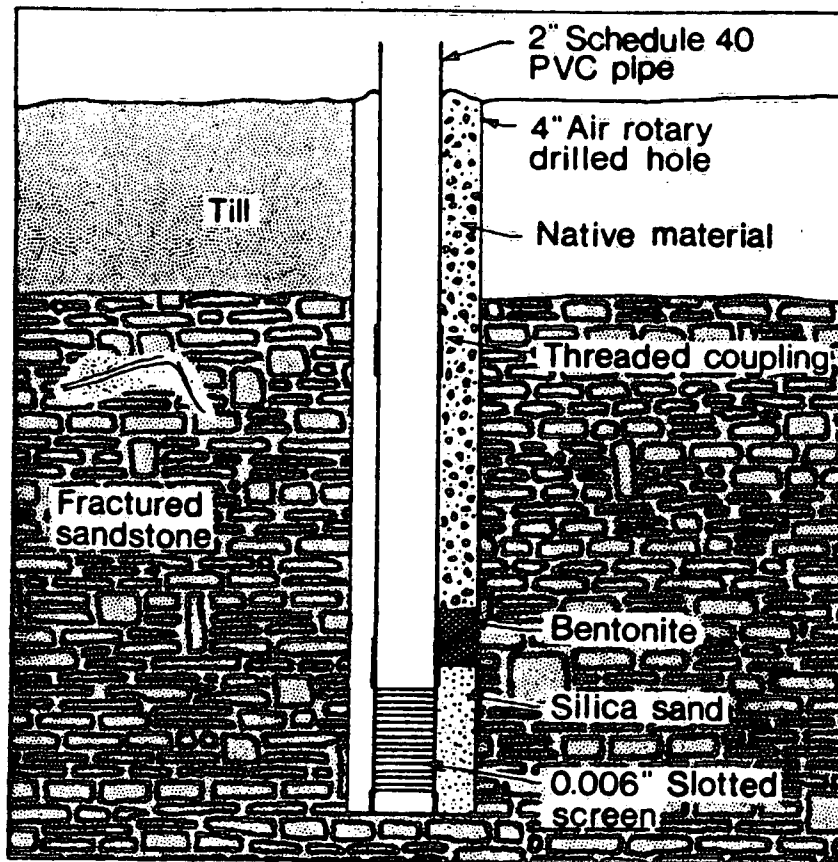


Figure 3. Schematic of a typical piezometer installation.

Ten piezometers were installed in June of 1985 in a similar pattern at a site near Mill Valley. The field is somewhat larger and thus the "T" is more spread out. Again the base of the "T" is located at the topographic high point of the field. Due to access problems only three more piezometers were installed in the spring of 1986. Figure 6 shows a plan view of the site with water table contours. Figure 7 is the cross section JLM showing the lines of equal head in the aquifer.

Measurements of soil organic carbon content have been made on samples from both sites. Except for one sample, taken at a depth of 15 cm in the field at Mill Valley, the fraction of organic carbon (FOC) in all samples was less than 2%. Organic carbon content dropped off rapidly below the root zone. At 70 cm, levels were below 0.2% and a sample of sandstone cuttings from just above the water table at Augustine Cove contained no detectable organic carbon (i.e. <0.004%). As Zhong et al. (1986) noted, the movement of aldicarb is unretarded in soils with FOC less than 2%. Consequently the migration of aldicarb in PEI sandstone should be controlled solely by the movement of water. Ground water velocities have not yet been calculated at either of the field sites because the complex nature of the fracture sandstone has not been studied in detail.

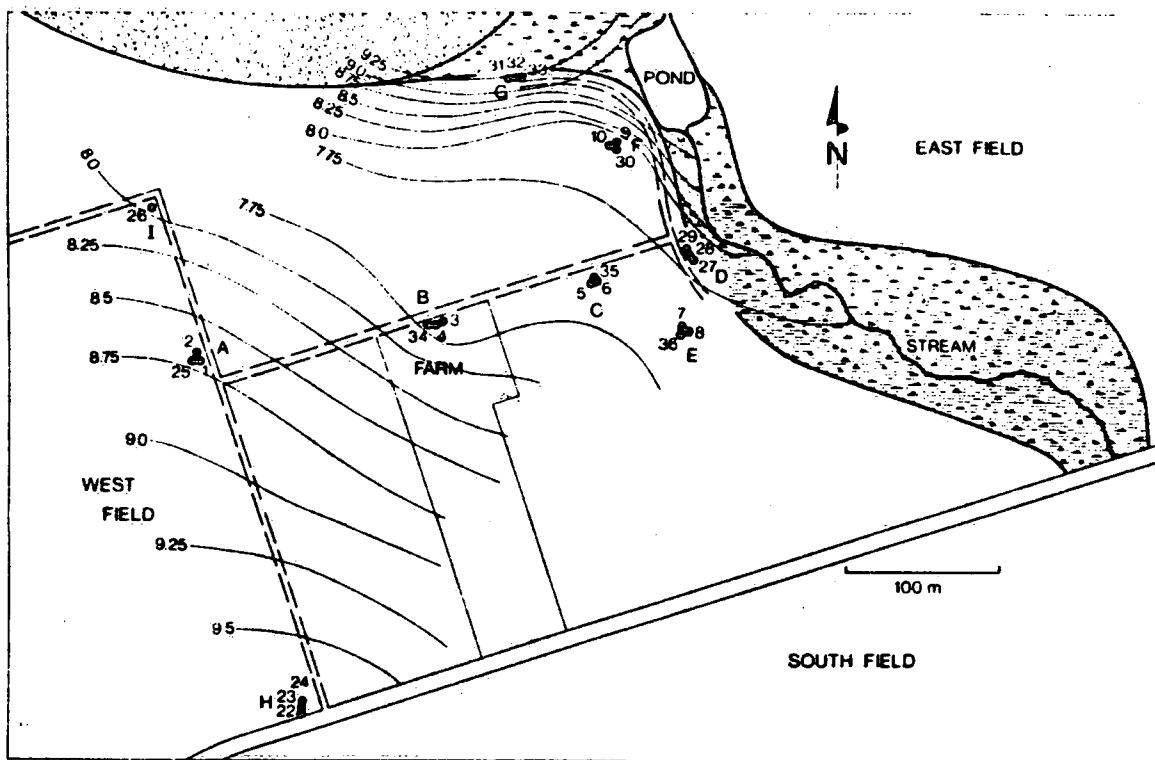


Figure 4 Water table in metres above mean sea level at Augustine Cove, PEI. Average of two water level measurements in June 1987.

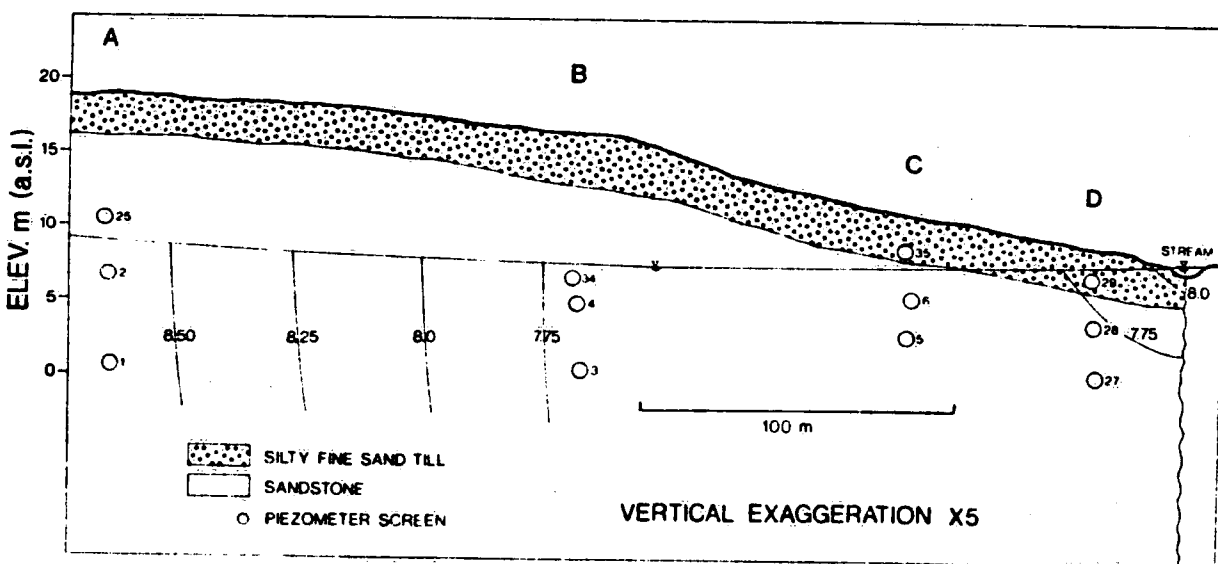


Figure 5 Equipotential map of hydraulic head in metres above mean sea level at Augustine Cove, PEI (cross section ABCD). Average of three water level measurements in September, 19868.

CHEMICAL METHODS

As many water quality parameters as possible were measured in the field in order to define in situ conditions and avoid possible changes during sample shipment. E_H and pH measurements were made in a flow cell using combination platinum and pH electrodes, respectively (Orion Research Inc., Cambridge, Massachusetts, USA). Dissolved oxygen (DO) was measured using an Orbisphere Oxygen Indicator, Model 2606 (Orbisphere Labs., Geneva, Switzerland). Specific conductance (YSI Scientific meter, Yellow Springs, Ohio, USA), temperature and ammonia (Orion gas-sensing electrode) were also measured in the field. A titration with normalized H_2SO_4 to a fixed end-point was performed in the field to determine alkalinity (as HCO_3^-).

After at least two well volumes had been purged, samples for aldicarb analysis were collected in 60 mL amber glass bottles using a Teflon bladder pump (Well Wizard, QED Systems, Ann Arbor, Michigan, USA). These samples were filtered, acidified to pH 5 and stored at 4°C prior to analysis. Samples for inorganic analysis were taken in plastic bottles and stored at 4°C. Samples for cations (Ca^{2+} , Mg^{2+}) were acidified to pH 3 with HNO_3 to prevent possible mineral precipitation prior to analysis.

The method of Chaput (1986) was used to analyse samples for the three toxic aldicarb species. This procedure combines on-line trace enrichment with fluorescence detection. Since only ASO and ASO₂ have been found in the subsurface, a modified procedure was developed that improved the separation of these two compounds and shortened the analysis. The mobile phase was changed to acetonitrile/water (15:85) to elute the two compounds in less than ten minutes. All samples taken in 1987 were analysed by this method.

ALDICARB AND NITROGEN CHEMISTRY

The environmental chemistry of aldicarb has been studied in detail by numerous workers (Jones, 1986b). Much of this research was conducted on a post-mortem basis as cases of ground water contamination arose in various part of the U.S.A. and Canada. Information from these studies and accompanying laboratory tests have been used to understand more fully the migration and fate of aldicarb in the subsurface. Modifications to agricultural practices to minimize contamination of ground water in problem areas have been developed from this work (e.g. Jones, 1985).

This section presents a review of aldicarb and nitrogen chemistry as it pertains to ground water pollution, with particular reference to the PEI sandstone aquifer. The reader is referred elsewhere (Lightfoot, 1987; Given and Dierberg, 1986) for a detailed discussion of the transformations of aldicarb, however a schematic of the degradation pathways is shown in Fig. 8. The three toxic compounds, aldicarb, aldicarb sulfoxide and aldicarb sulfone, are often referred to as either the total toxic residue or total aldicarb in ground water investigations. They shall be referred to as total aldicarb herein.

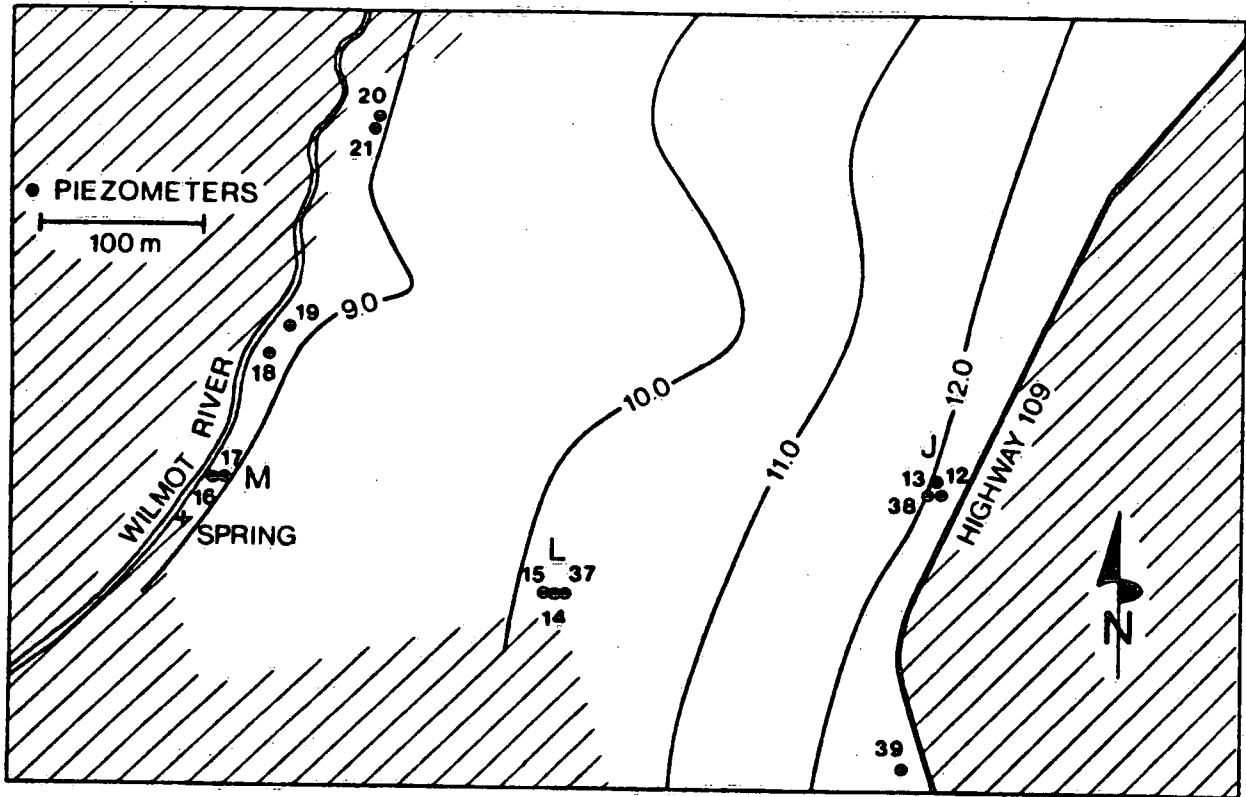


Figure 6 Water table in metres above mean sea level at Mill Valley, PEI (September, 1986).

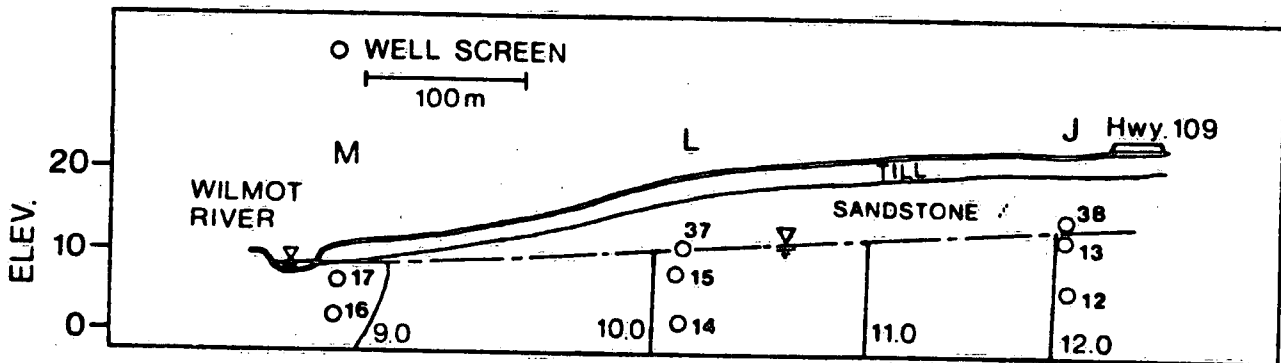


Figure 7 Equipotential map of hydraulic head in metres above mean sea level at Mill Valley, PEI (cross section JLM, September, 1986).

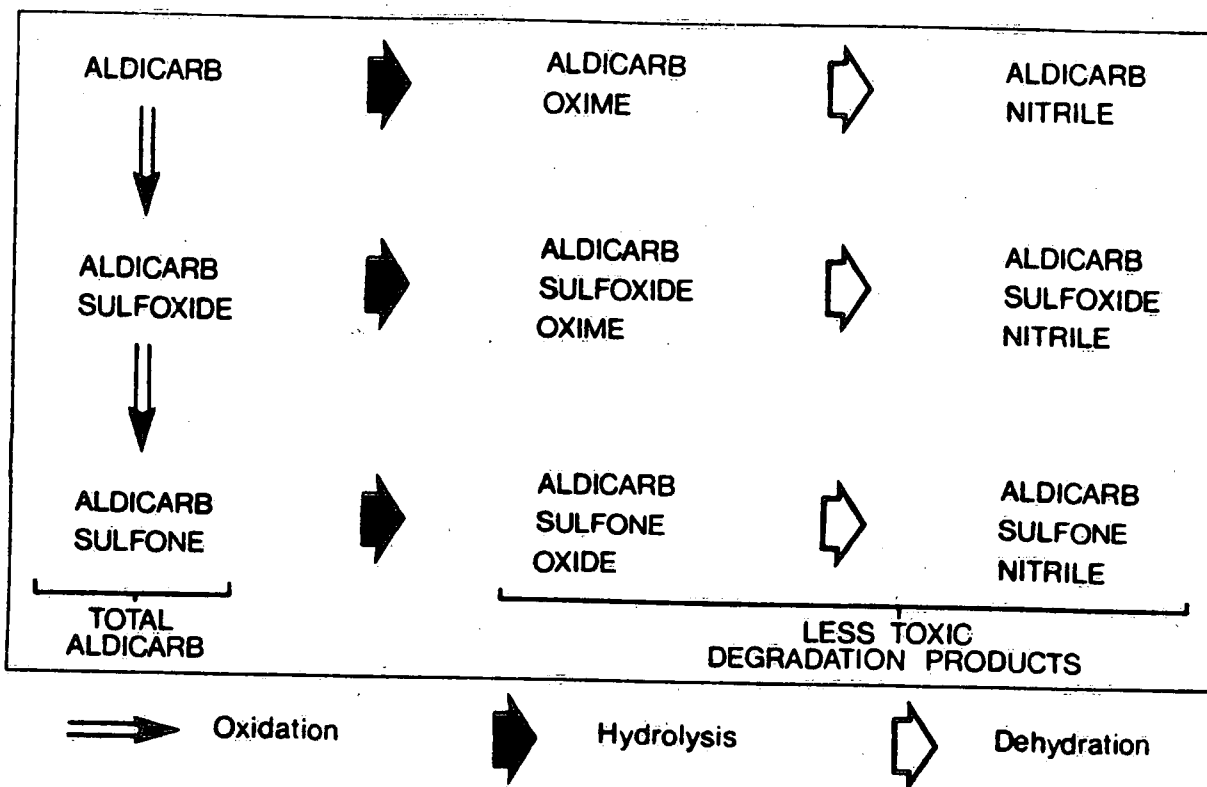
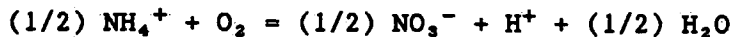


Figure 8 Simplified schematic of aldicarb degradation pathways

In summary, the two most important variables affecting the degradation of aldicarb are pH and temperature (Jones, 1986a and 1986b). The chemical hydrolysis reaction that degrades aldicarb (sulfoxide and sulfone) proceeds slowest in the pH range of 5 to 6 (see Fig. 9). Outside of this range, acid and base hydrolysis are more pronounced. Temperature also has a marked effect on the degradation of the three toxic products. Typically, the rate of most chemical reactions is approximately doubled with a 10°C rise in temperature, however, the aldicarb hydrolysis reactions are about 3.5 times as fast with a similar change in temperature (Lightfoot et al., 1987). As a consequence of these characteristics aldicarb contamination of ground water has been acute in the temperature regions of North America that have acidic soils (e.g. Long Island, N.Y., Maine, Wisconsin and eastern Canada).

Since parent aldicarb is oxidized so rapidly to aldicarb sulfoxide, it is rarely detected in ground water. The oxidation of the sulfoxide to the sulfone proceeds at a much slower rate, therefore these latter two compounds typically constitute total aldicarb in ground water. The proportions of these two compounds in the subsurface may vary within or between different sites.

The nitrogen cycle has been studied in detail from an agricultural point of view. The transformation of concern to ground water is the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-); i.e. nitrification. Nitrification is prevalent in oxygenated soil moisture beneath fields that have been treated with ammoniacal fertilizers. The reaction:



produces protons (acidity) and nitrate. As pointed out by Priddle et al., (1987), a pH of 3.6 will be produced in consuming 8 mg O_2/L and only 10% of the ammonium applied to the PEI fields. Needless to say, geochemical neutralization reactions will lessen this pH effect, however the reaction proceeds under a fairly wide variety of conditions. The two bacteria involved in nitrification are Nitrosomonas ($\text{NH}_4^+ \rightarrow \text{NO}_2^-$) and Nitrobacter ($\text{NO}_2^- \rightarrow \text{NO}_3^-$). Both are found in nearly all soils that are suited for agricultural purposes. Optimal conditions for these bacteria are in the pH range of 6 to 8 and at temperatures above 5°C and below 40°C depending on the type of soil. In addition to these two reactants (i.e. substrate NH_4^+ and oxygen), HCO_3^- must be present (Schmidt, 1982). Optimal conditions seem to vary quite widely but under conditions such as those found on PEI, nitrification is very rapid and a significant proportion of the ammonium applied at spring planting will be nitrified within 60 days (John MacLeod, Agriculture Canada, Charlottetown, PEI, pers. comm.).

GROUND WATER CHEMISTRY

Prince Edward Island is a rich farming province located on Canada's east coast. Its soils, being cool, sandy and well-drained, are particularly suited to the cultivation of potatoes. This also presents conditions conducive to aldicarb leaching and persistence. The pH of rainfall is low (<5) and the soils are acidic. The soil temperatures (at 15 cm) reach a maximum of 17°C during July or August (Macdougall et al., 1981).

Plan views of the two field sites that are being studied are shown in Figs. 4 and 6. Work has concentrated on characterizing the ground water chemistry and hydrogeology of the Augustine Cove site. In the summers of 1986 and 1987 water from the upper portion of the field and from the stream was being discharged through a fracture zone near piezometer nest D (out of the plane of the paper in Fig. 5). The effect of the losing stream is to alter drastically the ground water flow and chemistry in the lowland area. The ground waters in the recharge area are oxygenated ($>8 \text{ mg } \text{O}_2/\text{L}$), low in dissolved organic carbon (DOC) and iron but high in NO_3^- , whereas the stream water in the aquifer is strongly reducing hence containing no detectable NO_3^- or DO but much iron and DOC. A summary of chemical data from five representative wells at the Augustine Cove is shown in Table 1. Observation well 27 is close to the stream in the reducing zone. The other four wells are all completed to a depth of 1-3 m in the aquifer and are located away from the edges of the field. They are shown here because they appear to represent conditions beneath the field of interest without influences from the stream or inputs to adjacent fields.

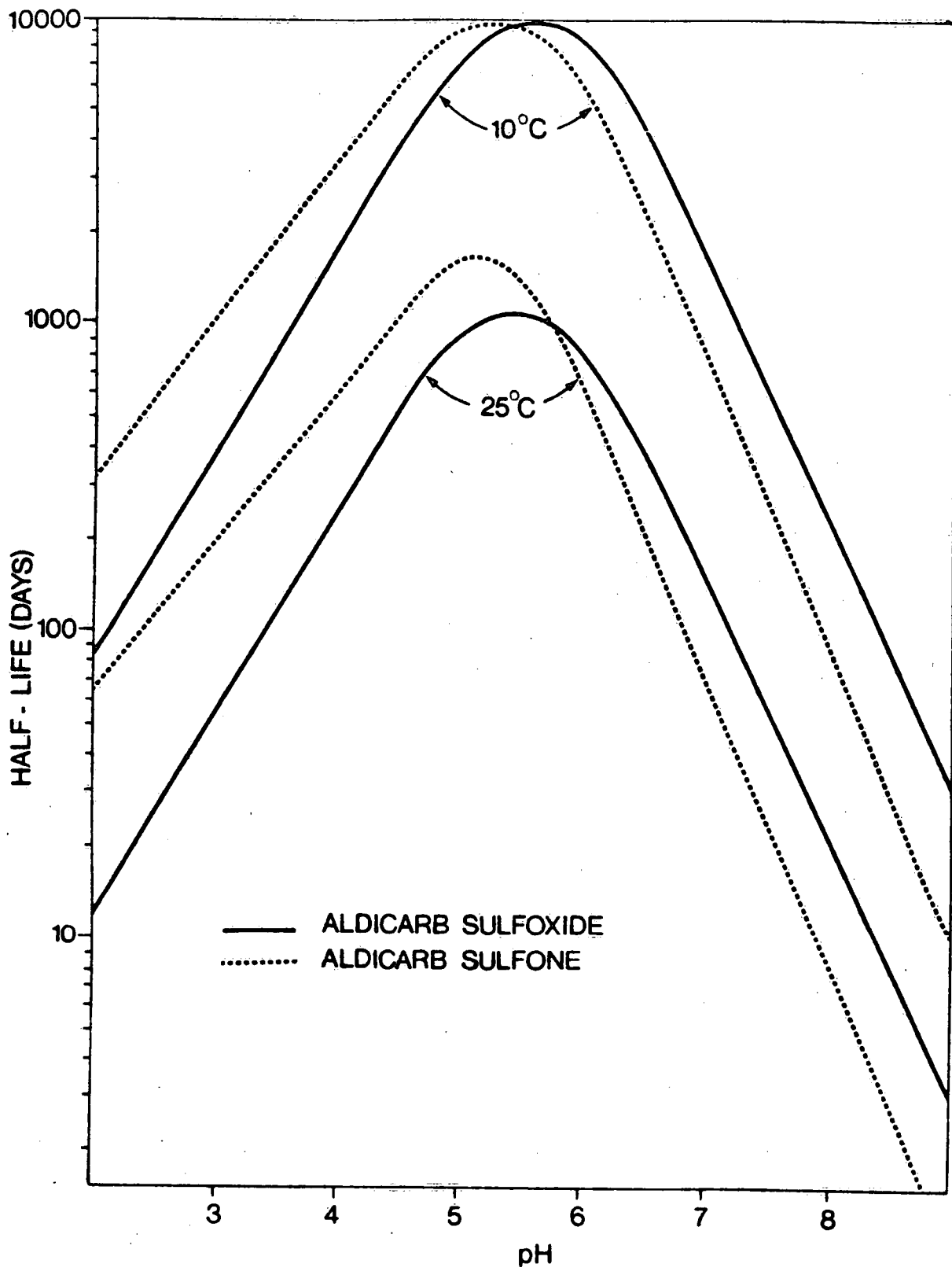


Figure 9 Effect of temperature and pH on the chemical hydrolysis of aldicarb sulfoxide and aldicarb sulfone (modified from Lightfoot et al., 1987).

Table 2 shows similar data for three representative wells and the spring at Mill Valley. The most striking difference is that, despite Temik applications in both 1985 and 1986 (Table 3), there is very little contamination of the ground water beneath this field. The 7.7 µg total aldicarb/L detected at MV-17 was the highest level at any well at Mill Valley during any sampling period. The only peculiar sampling point at this site has been the spring at the bottom of the field which discharges into the Wilmot River, and has had an average total aldicarb concentration of 4.4 µg/L over a three year period.

ALDICARB SPECIATION

Jones and Marquardt (1987) found that the ratio of aldicarb sulfone: total aldicarb remained constant at about 0.48 for five years following the cessation of aldicarb use on Long Island. A general ratio of 0.40 is mentioned by Jones (1986a) while the ratio in domestic and monitoring wells in Wisconsin was about 0.43 (Harkin et al., 1986). On the contrary, three years of data from PEI have shown that this ratio is generally much higher (i.e. >0.60) and can vary quite widely (0.43 to 1.0: see Table 3). As Priddle et al. (1987) noted, there appears to be a correlation between the ratio of aldicarb sulfone:aldicarb sulfoxide and the time after application.

TABLE 3 Fertilizer and aldicarb application (1983-1987)

Fertilizer or Pesticide	Year	Amount Applied (kg/ha)	
		Augustine Cove	Mill Valley
NH ₄ NO ₃ (as N)	1987	52	
Aldicarb	1986	1.96	2.02
NH ₄ NO ₃ (as N)		210	206
Urea (as N)			82
Aldicarb	1985		2.24
NH ₄ NO ₃ (as N)			27
CaCO ₃		2128	
CaMg (CO ₃) ₂		112	
NH ₄ NO ₃ (as N)	1984		27
(NH ₄) ₂ HPO ₄ (as N)		54	
Aldicarb	1983	1.96	
NH ₄ NO ₃ (as N)		190	27
Urea (as N)		5.9	

NH₄NO₃ - ammonium nitrate
 (NH₄)₂HPO₄ - diammonium phosphate
 Urea - CO(NH₂)₂

TABLE 1. Selected groundwater quality data, Augustine Cove, PEI, showing sampling date, pH, E_H , (measured Pt electrode potential vs. normal hydrogen electrode), dissolved oxygen, nitrate-nitrogen, bicarbonate, total aldicarb (sum of aldicarb, aldicarb sulfoxide and aldicarb sulfone), ratio (mole ratio of aldicarb sulfone: total aldicarb) and dissolved organic carbon. With the observation well number, screen refers to the depth to mid-screen below grade; unsaturated zone is the approximate depth to the water table. Blank - parameter not measured.

Date	pH	E_H (V)	DO (mg/L)	NO_3^- -N (mg/L)	HCO_3^- (mg/L)	Total Ald. (μ g/L)	Ratio	DOC (mg/L)
Observation Well #4 (Screen - 11.4 m, unsaturated zone - 10 m)								
7/85	7.5	0.47	9.0	7.6		4.0	0.61	
9/85				2.8	104	0.2		
9/86	7.0	0.43	8.7	7.6	101	3.6	0.68	0.8
6/87	7.1	0.55	10.0	11.0	96	3.1	0.79	<0.5
8/87						1.4		
Average	7.2	0.48	9.2	7.3	100	2.5	0.67	0.6
Observation Well #6 (Screen - 6.1 m, unsaturated zone - 4 m)								
7/85	6.3	0.54	2.8	14.0		12.0	0.74	
9/85				5.0	31	3.9	0.70	
9/86	6.4	0.42	5.7	8.4	49	7.1	0.76	1.0
6/87	6.3	0.56	9.0	12.0	45	6.9	0.74	<0.5
8/87						7.1	0.75	
Average	6.3	0.51	5.8	9.9	42	7.4	0.75	0.7
Observation Well #7 (Screen - 5.3 m, unsaturated zone - 3 m)								
7/85	6.4	0.49	9.0	12.0		10.8	0.69	
9/85				11.0	91	5.9	0.75	
9/86	5.6	0.48		8.0	50	4.7	0.77	0.6
7/87	6.6	0.51	8.0	11.0	76	3.7	1.0	<0.5
8/87						4.8	0.74	
Average	6.2	0.49	8.5	10.5	72	6.0	0.80	0.5
Observation Well #9 (Screen - 4.2 m, unsaturated zone - 3 m)								
7/85				14.0		14.2	0.70	
9/85				12.0	109	12.3	0.70	
9/86	6.6	0.48		13.6	94	12.8	0.72	0.9
7/87	7.5	0.51	6.0	13.0	151	15.0	0.71	1.0
8/87						12.8	0.71	
Average	7.1	0.50	6.0	13.2	118	13.4	0.71	0.95
Observation Well #27 (Screen - 7.0 m, unsaturated zone - 1 m)								
9/86	6.8	0.13	0.3	<0.05	207	<0.1		
7/87	6.8	0.15	0.4	<0.05	242	0.6		8.0
8/87						0.4		6.3
Average	6.8	0.14	0.35	<0.05	225	0.3		7.2

TABLE 2. Selected groundwater quality data, Mill Valley, PEI, showing sampling date, pH, E_H , (measured Pt electrode potential vs. normal hydrogen electrode), dissolved oxygen, nitrate-nitrogen, bicarbonate, total aldicarb (sum of aldicarb, aldicarb sulfoxide and aldicarb sulfone), ratio (mole ratio of aldicarb sulfone: total aldicarb). With the observation well number, screen refers to the depth to mid-screen below grade; unsaturated zone is the approximate depth to the water table. Blank - parameter not measured.

Date	pH	E_H (V)	DO (mg/L)	NO_3^- -N (mg/L)	HCO_3^- (mg/L)	Total Ald. (μ g/L)	Ratio
Observation Well #12 (Screen - 17.7 m, unsaturated zone - 12 m)							
7/85				3.5		<0.1	
9/85				4.3	65	<0.1	
9/86						<0.1	
6/87	7.8	0.49	10.0	4.7	90	<0.1	
8/87						<0.1	
Average				4.2		<0.1	
Observation Well #14 (Screen - 18.1 m, unsaturated zone - 9 m)							
7/85				5.4			0.1
9/85				6.0	77	<0.1	
9/86						<0.1	
6/87	7.3	0.49	10.0	6.1		3.7	0.55
8/87						0.7	
Average				5.8		0.9	
Observation Well #17 (Screen - 5.0 m, unsaturated zone - 2.5 m)							
7/85	7.9	0.47	5.3	5.4		0.1	
9/85				4.3	75		
9/86						1.1	
6/87	7.3	0.52	9.0	12.0		7.7	0.55
8/87						0.7	
Average				7.2		2.4	
Spring near Wilmot R.							
7/85				8.3		4.7	0.43
9/85				8.0		4.6	0.46
6/87	7.2	0.54	9.0			4.8	0.48
8/87						3.4	0.47
Average				8.2		4.4	0.45

Blank - parameter not measured

The mole ratio of aldicarb sulfone:total aldicarb (see data in Tables 1 and 2) will approach 1.0 as all the sulfoxide is oxidized to sulfone. It generally increases with depth and distance from the flow system. At the Augustine Cove site the ratio at a single well does not necessarily increase with time because residues from both the 1983 and 1986 Temik applications are being detected (see Table 3). A reason for the steadily increasing ratio seen here but not at other sites may be the highly oxygenated conditions of PEI ground waters, which tend to drive the microbial oxidation of sulfoxide to sulfone.

THE RELATIONSHIP OF NITROGEN AND ALDICARB RESIDUES

In contrast with results from other research sites (e.g. Harkin et al., 1986), the PEI data show a good correlation between aldicarb and nitrate residues in the saturated zone (see Fig. 10). This may of course be due strictly to physical reasons - both aldicarb and nitrate are essentially mobile and unretarded in the subsurface, hence their leaching characteristics are similar. Since favourable conditions exist for both aldicarb persistence and nitrification, there may also be a chemical explanation for the observed trend. Given that the oxidation of ammonium lowers pH and produces nitrate ions, the logical conclusion is that ground waters that inhibit aldicarb degradation (low pH) would also be high in nitrate as a result of this oxidation reaction.

It is also interesting to note that conditions inhibiting aldicarb degradation (low temperature and pH ~5) also slow the rate of nitrification. That is, nitrification proceeds fastest under conditions most suited to aldicarb degradation but it also affects the degradation of aldicarb. Therefore if these two processes can be separated by applying aldicarb and ammoniacal fertilizers at different times, the problem of aldicarb residues reaching ground water could possibly be reduced.

Various workers have studied the effects of pesticides on nitrification but not the reverse. Lin et al. (1972) noted that aldicarb would have to be applied at about 100 times its recommended rate before it would significantly inhibit nitrification. No other pesticide used on either of the two fields would inhibit nitrification at the rates applied.

If one assumes that nitrification conditions are similar at both sites and therefore equal amounts of nitrate are being produced by fertilizer application, then the effects should be the same. In the last five years (1983-1987), more nitrogen has been applied to the field at Augustine Cove (512 kg/ha) than at Mill Valley (367 kg/ha). This seems to be reflected in the lower NO_3^- -N levels in ground water at Mill Valley. Total aldicarb levels are also lower but seem to be rising in the period after the 1985-86 applications. This may be due to the slow leaching of aldicarb residues from the unsaturated zone as found by Pacenka and Porter (1987) on Long Island. This situation is more likely at Mill Valley because of the two consecutive years of Temik application and the thicker unsaturated zone. This hypothesis is supported by the steady concentration of total aldicarb found in the spring at the bottom of the Mill Valley field.

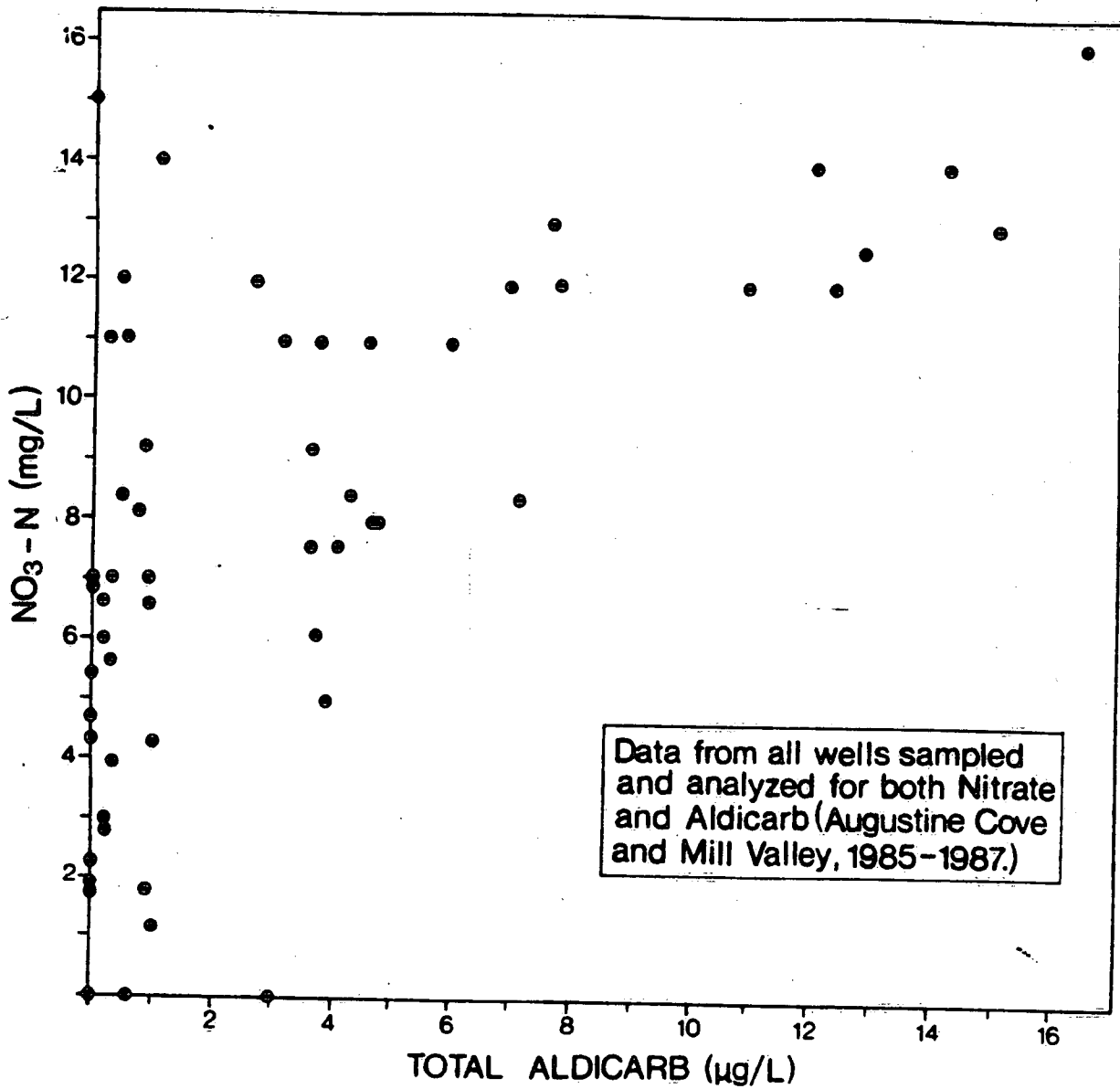


Figure 10 Nitrate-N versus total aldicarb from PEI field sites.

As Jones et al. (1987) have reported, a shallow water table allowed for rapid infiltration of aldicarb residues without time for degradation even under warm conditions in Florida. Similarly total aldicarb concentrations at both field on PEI are highest where the water table is shallowest. The importance of a thick unsaturated zone is also noticed when the pH values from both sites are examined. At Mill Valley no wells have had a pH below 7.3, whereas there are several wells at Augustine Cove that are consistently below 7.0. Recharge water, that is acidic from both rainfall and nitrification, has therefore more time to be neutralized before reaching the water table at Mill Valley.

In order to examine the effect of ammonium oxidation on the pH of these ground waters, a series of geochemical simulations were undertaken with the numerical code, PHREEQE (Parkhurst et al., 1980). Thermodynamic data (ΔG_f° , ΔH_f° , ΔC_p) for determining the equilibrium constants for the dissociation reactions of nitrogen species at 7°C was obtained from the CRC Handbook of Chemistry and Physics (1986). The simulations involved titration of a water, representing rainfall on PEI, with a solution containing varying concentrations of ammonium. A second series of analyses shows the neutralizing effect of calcite dissolution on the pH of the ammonium rich ground waters.

The results of the first analyses, shown in Figure 11, indicate that as ammonium is dissolved in pure water, it is oxidized and significantly lowers the pH. For example, a 0.0001 m solution of NH_4^+ in pure water will lower the pH from a background level of approximately 7 to a pH of 4. Increasing the ammonium concentration in solution to 0.01 m will further decrease the pH to 2.

A major factor influencing the chemistry of ground water is the presence of calcite (CaCO_3) in the soil. Thus, the pH of ground water under natural conditions will be controlled by the amount of calcite available for dissolution. Simulating the dissolution of calcite in pure water under equilibrium conditions will raise the background pH from a value of 7 to approximately 10. However, the addition of ammonium will again cause a decrease in the pH of the ground water (Figure 11). For example, a 0.01 m solution of NH_4^+ in water in equilibrium with calcite, has a pH of approximately 7.

An equilibrium model was used here in order to bracket the range of expected pH's which might be produced under natural conditions. Under conditions typical of PEI, calcite dissolution may not reach equilibrium, thus the actual pH of the solution will be below the calcite equilibrium curve (Figure 11). The amount of calcite dissolved represents approximately 1.0×10^{-4} to 5.8×10^{-2} mol for 0.0 to 0.1 mol of NH_4^+ dissolved respectively. These values correspond to about 3.7×10^{-3} to 2.1 cm³ of calcite being dissolved for each litre of solution. This large amount of calcite is probably not available for dissolution. Therefore the actual pH of the solution will again be less than that obtained under optimum equilibrium conditions. In our study area the NH_4^+ concentration of infiltrating water after fertilizer application is about 0.001 M. The corresponding maximum and minimum values of pH for this concentration of NH_4^+ are approximately 8 and 3 respectively. Due to natural geochemical factors that influence the ground water chemistry, this range is probably smaller. A more detailed discussion of the modeling of these reactions is in preparation (Crowe et al.).

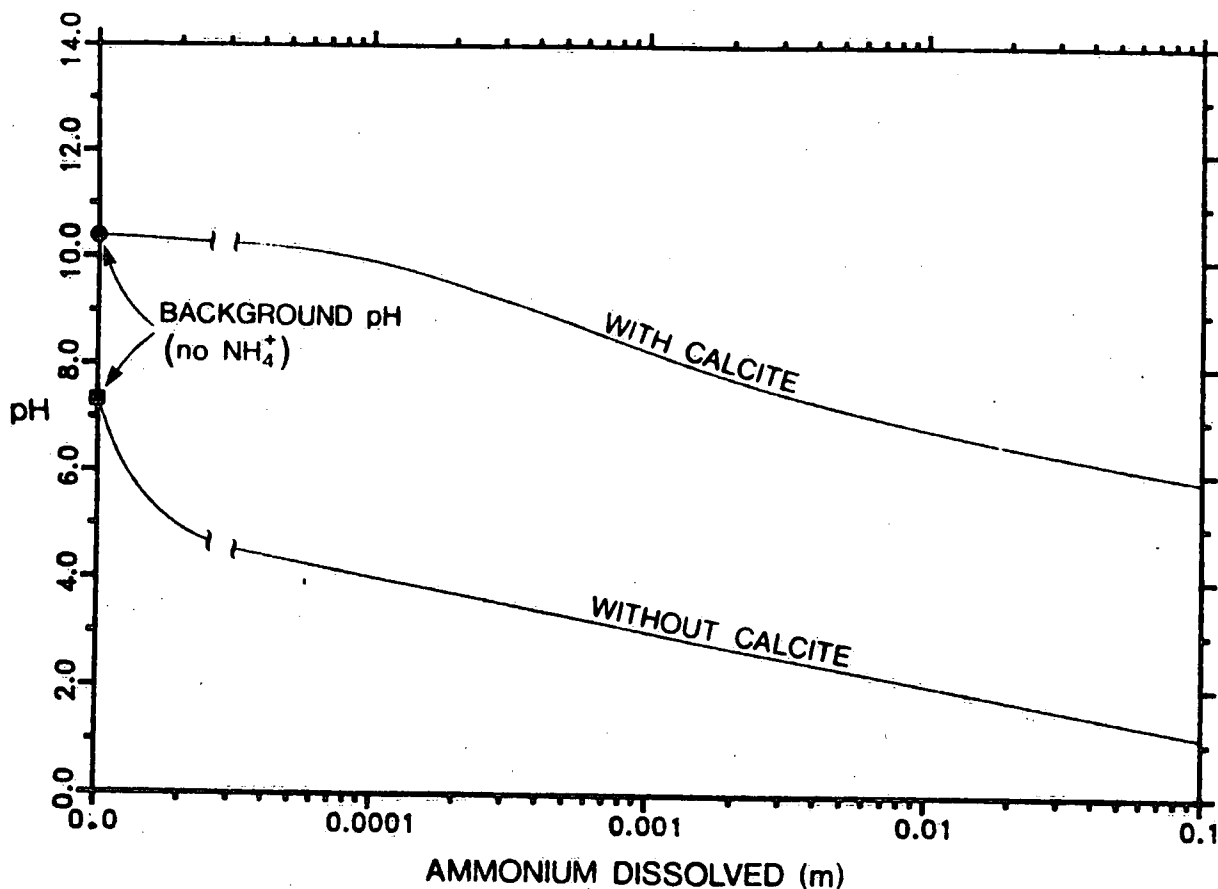


Figure 11 PHREEQE results plotted as pH versus ammonium dissolved (molality) in pure water and water in equilibrium with calcite.

In summary, nitrification seems to be lowering the pH in PEI soils resulting in further inhibition of aldicarb degradation in an environment that is already conducive to aldicarb persistence. With data from two sites showing that high total aldicarb levels rarely ever occur without high nitrate, a link between nitrification and aldicarb persistence is postulated.

REFERENCES

- Chaput, D. 1986. On-line trace enrichment for the determination of aldicarb species in water, using liquid chromatography with post-column derivatization. *J. Assoc. Off. Anal. Chem.*, 69(6), 985-989.
- CRC Handbook of chemistry and physics, 67th edition. 1986. Weast, R.C. Ed., CRC Press Inc., Boca Raton, Florida.
- Francis, R.M. 1981. Hydrogeological properties of a fractured porous aquifer, Winter River Basin, Prince Edward Island. M.Sc. Thesis, University of Waterloo, Waterloo, Ontario.

- Given, C.J. and Dierberg, F.E. 1986. Effect of pH on the rate of aldicarb hydrolysis. *Bull. Environ. Contam. Toxicol.*, 34, 627-633.
- Hallberg, G.R. 1986. From hoes to herbicides: Agriculture and ground water quality. *J. Soil Water Cons.* Nov.-Dec. 1986, 357-364.
- Harkin, J.M., Jones, F.A., Fathulla, R.N., Dzantor, E.K. and Kroll, D.G. 1986. Fate of aldicarb in Wisconsin groundwater. In *Evaluation of Pesticides in Groundwater*, ACS Symposium Series No. 315, 219-255.
- Jones, R.L. 1985. Effect of application methods on movement and degradation of aldicarb residues in Maine potato fields. *Environ. Toxicol. Chem.*, 5, 167-173.
- Jones, R.L. 1986a. Field, laboratory and modeling studies on the degradation and transport of aldicarb residues in soil and groundwater. In *Evaluation of Pesticides in Groundwater*, ACS Symposium Series No. 315, 197-218.
- Jones, R.L. 1986b. The aldicarb experience: 1. Conduct and impact of monitoring and research programs. Presented at Workshop on Groundwater Contamination from Agriculture, Soil Sci. Soc. Am. (Madison, Wisconsin), New Orleans, Louisiana, Dec. 5-6, 1986.
- Jones, R.L. and Marquardt, T.E. 1987. Monitoring of aldicarb residues in Long Island, New York potable wells. *Arch. Environ. Contam. Toxicol.* 16, 643-647.
- Jones, R.L., Hornsby, A.G., Rao, P.S.C. and Anderson, M.P. 1987. Movement and degradation of aldicarb residues in the saturated zone under citrus groves on the Florida ridge. *J. Cont. Hydrol.* 1, 265-285.
- Lightfoot, E.N., Thorne, P.S., Jones, R.L., Hansen, J.L. and Romine, R.R. 1987. Laboratory studies on the degradation mechanisms of aldicarb, aldicarb sulfoxide, aldicarb sulfone. *Environ. Toxicol. Chem.*, 6(5).
- Lin, S., Funke, B.R. and Shulz, J.T. 1972. Effects of some organophosphate and carbamate insecticides on nitrification and legume growth. *Plant Soil*, 37, 489-496.
- MacDougall, J.I., Veer, C. and Wilson, F. 1981. Soils of Prince Edward Island. LRRI Contribution Number 141, Minister of Supply and Services Canada.
- Matheson, R.A.F., Francis, R.M., Jardine, D.E., Gill, M.N. and Ernst, W.P. 1987. Assessment of PEI groundwater for the pesticide aldicarb. Environment Canada, Environmental Protection Service, Atlantic Region.
- Pacanka, S. and Porter, K.S. 1981. Preliminary regional assessment of the environmental fate of the potato pesticide, aldicarb, eastern Long Island, New York. Water Resources Program, Centre for Environmental Research, Cornell University, Ithaca, N.Y.

Parkhurst, D.L., Thorstenson, D.C. and Plummer, N.L. 1980. PHREEQE - A computer program for geochemical calculations. U.S. Geological Survey, Water Resources Investigations 80-96.

Priddle, M.W., Jackson, R.E., Novakowski, K.S., Denhoed, S., Graham, B.W., Patterson, R.J., Chaput, D. and Jardine, D. 1987. Migration and fate of aldicarb in the sandstone aquifer of Prince Edward Island. Water Poll. Res. J. Can. 22(1), 173-185.

Toft, P. Oct. 9, 1986. Memo: "Interim drinking water guideline for aldicarb". Health Protection Branch, National Health and Welfare, Ottawa, Ont.

van de Poll, H.W. 1983. Geology of Prince Edward Island. Queen's Printer, Charlottetown, PEI.