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## PERSISTENCE OF ALDICARB RESIDUES IN THE SANDSTONE AQUIFER OF PRINCE EDWARD ISLAND, CANADA

by

R.E. Jackson<sup>1</sup>, J.P. Mutch<sup>2</sup> and M.W. Priddle<sup>1</sup>

<sup>1</sup>National Water Research Institute Canada Centre for Inland Waters Burlington, Ontario, L7R 4A6 <sup>2</sup>Ground Water Studies Group Dept. of Civil Engineering University of New Brunswick

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## ABSTRACT

Aldicarb residues are found in the shallow ground waters of the fractured, sandstone aquifer of Prince Edward Island, Canada, well over two years after the last application of this pesticide. Furthermore, the concentrations of aldicarb measured are relatively constant with time. The chemical and hydrogeological mechanisms by which such persistence occurs are discussed. It is deduced that aldicarb degradation is inhibited by the low pH and temperature of the soil and ground water, the former being partly due to the pH buffering effects of ammonium fertilizer oxidation on the hydrolytic degradation of aldicarb. The aldicarb residues are prevented from migrating from beneath the fields on which they were applied by in-situ storage processes associated with diffusion from the aquifer fractures into the interstitial matrix of the sandstone and reverse diffusion into the fractures, thereby maintaining constant and relatively high concentrations in ground water.

Attempts to simulate the observed persistence of aldicarb in this hydrogeologic environment using a one-dimensional, solute transport simulation code were unsuccessful, probably because of the three-dimensional nature of the matrix diffusion process. The simulations suggested that the overall half life for aldicarb in the till/sandstone system approaches 150 days.

## RÉSUMÉ

On a constaté que l'aquifère dans des grès fracturés situé à faible profondeur dans l'Île-du-Prince-Édouard au Canada, contenait encore des résidus d'aldicarbe bien plus de deux ans après la dernière application de ce pesticide. Fait plus inquiétant, les concentrations d'aldicarbe mesurées étaient relativement constantes au fil du temps. Les mécanismes chimiques et hydrogéologiques qui expliquent cette persistance sont traités. Les auteurs en déduisent que la dégradation de l'aldicarbe est limitée par la température et le pH faibles du sol et des eaux souterraines; le faible pH serait dû en partie aux éffets tampons de l'oxydation du fertilisant à base d'ammmonium sur la dégradation hydrolitique de l'aldicarbé. La migration des résidus d'aldicarbe qui se trouvaient sous les champs sur lesquels le pesticide a été appliqué est stoppée par l'emmagasinement in situ associé à la diffusion depuis les fractures vers la matrice de grès et à la diffusion inverse vers les fractures: les concentrations restent donc constantes et relativement élevées dans les eaux souterraines.

Les essais visant à simuler, à l'aide d'un code de simulation unidimensionnel du transport en solution, la persistance observée de l'aldicarbe dans ce milieu hydrogéologique, n'ont pas bien fonctionné, probablement à cause de la nature tridimensionnelle du processus de diffusion dans la matrice. Les simulations ont cependant permis de montrer que la demi-vie globale de l'aldicarbe dans un système grès/till serait voisine de 150 jours.

### MANAGEMENT PERSPECTIVE

Prince Edward Island is wholly dependent upon ground water for all domestic, agricultural, industrial and potable uses. The "sole source aquifer" is a fractured sandstone of high permeability, which yields ground water of otherwise good quality. The contamination of this aquifer by agricultural residues, principally aldicarb and nitrate, has caused much concern among Islanders. Beginning in 1985, hydrogeologists from NHRI and then NWRI, have been monitoring ground water quality beneath three potato fields to which aldicarb (Temik) had been applied in May of 1983 and 1986, together with the seed potatoes. Ground water monitoring in May 1988 indicated that 10% of all samples from these three fields exceeded the NH&W drinking water guidelines of 9 ppb. The physical and chemical processes controlling the persistence of aldicarb in this aquifer are discussed.

## PERSPECTION - GESTION

L'Île-du-Prince-Édouard dépend en totalité des eaux souterraines pour répondre à ses besoins en eau potable et pour les usages domestiques, agricoles et industriels. Le seul aquifère exploité est un grès fracturé à perméabilité élevée qui fournit une eau souterraine de bonne qualité. La contamination de cet aquifère par les résidus agricoles, surtout l'aldicarbe et le nitrate, cause beaucoup d'inquiétude chez les habitants de l'île. À partir de 1985, des hydrogéologues de l'INRH, puis de l'INRE surveillent la qualité des eaux souterraines sous trois champs de pommés de terre sur lesquels de l'aldicarbe (Temik) a été appliqué en mai 1983 et mai 1986 en même temps que les pommes de terre de semence. Les mesures réalisées en mai 1988 montrent que 10 % de tous les échantillons de ces trois champs renferment des teneurs en aldicarbe supérieures aux directives de 9 ppb établies par Santé et Bien-être Canada pour l'eau potable. Les processus physiques et chimiques qui exercent un contrôle sur la persistance de l'aldicarbe dans cet aquifère sont traités.

### INTRODUCTION

Prince Edward Island (PEI) is situated in the Gulf of St. Lawrence (see Figure 1) and is composed of Permo-Pennsylvanian sandstone redbeds. The fractured sandstone constitutes the solesource aquifer of this the smallest province of Canada (5660 sq.km., 127,000 population). The annual precipitation is 1120 mm with average mean temperatures of  $-7^{\circ}$ C in January and 18°C in July.

Surveys of domestic wells on PEI in 1983 and 1984 indicated that aldicarb contamination of ground water was widespread, however levels of contamination were low, i.e., <9  $\mu$ g/L. This pesticide, which is the active ingredient of Temik 10G, has been widely used to control aphids and the Colorado potato beetle on the PEI potato crop. A research project was begun in 1985 to determine the fate of the aldicarb in order to learn more about the vulnerability of ground waters to pesticides. Knowledge gained from this project is to provide advice to regulatory agencies within the Government of Canada.

Three field sites were established in 1985 and 1986, one of which is described in the following pages. The sites were chosen on evidence from the 1983 and 1984 surveys which indicated that Temik had been used on nearby fields and would therefore provide suitable study sites. Aldicarb was applied to the field in question at Augustine Cove, PEI, with the seed potatoes in 1983 and 1986. The field was in hay or clover in the intervening and subsequent years. In the following pages it is shown that aldicarb has persisted in PEI ground waters due to both chemical and hydrogeologic mechanisms.

a very toxic carbamate 15 pesticide with an Aldicarb  $LD_{50} = 0.9 \text{ mg/kg}$  (rat) and a solubility of 6,000 mg/L (Moye and Miles, Following application in granular form, aldicarb undergoes 1988). rapid dissolution and subsequent microbially-catalyzed oxidation to first aldicarb sulfoxide  $(LD_{50} = 0.9 \text{ mg/kg} (rat) \text{ and solubility} =$ 330,000 mg/L), then aldicarb sulfone  $(LD_{50} = 24 \text{ mg/kg} (rat) \text{ and}$ solubility = 8,000 mg/L). The degradation pathway of these three aldicarb species is shown in Figure 2. Aldicarb is detoxified by hydrolysis to the respective oxime species, a process which is strongly temperature and pH dependent. The Canadian drinking water guideline for the total of these three toxic species, referred to hereafter as total aldicarb, is  $9 \mu g/L$ .

# METHODS OF SAMPLING AND ANALYSIS

1.

Groundwater monitoring was conducted using PVC piezometers with 1 or 1.5 m screens that were installed using an air rotary drilling rig. Samples were collected from these 5 cm monitoring wells using either an all Teflon or a Teflon/stainless steel bladder pump (QED Systems, Ann Arbor, MI, U.S.A.). These pumps were not dedicated and had to be cleaned by flushing with distilled water between wells.

After about two well volumes were removed from each well, flow cell analyses were begun. These included Eh and pH using combination platinum and glass electrodes, respectively (Orion, Cambridge, MA, U.S.A.). An Orbisphere Model 2606 Oxygen meter was used to measure dissolved oxygen. Samples were also taken for a titration to determine alkalinity (as  $HCO_3^-$ ) and in some cases to measure ammonia with an Orion gas-sensing electrode. Conductivity and temperature were also measured in the field.

After field analyses were completed, samples for aldicarb were filtered, acidified to pH 5 and stored in amber glass bottles until analysis. Field blanks of distilled water and water from the pump cleaning procedure were taken and stored in a similar fashion. Samples for inorganic parameters were collected in plastic bottles and stored at about 4°C until analysis. Cation samples were collected separately and acidified to pH 3 with nitric acid to prevent possible mineral precipitation.

Aldicarb analysis was initially conducted using the method Chaput (1986). Since only aldicarb sulfoxide and aldicarb sulfone were detected in the samples from 1985 and 1986, a modified procedure was used in 1987 and 1988. An isocratic elution similar to that of Lesage (1989) was used to separate these two compounds in less than 10 minutes.

#### HYDROGEOLOGY

The site at Augustine Cove, PEI, was established in 1985, and has been continually expanded since that time. It now has 25-5 cm piezometers, 3 Solinst multilevel bedrock monitors, and a continuously recording observation well. The sandstone aquifer is usually overlain by 2-3 m of sandy till.

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The hydraulic properties of the aquifer are controlled by the spacing, orientation and aperture of the fractures. The bulk hydraulic conductivity of the sandstone varies from  $4\times10^{-5}$  m/s in the shallow bedrock to  $5\times10^{-6}$  m/s below the first 5 m (Lapcevic and Novakowski, 1988). By contrast, Francis (1981) measured values of  $5\times10^{-8}$  m/s in the matrix of the sandstone, i.e., that part of the sandstone unaffected by fracturing, together with a matrix porosity ranging from 12 to 20%. Lapcevic and Novakowski estimated the transmissivity of the bedrock to be of the order of  $6\times10^{-4}$  m<sup>2</sup>/s with a storativity of  $2\times10^{-4}$ .

The ground water flow pattern at the Augustine Cove site is shown in Figures 3 and 4 at two different periods of time. Figure 3 shows the flow pattern during June 1987, at which time the water table was at a relatively low level. Recharge to the ground water flow system came from both the upland area around the farm house and from the losing stream. Discharge from the cross section occurred through a fracture zone, normal to the plane of the figure, around piezometers 5 and 6. Figure 4 shows the flow pattern during a period with a high water table in May 1988. Recharge occurs in the upland area with discharge occurring to the stream. Because of the high hydraulic gradients at the site during May 1988, and the very low fracture porosities (perhaps 1%), ground water velocities may have reached as high as three metres per day. It appears probable that the high water table regime occurs each spring, but that the low water table regime describes discharge at other times of the year.

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## GROUND WATER QUALITY MONITORING

Ground water quality samples collected from the first ten metres of saturated bedrock generally contain measurable dissolved oxygen and abundant nitrate with a wide range of pH values (see Table 1). Figures 5 and 6 show the time series of nitrate and total aldicarb, respectively, for the period 1985-88 in four monitoring wells whose locations are shown in the upper part of Figure 5. Also shown are the aldicarb and fertilizer inputs.

There are three significant features in these figures. First, there is a pronounced drop in both nitrate and total aldicarb levels in 1985 following the drilling and instrumentation of the boreholes. This is probably due to infiltration of shallow, highly contaminated ground waters into the new boreholes during drilling and to the rapid flushing of this water during the following month. Second, from 1986 to 1988, these time series have displayed relatively constant concentrations of both nitrate and total aldicarb despite the fact that only one application of aldicarb was made during this period. about 2 kg/ha in mid-May 1986. Irrespective of the solubility and mobility of both contaminants, the time series show remarkable persistence in both. Third, short term variations are minor. Continual sampling of the four monitoring wells shown in Figures 5 and 6 during May 1988 showed little day-to-day variation in either nitrate aldicarb concentrations. or The relative standard deviation (= standard deviation x 100 divided by the mean) of total aldicarb at

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each of the four monitoring wells ranged from 6% to 19% during the course of the month with an average of about 10% for all four wells.

Figure 7 shows the time series of the ratio of aldicarb sulfone to total aldicarb. In this case, total aldicarb is the sum of the sulfoxide and sulfone species only, due to the rapid oxidation of the parent aldicarb. This time series also shows relatively constant ratios. Furthermore, there was little change in the sulfone ratio with time during the intensive sampling period in May 1988; the average relative standard deviation for all four monitoring wells during May 1988 was only 2%.

It is noteworthy that the other two instrumented sites on PEI show similar persistence in both the concentration and ratio during the same period, although absolute values for nitrate and total aldicarb differ.

## SIMULATION OF ALDICARB INFILTRATION

Attempts were made to simulate the persistence of aldicarb, as shown in Figures 6 and 7, to determine whether it would have been possible, a priori, to have predicted the fate of the applied aldicarb using the published soil properties for the relevant soil series and an advanced transport code. The code chosen was LEACHMP, which was developed by Wagenet and Hutson (1986) especially for aldicarb transport. It is a one-dimensional code simulating water and solute transport through porous media under transient conditions and which allows for the relevant oxidation and hydrolysis reactions shown in Figure 2.

The simulations were based upon a 4.4 m soil profile depth with the water table initially set at 3.0 m for January 1, 1983. The soil profile was assumed to be approximately 54% sand, 36% silt and 10% clay, for which the hydraulic properties were taken from the Canada Department of Agriculture report for PEI soils (MacDougall <u>et al.</u>, 1981). The dispersivity was set at 10 cm so that no aldicarb residues would remain in the first meter of the simulated soil profile, as was observed in the field. Daily climatic data from nearby meteorological stations were used as input to the model. The oxidation and hydrolysis rate constants were taken from Zhong <u>et al</u>. (1986), corrected for temperature to 10°C, and then further adjusted in the calibration step in an attempt to replicate the observed, field values of total aldicarb (4-12  $\mu$ g/L) and the sulfone/total aldicarb ratio (70-80%).

Figure 8 shows a typical output of the LEACHMP simulations. While reasonable predictions of the aldicarb sulfone ratio are produced throughout the period of simulation, the model suggests that pulses of aldicarb infiltrate to the water table then drain away or degrade very quickly, and that the water table aquifer then appears to become uncontaminated. Therefore, the model displays none of the persistence or dampened response noted in the field data (Figures 6 and 7) in which high concentrations persist in the shallow bedrock for several years. Furthermore, the calibrated values of the half lives for the various oxidation and hydrolysis reactions are about three times the temperature adjusted values of Zhong <u>et al</u>. indicating that aldicarb degradation rates appear to be very slow in PEI soils (Mutch, 1989). We estimate its overall half life in PEI soils and ground waters to be on the order of 150 days, as opposed to the estimated 100 day half life estimated by Jones <u>et al</u>. (1986) for aldicarb in Maine potato fields.

#### DISCUSSION

The very long half lives predicted for the oxidation and hydrolysis reactions and the failure of the model to reproduce the persistence of the field data demonstrate that (1) aldicarb is not readily degraded in the hydrologic system and (2) some in-situ storage mechanism is retaining undegraded aldicarb species and slowly releasing them over time, thereby maintaining relatively high concentrations in the monitoring wells. There are several possible mechanisms which may play a role: sorption of aldicarb and its slow release, downslope migration of aldicarb within the flow system, inhibition of degradation, slow infiltration through the unsaturated till and, finally, matrix diffusion within the sandstone and slow release.

Due to the solubility of the aldicarb species, it is very unlikely that significant sorption of aldicarb takes place. Laboratory column tests, using a methodology similar to that described by Zhong <u>et al</u>. (1986), showed that aldicarb and aldicarb sulfoxide had retardation factors of 1.25 and 1.26, respectively. That is, they migrate at an average of 80% of the ground water velocity. Therefore, this process alone cannot explain the persistence of aldicarb in the PEI soils and aquifer.

Similarly, the downslope migration of aldicarb from further up the ground water flow system does not explain the problem of persistence. Generally, the concentrations of total aldicarb in the monitoring wells from the upland recharge area (e.g., #4 in Table 1) are significantly lower than the concentrations in the wells along the slope of the flow system (e.g., #6, 7 and 9). Furthermore, the ground water pH upslope tends to be neutral or even higher (see Table 1), thus resulting in relatively rapid degradation of aldicarb species. Therefore, downslope migration of aldicarb would have to be coupled with a much higher continuous flux of aldicarb percolating from the vadose zone in the direct vicinity of the downslope wells if the observed persistence is to be explained. Therefore, this process does not explain the persistence of the aldicarb.

In previous papers (Priddle <u>et al.</u>, 1987 and 1988) it has been argued that aldicarb hydrolysis, and therefore detoxification, is strongly inhibited because of the chemical environment within which migration is taking place. Figure 9 shows that aldicarb hydrolysis is very dependent upon temperature and pH and that aldicarb species are most persistent in the pH range of 5 to 6. Because spring rains and

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snowmelt in PEI are acid (< pH 5) and cold, and because the soil itself is acidic, aldicarb is inherently persistent in this environment and long degradation rates might be expected. Additionally, the acidity of the soil water environment is maintained by the pH buffering effects of the oxidation of ammonium fertilizers:

 $0.5 \text{ NH}_4^+ + 0_2 = 0.5 \text{ NO}_3^- + \text{H}^+ + 0.5 \text{ H}_20$ 

for which the optimum microbial and chemical conditions are readily satisfied in PEI soils. Given that there is abundant oxygen and even some dissolved ammonium remaining (mean = 0.14 mg  $NH_4$ +-N/L) in PEI ground waters, the above reaction probably plays an important role in inhibiting aldicarb degradation processes in the vadose zone.

There can be little doubt that slow infiltration through the unsaturated till can create a reservoir of aldicarb that slowly leaches aldicarb species to the water table. Even in much more permeable sediments, such as those on Long Island (Pacenka <u>et al.</u>, 1987), large amounts of aldicarb were retained and were being slowly leached through the thick vadose zone some five years after the last application of aldicarb.

Finally, it has been shown by both Grisak and Pickens (1980) and Neretnieks (1980) that diffusion of relatively high concentrations of solutes from rock fractures into the porous matrix of a bedrock can result in the storage of the solute over time (see Figure 10). When hydrologic conditions cause the water in the fractures to have a lower solute concentration than that in the matrix, diffusion will produce a net flux from the rock matrix to the fractures that will restore the aldicarb levels of ground water in the fractures. Clearly, this could account for aldicarb storage in the PEI sandstone in which intergranular porosities average 16% (Francis, 1981). Naturally, a onedimensional, porous media-based model, such as LEACHMP, could not be expected to mimic the retention of solutes by matrix diffusion. However, the simulations were helpful in indicating what hydrologic processes are unlikely to be occurring and what magnitude of reaction constants are required to produce the observed total aldicarb and aldicarb speciation data.

## SUMMARY AND CONCLUSIONS

Aldicarb residues persist in the shallow ground waters of the fractured sandstone aquifer of Prince Edward Island well over two years after the last application of the pesticide. The persistence appears to be the consequence of two processes - one chemical, the other hydrological.

Aldicarb species are not rapidly transformed by hydrolysis to much less toxic species due to the low pH and temperature of the soil/water environment. Low pH levels are probably maintained by the oxidation of ammonium fertilizers which may well buffer the pH in the 5-6 range and therefore inhibit the hydrolytic degradation of aldicarb sulfoxide and sulfone.

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Given the relatively high ground water velocities at the field site, high concentrations of aldicarb species would have to be stored in-situ to prevent their discharge from the flow system. Such in-situ storage could well occur due to matrix diffusion from fractures to the integranular matrix. Reverse diffusion could then maintain relatively constant levels of aldicarb species and nitrate in the fracture waters sampled by the monitoring wells and displayed in Figures 5 and 6. In addition, slow infiltration of aldicarb through the thin till would provide additional storage of solute and would act to produce the dampened monitoring well response of aldicarb to the pulse inputs to the system.

The inability of the solute transport code LEACHMP to simulate the persistent behaviour of aldicarb in this hydrogeological environment points out the need for detailed field testing of mobile pesticides in the principal areas of their use. Furthermore, threedimensional versions of the model will be required if the behaviour of such pesticides is to be modeled in dual-porosity hydrogeological systems.

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# Figure 4



















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Figure 9

