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**THE FATE OF ALDICARB IN AN  
UNSATURATED-SATURATED FLOW SYSTEM  
ON PRINCE EDWARD ISLAND, CANADA**

by

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## ABSTRACT

Aldicarb (a highly toxic, soluble and persistent pesticide) has been detected in the ground waters of Prince Edward Island (PEI), Canada. Three field sites were established on PEI to investigate the processes controlling the fate of aldicarb in the sandstone. A four-year ground water quality monitoring program was conducted, and results indicate that aldicarb residues have persisted much longer than had been expected. Attempts to calibrate a 1-D solute transport model to the observed field data were unsuccessful. The persistent nature of the pesticide observed, as well as the inability of the model to reproduce the observed data, suggests that the degradation of the pesticide may be inhibited, and that there may be a storage mechanism involved, acting to retain the undegraded pesticide and slowly releasing it over time. It has been shown by others that the degradation of aldicarb is inhibited by the low temperatures and pH of the soil and ground water. Pesticide concentration fluctuations have been dampened by diffusion of the pesticide into and out of the sandstone matrix. Simulations performed with the 1-D model indicate that an application at plant emergence, rather than at planting, could significantly reduce the amount of pesticide reaching the water table.

## RÉSUMÉ

L'aldicarbe (un pesticide soluble, persistant et très toxique) a été détecté dans l'eau souterraine de l'Île-du-Prince-Édouard (Î.-P.-É.), Canada. Trois stations sur l'île ont été établies afin qu'on puisse étudier les mécanismes qui déterminent l'évolution de l'aldicarbe dans le grès. On a fait un programme de surveillance de la qualité de l'eau souterraine d'une durée de quatre ans; les résultats montrent que des résidus d'aldicarbe ont persisté beaucoup plus longtemps qu'on ne s'y attendait. Les essais pour étalonner le modèle 1-D de transport des solutés à partir des observations sur le terrain n'a rien donné. Le caractère persistant du pesticide ainsi que l'incapacité du modèle à reproduire les résultats observés indiquent que la décomposition du pesticide peut être inhibée et qu'il peut y avoir un mécanisme d'entreposage par lequel une partie du pesticide non décomposé est retenue pour être libérée d'une manière progressive. D'autres chercheurs ont montré que la décomposition de l'aldicarbe est inhibée par les basses températures ainsi que le pH du sol et de l'eau souterraine. Les fluctuations de la concentration en pesticides ont été atténuées par la diffusion du pesticide dans le grès et hors de ce dernier. Des simulations sur le modèle 1-D indiquent qu'une application à la levée plutôt qu'à la plantation pourrait réduire de manière importante la quantité de pesticides qui atteint le niveau phréatique.

## MANAGEMENT PERSPECTIVE

Prince Edward Island is 100% dependent on ground water from the "sole source", fractured sandstone, aquifer for all its domestic agricultural, industrial and potable water needs. The portion of the "sole source" aquifer closest to the surface is the most productive, but, is also the first and most readily contaminated. Aldicarb (Temik) has been detected in the ground waters of Prince Edward Island, as the result of the application of this pesticide to potato crops beginning in 1978. Three field sites have been established on PEI, by hydrogeologists from NHRI and NWRI, to investigate the processes controlling the fate of aldicarb in the sandstone. A ground water quality monitoring program has been conducted, and results indicate that aldicarb residues are persisting much longer than had been expected. Attempts to calibrate a 1-D solute transport model to the observed field data were unsuccessful due to the dual porosity nature of the flow system. Storage mechanisms appear to be involved, acting to retain the pesticide, and slowly releasing it over time. Degradation of the pesticide is also inhibited by the low temperatures and pH of the soil and ground water beneath the three field sites.

## PERSPECTIVE-GESTION

L'Île-du-Prince-Édouard dépend entièrement de l'eau souterraine produite par un aquifère unique, un grès fracturé, pour tous ses besoins domestiques, agricoles, industriels et potables en eau. La portion de l'aquifère unique qui est le plus près de la surface est la plus productive, mais c'est aussi la première à être contaminée et celle qui l'est le plus facilement. De l'aldicarbe (Temik) a été détecté dans l'eau souterraine de l'Île-du-Prince-Édouard par suite de l'application de ce pesticide à des cultures de pommes-de-terre à partir de 1978. Trois stations ont été choisies sur l'île par des hydrogéologues de l'INRE et de l'INRH afin d'étudier les mécanismes qui déterminent l'évolution de l'aldicarbe dans le grès. Un programme de surveillance de la qualité de l'eau a été appliqué; les résultats montrent que les résidus d'aldicarbe persistent beaucoup plus longtemps qu'on ne l'avait pensé. Il a été impossible d'étalonner le modèle 1-D de transport des solutés à partir des données d'observation à cause du double caractère de porosité du réseau d'écoulement. Il semble y avoir des mécanismes d'entreposage qui retiennent le pesticide pour le libérer lentement par la suite. La décomposition du pesticide est également inhibée par les basses températures et le pH du sol et de l'eau souterraine sous les trois stations.

The Fate of Aldicarb in an  
Unsaturated-Saturated  
Flow System on Prince Edward Island, Canada

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#### ABSTRACT

Aldicarb (a highly toxic, soluble and persistent pesticide) has been detected in the ground waters of Prince Edward Island (PEI), Canada. Three field sites were established on PEI to investigate the processes controlling the fate of aldicarb in the sandstone. A four-year ground water quality monitoring program was conducted, and results indicate that aldicarb residues have persisted much longer than had been expected. Attempts to calibrate a 1-D solute transport model to the observed field data were unsuccessful. The persistent nature of the pesticide observed, as well as the inability of the model to reproduce the observed data, suggests that the degradation of the pesticide may be inhibited, and that there may be a storage mechanism involved, acting to retain the undegraded pesticide and slowly releasing it over time. It has been shown by others that the degradation of aldicarb is inhibited by the low temperatures and pH of the soil and ground water. Pesticide concentration fluctuations have been dampened by diffusion of the pesticide into and out of the sandstone matrix. Simulations performed with the 1-D model indicate that an application at plant emergence, rather than at planting, could significantly reduce the amount of pesticide reaching the water table.

#### INTRODUCTION

The widespread use of pesticides in today's society poses a serious threat of contamination to ground water supplies. Because of the areal extent to which these agricultural chemicals are applied, the emphasis must be placed on prevention, rather than relying on remedial action after the contamination has occurred. Prevention of contamination requires a thorough knowledge of the processes that control the fate of a pesticide in the subsurface environment. It is too late to apply this reasoning to the application of the pesticide, Temik (active ingredient: aldicarb), to potato

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fields on Prince Edward Island (PEI) (Figure 1). Temik (aldicarb) has been applied to potato crops on PEI since 1978, and as a result, a number of domestic wells on PEI have been found to contain traces of aldicarb (Matheson et al., 1987). However, to gain a better understanding of the processes and mechanisms that control the fate of aldicarb under the particular conditions that exist on PEI, a post-mortem study of the transport and transformation of aldicarb in the sandstone aquifer of PEI was undertaken. The results of part of this study, along with numerical simulations of fate of the pesticide in the subsurface, are presented.

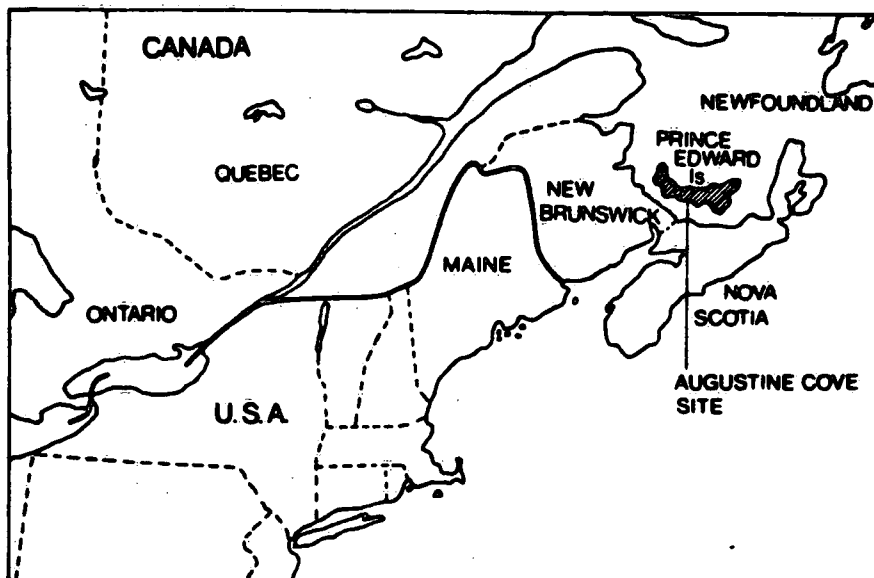


Fig. 1. Location of Prince Edward Island, Canada in eastern North America.

#### ALDICARB

Aldicarb belongs to the oxime carbamate insecticide family and is one of the most toxic pesticides registered for use today. Aldicarb has an oral LD<sub>50</sub> (rats) of 0.9 mg/kg and an aqueous solubility of 6000 mg/L at 25°C (Ware, 1978), and because of its extreme toxicity, it is formulated as a granular systemic pesticide. Upon dissolution in the soil moisture, aldicarb degrades via two possible pathways: oxidation and/or hydrolysis. Aldicarb (AS) may first, undergo a microbially-catalyzed oxidation to form aldicarb sulfoxide (LD<sub>50</sub> = 0.9 mg/kg and an aqueous solubility of 330,000 mg/L) (Moye and Miles, 1988). This oxidation process occurs quickly and the parent pesticide is rarely found in any ground water monitoring programs. Aldicarb sulfoxide (ASO), may then be more slowly oxidized to aldicarb sulfone (ASO<sub>2</sub>) (LD<sub>50</sub> = 24 mg/kg and aqueous solubility = 8000 mg/L) (Figure 2). The two transformation products (daughter products) are also highly soluble, toxic, and persistent in the environment, and therefore, must be considered in any study of aldicarb. The Canadian drinking water limit for the total of these three products (referred to as total aldicarb) is 9 µg/L (Health and Welfare Canada, 1988).

Aldicarb and its two daughter products (ASO and ASO<sub>2</sub>) may also

degrade via hydrolysis to their respective oximes species and dehydrate to nitrile species. The degradation products are much less toxic and do not create a health concern. The rate of the detoxifying hydrolysis reaction has been found to be dependent on a number of physical and chemical conditions (most notably temperature and pH) and is highly site specific (Lightfoot et al., 1987). Degradation half-lives reported for aldicarb have ranged from as little as two weeks, to more than two years (Jones, 1986).

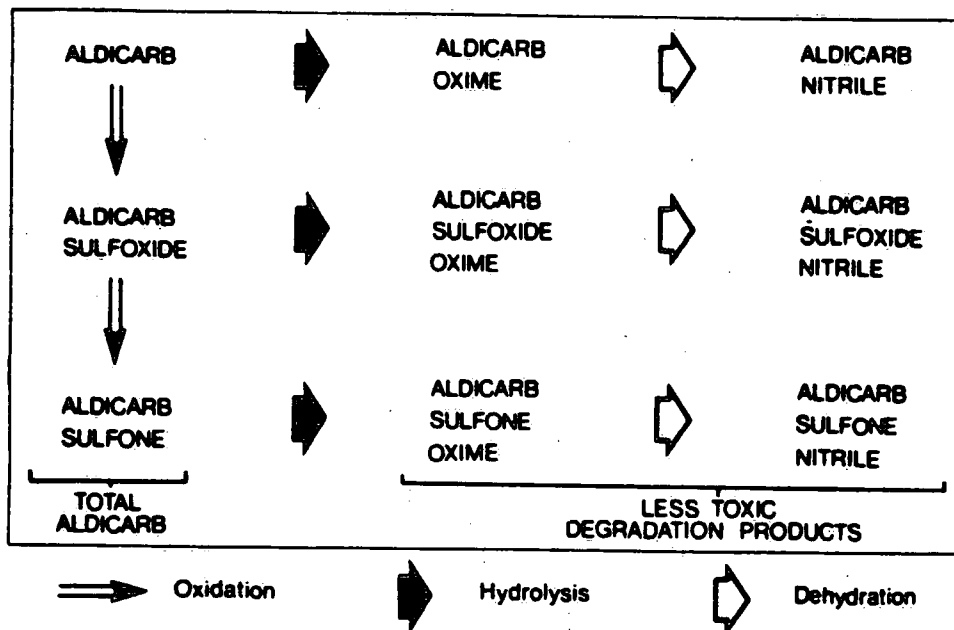


Fig. 2. Simplified schematic of aldicarb degradation pathways.

#### ALDICARB CONTAMINATION ON PRINCE EDWARD ISLAND

Prince Edward Island (5660 sq. km., 127,000 population) is 100% dependent on the fractured sandstone redbeds, of which it is formed, as a sole source aquifer for all of its water needs. Aldicarb was first applied to potato fields on PEI in 1978 to control aphids and the Colorado potato beetle. By 1983, it was estimated that between 5000 and 10000 kg of the active ingredient was applied to 3000 hectares of potatoes (Matheson et al., 1987). A survey was conducted in 1983 and 1984 to assess the presence of aldicarb in the ground waters of PEI and aldicarb residues were found in 20 of the 103 (19.4 %) domestic wells tested. However, all concentrations were found to be below the Canadian drinking water limit of 9 µg/L. The maximum concentration detected was 5.4 µg/L and most measured values were in the range of 1.3 to 2.2 µg/L.

#### FIELD SITES

Three field sites were established on PEI to investigate the fate of aldicarb in the sandstone aquifer and overlying till. However, this paper will be limited to a discussion of results from one of the sites, located at Augustine Cove, in the main potato growing region on PEI. The Augustine Cove (AC) field site was chosen because of (1) the availability of good



pesticide and fertilizer applications records, (2) the cooperation of farm managers, and (3) evidence of aldicarb residues in a well surrounded by the field in question.

The climate on PEI is cool and humid. The average annual precipitation is 1120 mm and mean monthly temperatures range from  $-6.8^{\circ}\text{C}$  in February to  $19.1^{\circ}\text{C}$  in July (MacDougall et al., 1981).

The hydrostratigraphy of the site consists of a 2-5 metres of glacial till overlying a sequence of fractured Permo-Carboniferous sandstone redbeds (van der Poll, 1983). The surface relief of the Island is gently undulating and the till covering the Augustine Cove site is classified as a Charlottetown Series soil (MacDougall et al., 1981). The soil is described as an Orthic Humo-Ferric Podzol, derived from a reddish brown, medium to strongly acidic, fine sandy loam. The surface soil is well drained, while drainage in the subsoil varies from moderately to poorly drained. The sandstone aquifer underlying the site acts as a semi-confined to unconfined aquifer (Priddle et al., 1989). Fractures in the sandstone decrease in both number and aperture with depth, and as a result, the permeability of the aquifer also decreases with depth. Zones in the aquifer closest to the surface are therefore the most productive, but are also the first and most readily contaminated (Francis and Gale, 1988).

The field site was instrumented for geochemical and hydraulic testing. Twenty five piezometers were installed using an air rotary drill rig, and are constructed of 50 mm, Schedule 40, PVC, with either a 1.0 or 1.5 metre length of #6 slot screen. The screens were packed with #2 silica sand and capped with a one-metre bentonite seal. The remainder of the hole was back filled with native material collected during drilling (Priddle et al., 1988). Figures 3 and 4 show a plan view and cross section of the Augustine Cove site, respectively.

#### HYDROGEOLOGY

Slug tests performed in the piezometers at Augustine Cove resulted in hydraulic conductivities that ranged from  $2.4 \times 10^{-6}$  m/s to  $6.0 \times 10^{-4}$  m/s. In general, the hydraulic conductivities increased with proximity to the stream, and decreased with depth (Mutch 1989). Open-hole slug tests and pump tests were performed in three 76 mm inclined boreholes installed at the site and hydraulic conductivities ranged from  $4 \times 10^{-5}$  m/s, in the shallow bedrock, to  $5 \times 10^{-6}$  m/s, at bedrock depths greater than 5 metres (Lapcevic and Novakowski, 1988). Francis and Gale (1988), in contrast, found hydraulic conductivities of  $5 \times 10^{-8}$  m/s in the sandstone matrix, with intergranular porosities averaging 16 percent. Transmissivity and storativity values in the bedrock were estimated as  $6 \times 10^{-4}$  m/s and  $2 \times 10^{-4}$ , respectively (Lapcevic and Novakowski, 1988).

Water levels were taken periodically, and revealed that two distinct ground water flow patterns exist at the Augustine Cove site at different times of the year. The first pattern, representative of a period with a high water table, is a

typical one with recharge occurring in the upland areas and a subsequent discharge to the stream. During periods of the year with a low water table, in addition to deriving recharge water from the upland areas, water is also being recharged directly to the fractured sandstone aquifer from the stream. It appears that there is a highly fractured zone running roughly parallel to the stream in Figure 3, and extending out of the plane of the paper in Figure 4, near piezometers AC5 and AC6 (Nest C). Ground water beneath the field flows through this fracture zone and is discharged from the field in the south-east corner (Mutch, 1989). It appears probable that the high water table regime occurs each spring but that the low water table regime is more representative for the remainder of the year.

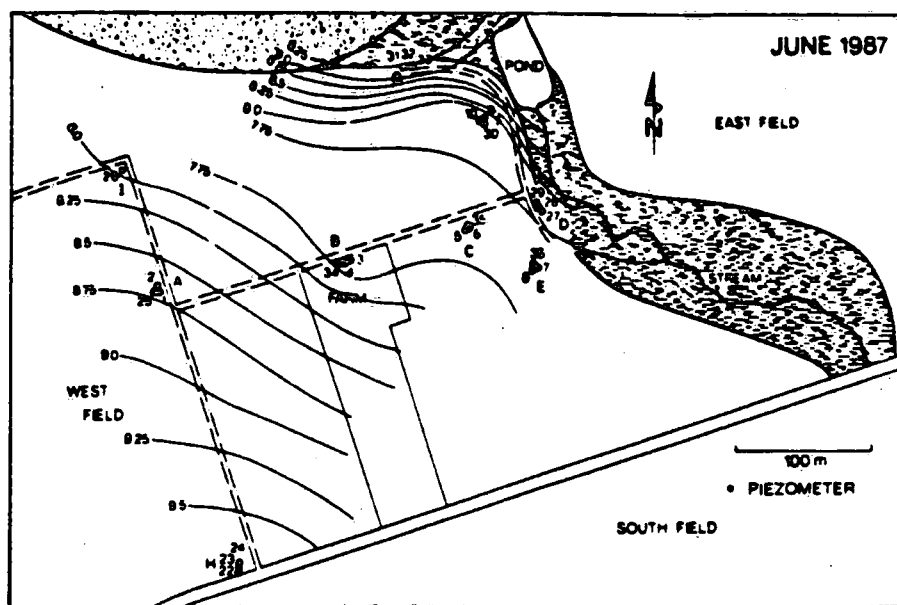


Fig. 3. Field site at Augustine Cove, PEI, showing ground water flow pattern and location of monitoring wells.

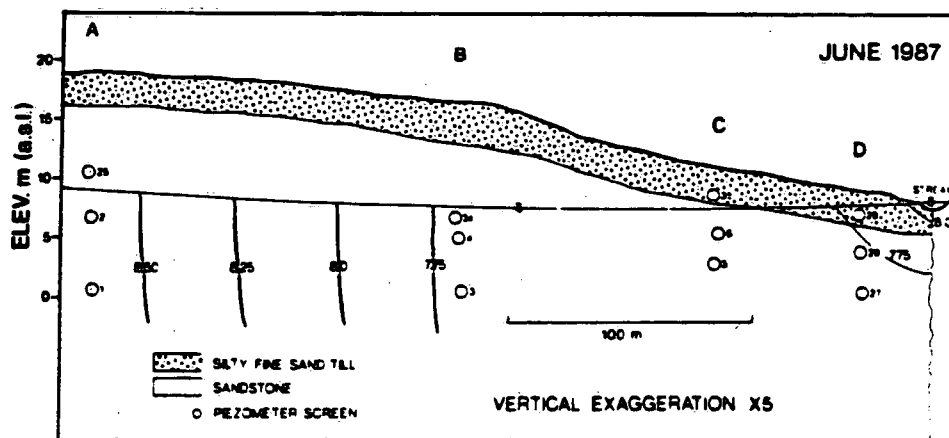


Fig. 4. Cross section of Augustine Cove site, showing equipotential lines of hydraulic head (June 1987).

## METHODS OF SAMPLING AND ANALYSIS

Two to three well volumes were purged from the 50 mm diameter piezometers prior to the initiation of geochemical testing and sampling. A Teflon or Teflon/stainless steel submersible bladder pump (Well Wizard, QED Systems, Ann Arbor, MI, U.S.A.) was used for sample extraction and geochemical testing. The pumps were not dedicated and were rinsed with distilled water after each well was tested and sampled. The discharge line from the pump was connected directly to a flow cell and measurements of the redox potential (Eh) and pH of the ground water were taken with combination platinum and glass electrodes, respectively (Orion, Cambridge, MA, U.S.A.). Specific conductance and temperature measurements were also monitored (YSI Scientific meter, Yellow Springs, Ohio, U.S.A.). Ammonia (NH<sub>3</sub>) measurements were obtained with an Orion 701 meter (Orion, Cambridge, MA, U.S.A.) and an NH<sub>3</sub> specific electrode. A field titration was performed on a filtered sample (0.45 µm) to determine alkalinity and dissolved oxygen levels were measured with an Orbisphere Model 2606 Oxygen meter (Orbisphere Labs, Geneva, Switzerland).

Filtered (0.45 µm) samples for aldicarb analysis were collected in triple rinsed 60 mL amber bottles, acidified to approximately pH 5 (100 µL of dilute H<sub>3</sub>PO<sub>4</sub>), and stored in the dark at approximately 4°C until analyzed. Samples of the rinse water, as well as field blanks were collected for quality control, and were stored and analyzed in the same manner as the aldicarb samples. Aldicarb residues were not detected in any blanks or in the cleaning water that passed through the pump. Ground water samples were also collected for major ion analysis in 500 mL plastic sample bottles.

Aldicarb analysis was initially (1985 and 1986) conducted using the method of Chaput (1986). However, only aldicarb sulfoxide and aldicarb sulfone were detected in these samples so analysis in 1987 and 1988 was conducted using an isocratic elution method similar to that of Lesage (1989), that separates the two aldicarb transformation products in less than 10 minutes.

## GEOCHEMICAL RESULTS

A statistical summary of the results (1985-1988) of the in situ measurements for pH, Eh, dissolved oxygen (D.O.), temperature, and nitrate is presented in Table 1. In general, the ground water beneath the site contains appreciable amounts of dissolved oxygen, abundant nitrate and a wide range of pH values. The mean pH value was 7.0, however, 11 of the 25 piezometers at the Augustine Cove had pH levels below 7.0 at some point during the monitoring program, with a minimum of 5.6. Values of pH tended to increase with the depth, and although pH values varied over a wide range, a decreasing trend was noticed with distance down the flow path. The ground water contains appreciable oxygen (mean dissolved oxygen values = 5.8 mg/L) while mean Eh values were 417 mV, indicating that highly oxygenated conditions exist.

Table 1 Statistical summary of in situ geochemical results. (Augustine Cove, 1985-1988)

GEOCHEMICAL SUMMARY - AUGUSTINE COVE					
	pH	EH (mV)	TEMP. (°C)	D.O. (mg/L)	NITRATE (mg/L)
NO. SAM.	37	37	16	31	64
MEAN	7.0	417	11.6	5.8	7.6
STD.DEV.	0.6	153	2.9	4.0	5.4
RELATIVE STD.DEV.	8.6%	36.7%	25.0%	68.9%	71%
MEDIAN	6.9	440	12.0	8.0	9.0
MAXIMUM	8.2	690	16.0	10.0	22.0
MINIMUM	5.6	120	7.0	0.2	0.0

Time series for the total aldicarb concentration and the aldicarb speciation ratio (defined as ASO<sub>2</sub>/total aldicarb) for the four individual wells, located towards the centre of the field (see Figure 3), are displayed in Figures 5 and 6. A time series of nitrate concentrations is shown in Figure 7. The amount, and timing, of pesticide applications are shown on each of these figures. As previously mentioned, aldicarb is quickly oxidized to aldicarb sulfoxide (ASO) and is rarely detected in ground water. As a result, the total aldicarb concentrations displayed in Figure 5 are simply the sum of aldicarb sulfoxide (ASO) and aldicarb sulfone (ASO<sub>2</sub>).

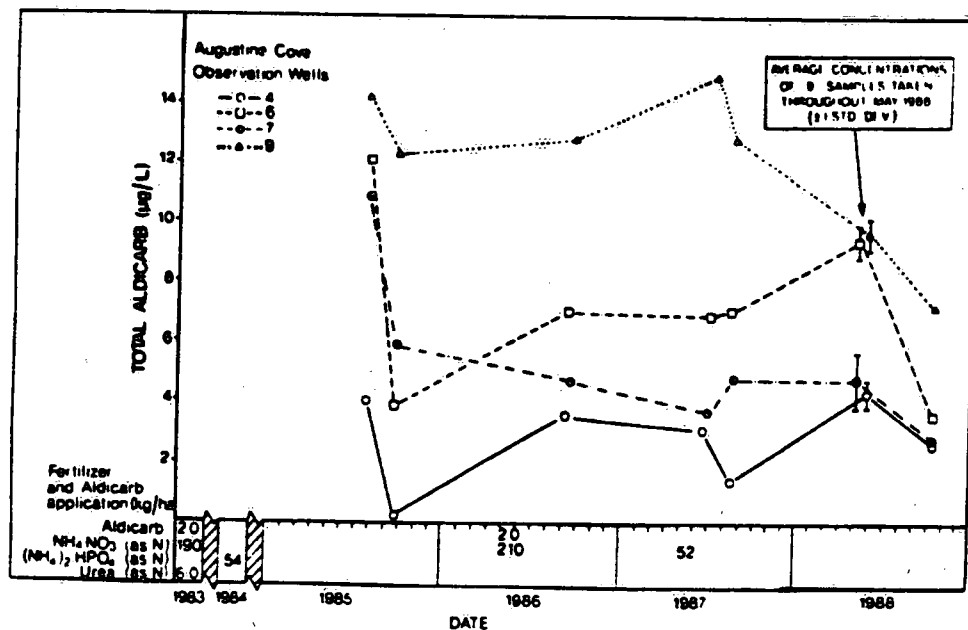


Fig. 5. Time series of total aldicarb concentrations in four observation wells from Augustine Cove, PEI.

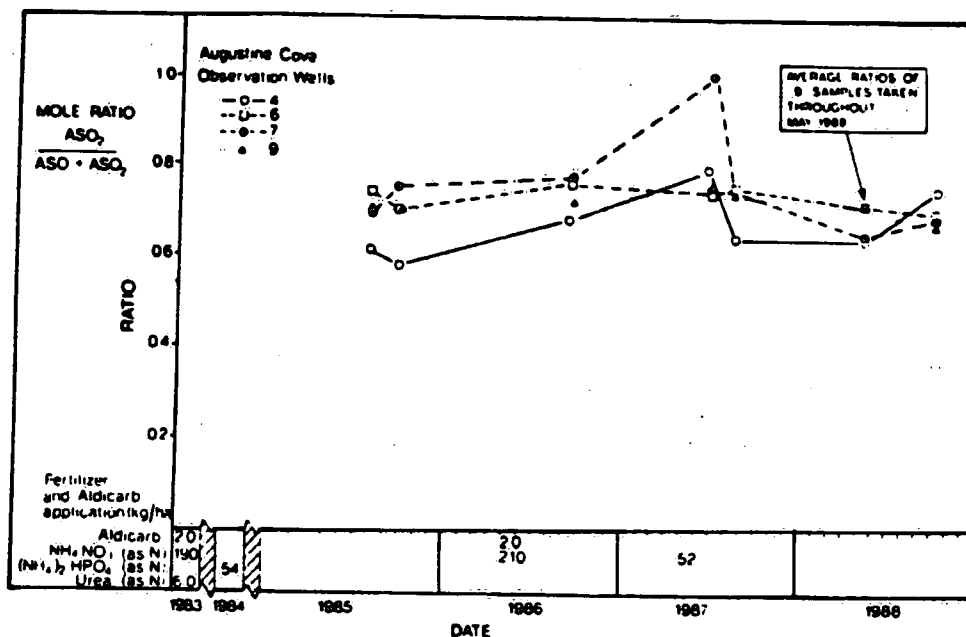


Fig. 6. Time series of aldicarb speciation ratio in four observation wells from Augustine Cove, PEI.

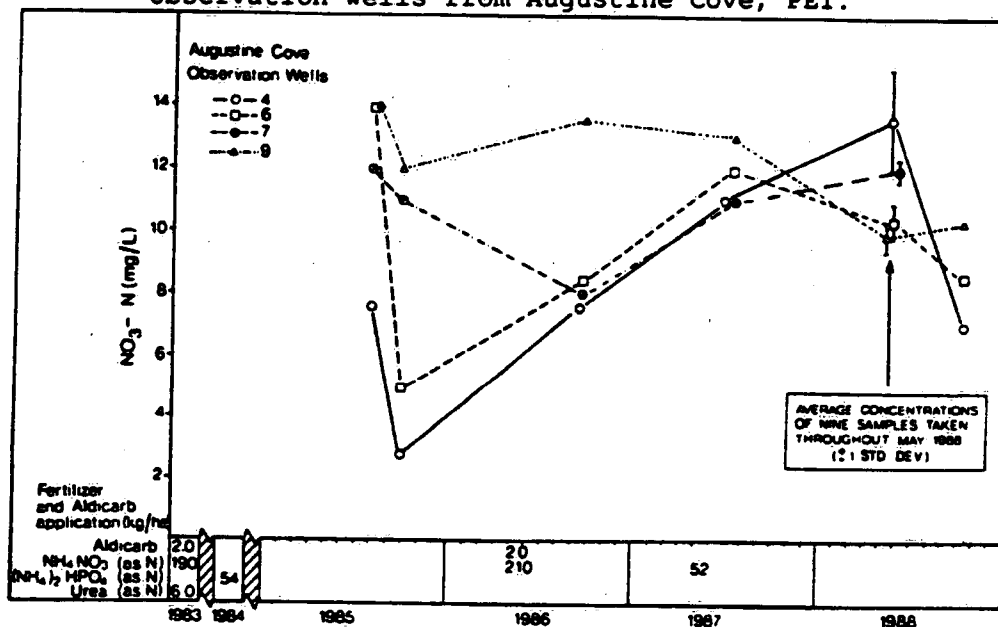


Fig. 7. Time series of total aldicarb concentrations in four observation wells from Augustine Cove, PEI.

Total aldicarb concentrations (Figure 5), the aldicarb speciation ratio (Figure 6), and the nitrate concentrations (Figure 7), all remained relatively constant over the sampling period, despite the fact that there was only one pesticide application during this time. The chemical species, ASO and ASO<sub>2</sub>, are both considered to be relatively unretarded (retardation factors of 1.25 and 1.26, respectively (Jackson et al. 1990)). Yet they, and nitrate, show a remarkable persistence (Figures 5-7) over the sampling period. The pronounced drop that does occur in the concentration of total aldicarb and nitrate 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 concentrations more characteristic of the depth of each piezometer. Concentrations of aldicarb in the upland, recharge areas (i.e. AC4), with an unsaturated zone depth of approximately 10 metres, are typically lower than those in the lowland, discharge areas (i.e. AC6, AC7, and AC9). The highest concentrations were observed in the shallowest piezometer (AC9). The four piezometers (AC4, AC6, AC7, and AC9) were sampled frequently during May, 1988 to observe short-term fluctuations in the parameters being investigated (total aldicarb and aldicarb speciation ratios). Fluctuations were minor, with a relative standard (standard deviation  $\times$  100 divided by the mean) deviations for total aldicarb ranged from 5.1% to 18.8%, with a mean of 9.6%, and from 1.4% to 3.1%, with a mean of 1.9% for the speciation ratio (Mutch 1989).

The aldicarb speciation ratios (mole ratio of  $\text{ASO}_2$ /total aldicarb) found on PEI are appreciably different from the average ratio reported by Jones (1986) (0.4) and Harkin et al. (1986) (0.31) for studies conducted in the US. The speciation ratio at Augustine Cove covered the full range from 0.00 to 1.00, however, the mean was 0.73. The high speciation ratios found on PEI may be a result of the highly oxygenated conditions and relatively low pH environment in the ground water. The low pH would inhibit hydrolysis of ASO and  $\text{ASO}_2$ , while the abundance of oxygen may act to enhance the microbial catalyzed oxidation of ASO to  $\text{ASO}_2$ . As  $\text{ASO}_2$  becomes the pre-dominant toxic species, the speciation ratio approaches 1.0.

A good relationship between high concentrations of total aldicarb and nitrate in the saturated zone is demonstrated in Figure 8 (Priddle et al. 1988; 1989). In 10 of the 11 samples containing concentrations of total aldicarb above its maximum acceptable concentration (9  $\mu\text{g/L}$ ), nitrate levels were also in excess of its maximum acceptable concentration (10  $\text{mg/L NO}_3^- \text{-N}$ ). It may therefore, be possible to use nitrate as an indicator of domestic wells that are susceptible to aldicarb contamination.

#### **SIMULATING OF THE FATE OF ALDICARB**

Attempts were made to simulate the fate of aldicarb in the subsurface environment on PEI with a 1-D pesticide transport model, LEACHMP (Wagenet and Hutson, 1987). LEACHMP was developed specifically to simulating the fate of aldicarb and its two daughter products (ASO and  $\text{ASO}_2$ ) as they migrate through a porous medium.

Data was derived for this study from a number sources. Climatic data were obtained from weather stations located approximately 30 km from the site. Soil parameters (for a sandy loam) were taken from MacDougall et al. (1981) and the model was set up to simulate a 4.4 metre soil column, with a water table placed at 3.0 metres on the starting date (January 1, 1983). The dispersivity value was set to 10 cm so that no aldicarb would remain in the first metre of the simulated soil profile (corresponding to what was observed in the field). Initial oxidation and hydrolysis rate constants were taken

from Zhong et al. (1986) and adjusted for a temperature of 10°C.

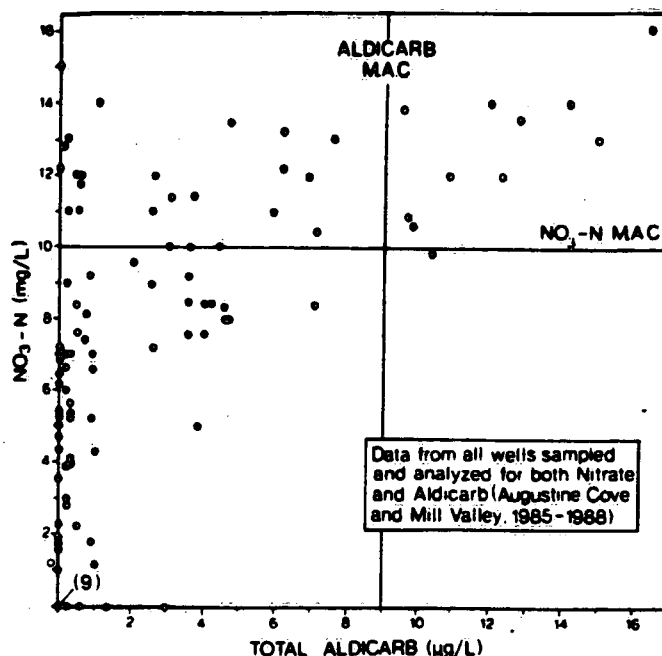


Fig. 8. Nitrate-N vs. total aldicarb concentrations from PEI field sites.

Attempts to calibrate LEACHMP to the field data obtained were unsuccessful (Figure 9). Reasonable predictions are provided by LEACHMP for the aldicarb speciation ratio. However, the model predicts that the pesticide will migrate through the soil profile in a large pulse, with concentrations quickly returning to very low levels (via degradation and leaching of the pesticide past the water table). The model is unable to accurately simulate the persistent nature of the pesticide in the shallow bedrock seen in Figure 5.

The transformation (oxidation) and degradation (hydrolysis) rate constants in the best model calibration corresponded to half-lives that were approximately three times the temperature adjusted values presented by Zhong et al. (1986), suggesting that aldicarb degradation is very slow in the PEI soils and shallow bedrock. The half-life of total aldicarb in the PEI soils and ground waters is estimated to be on the order of 150 days, in contrast to the 100 day estimation given by Jones (1985) for aldicarb applied to potato fields in Maine.

#### PESTICIDE APPLICATION DATE

Aldicarb is presently applied on PEI at planting. LEACHMP was used to investigate the affect of delaying the application of the pesticide until plant emergence (Figure 10). Two factors were considered in determining the influence of the date of application on the total aldicarb concentration. The first, was the change in the amount of infiltration that occurs as the date of application is extended from planting (May 17 - Day 137) to emergence (June 21 - Day 172). Infiltration amounts at the site are generally greater at the time of planting due

to the large spring recharge at the site. The top three curves in Figure 10 demonstrate the change in the total aldicarb concentration, due solely to the change in the amount of infiltration as the application date was extended. For the period under study (1983-1985), total aldicarb concentration do not change appreciably due to a change in the amount of infiltration as the application date is extended.

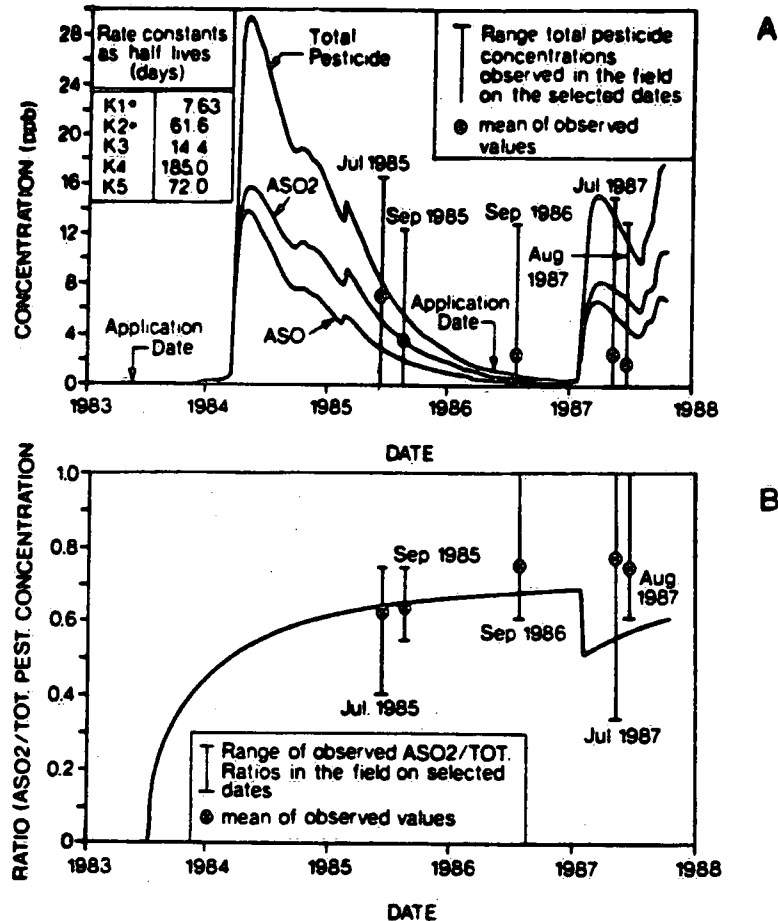


Fig. 9. Total aldicarb, ASO and ASO<sub>2</sub> concentrations and the speciation ratio predicted by the LEACHM model.

The second factor which must be considered, is the temperature effect. Degradation of aldicarb is strongly dependent on temperature (Lightfoot et al., 1987). Mean monthly soil temperatures on PEI (at a depth of 150 mm) increase by approximately 5°C between the months of May and June (MacDougall et al., 1981). A simulation performed to investigate the influence that the change in temperature (because of a later application date - Day 172 = June 21) was run with the degradation rate constants in the top 400 mm of the soil adjusted to reflect a soil temperature of 15°C rather than a 10°C, as was the case in the earlier simulations. The results (bottom curve in Figure 10) show an appreciable decline in the total aldicarb concentration, indicating that the change in the soil temperature, rather than a change in the amount of infiltration, is the most important factor in the significant reduction of the total aldicarb concentration



with a pesticide application at seedling emergence.

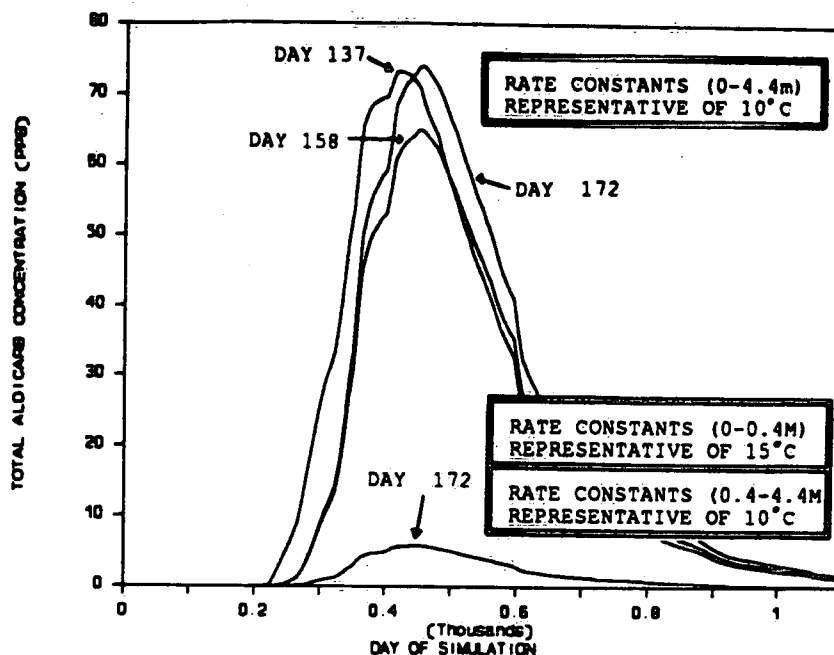


Fig. 10. Time series of total aldicarb concentrations for different pesticide application dates. The top three curves show differences due to the change in the amount of infiltration only. The bottom curve also takes the temperature effect into account.

#### DISCUSSION OF RESULTS

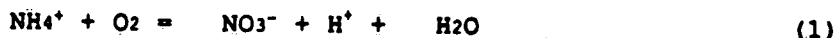
The inability of the model to reproduce the stable persistent nature of the pesticide concentration and ratio lends support to the theory that other mechanisms, not accounted for in the LEACHMP model, are involved in the determining the fate of aldicarb in sandstone aquifer of PEI. The long half-lives predicted for aldicarb by LEACHM also suggests that aldicarb degradation is being inhibited. The persistence of high, and relatively consistent concentrations observed in the field indicates that there may be some in situ storage mechanism retaining the pesticide and slowly releasing it over time. There are several possible mechanisms which may be involved:

1. pH and temperature conditions that lead to the inhibition of aldicarb degradation,
2. non-equilibrium sorption of the pesticide,
3. downslope migration of aldicarb,
4. slow infiltration through the overlying till, and
5. matrix diffusion in the sandstone unit.

The likelihood of each of these mechanisms accounting for the differences between the observed concentrations in the field and the computed concentrations are discussed below.

There are a number of natural and anthropogenic conditions existing at the sites which may lead to the inhibition of aldicarb degradation. The soils, ground water (in the low land, discharge areas), and the spring rains and snowmelt at

the site are all acidic (in the range of pH = 4 to 7), and contribute to the inhibition of aldicarb degradation by maintaining the pH at a level where degradation of aldicarb to less toxic products is slowest (pH 5-6). In addition, anthropogenic factors also lead to the inhibition of pesticide degradation. The pesticide is applied at planting, when soil temperatures are low and there is not plant root system to take up the pesticide. Ammonium based fertilizers [ $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$ ] have been applied to the field site (see Figure 7). In the oxygen-rich ground water, nitrification of the applied  $\text{NH}_4^+$  occurs according to the equation:



The nitrification of ammonia based fertilizers produces protons ( $\text{H}^+$ ), which lower the pH of the water buffering it in the range where aldicarb degradation is slowest. All these factors contribute to the inhibition of aldicarb degradation.

#### Non-equilibrium sorption

It is unlikely that sorption of aldicarb is an important process at the site. In previous studies, little evidence of significant sorption of the three aldicarb species has been found (Lemley et al., 1988; Zhong et al., 1986). Laboratory column tests performed on samples collected from the field site support this premise. Retardation factors for ASO and ASO<sub>2</sub> were 1.25 and 1.26, respectively (Jackson et al., 1990). Sorption of aldicarb with a slow, subsequent desorption can therefore 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 (AC4) were significantly lower than the concentrations found in the wells further down the flow path (Figure 5). In addition, pH levels in the upland recharge areas tend to be in the range (>7.0) where aldicarb degradation is relatively rapid (Lightfoot et al., 1987). Any contributions supplied to the wells in the discharge areas by downslope migration, would be significantly lower than the concentrations observed in the wells in the upland areas. Again, this process alone, cannot account for the high and relatively consistent concentrations observed in the field.

#### Slow infiltration through the unsaturated till

A relatively high, and continuous flux of pesticide percolating from 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. It is likely that processes similar to those described for tritium in the British Chalk (Foster, 1975) may be present in the till and unsaturated portion of the sandstones at the sites. A reservoir of aldicarb residues may have accumulated in the vadose zone by the diffusion process and may be slowly 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 a coarse grained and very permeable vadose zone. Aldicarb residues were still being leached to the water table five years after the last application of the pesticide.

#### Matrix diffusion in the saturated sandstone

Matrix diffusion processes may also be 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 bedrock. Large amounts of solute storage over time are possible. As conditions change and water of 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 percent in the fractured sandstones on the Island, indicating that the matrix diffusion mechanism could provide large amounts of storage for aldicarb residues and could account for the persistence of aldicarb observed in the field.

#### CONCLUSIONS

Results from the four-year ground water quality monitoring program (1985-1988) reveal that aldicarb residues persisted at relatively high, and consistent, concentrations and little short term variation is evident. The persistence and dampened response observed in the transport of aldicarb appears to be the consequence of two factors, low soil temperatures and pH values (that inhibit the degradation of aldicarb), and diffusion of aldicarb residues into the sandstone matrix, with the a slow release of the pesticide as the concentration begins to fall. Slow infiltration of the pesticide through the over lying till also acts to provide temporary (in situ) storage of the pesticide. These processes may account for the dampened response observed for aldicarb migration.

Aldicarb speciation ratios were also relatively consistent over the four-year sampling period and were higher (mean = 0.73) than values reported for studies conducted in the US ( 0.4). This may be due to the highly oxygenated ground waters (promoting oxidation of ASO to ASO<sub>2</sub>), and the low pH values (inhibiting hydrolysis of ASO and ASO<sub>2</sub>) causing ASO<sub>2</sub> to become the predominant species, thereby raising the speciation ratio.

Nitrate concentrations follow the trends established by aldicarb. Although nitrate is considered to be unretarded in nature, it too, demonstrated a remarkable persistence. The field data collected demonstrates a good relationship between high aldicarb concentrations and high levels of nitrate.

The inability of the LEACHMP model to reproduce concentrations observed in the field also lends support to the theory that there may be a storage mechanism (matrix diffusion and slow

infiltration through the till) acting to retain the pesticide, with a slow release to the water table over time. The long total aldicarb half-lives (150 days) predicted by the model also indicates that processes are acting that inhibit the degradation of aldicarb residues.

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