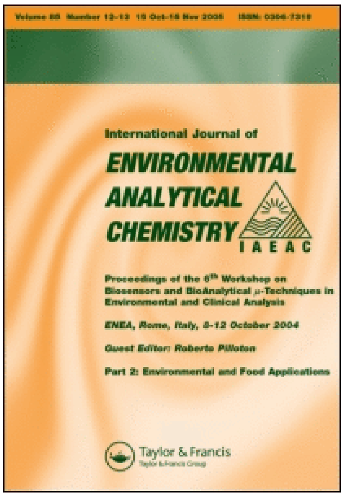

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A Study of Physical and Chemical Parameters that may Contribute to the Degradation of Aminocarb (4-dimethylamino-3-methylphenyl N-methylcarbamate) in Water

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In this study the effects of several physical and chemical parameters on the chemical degradation of aminocarb in water were measured. The parameters were: pH, temperature, oxygen, sodium chloride, iron(III) and copper(II) ions, sunlight and environmental water. A half-line of 342 h ± 3.3% was obtained for aminocarb in reference or standard water.

The study shows that a basic pH, an increase in temperature, the presence of oxygen, and sunlight caused significant decrease in the half-life of aminocarb. There is also a decrease in environmental water. The other parameters do not show any effect.

INTRODUCTION

The chemical insecticide aminocarb, 4-dimethylamino-3-methylphenyl N-methylcarbamate (Bayer 44646), has been used increasingly in Canada since 1973 to help control epidemics of spruce budworm (*Choristoneura fumiferana* Clemens). It is usually sprayed aerially as the formulation MATACIL^{R} at a dosage of 70 g of active ingredient

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per hectare. In New Brunswick alone, 0.74 and 2.14 million hectares were sprayed with MATACIL^R in 1978 and 1979, respectively (1).

General reviews dealing with the chemistry and biochemistry of aminocarb have been prepared (2,3). Hydrolysis seems to be prominent in alkaline medium. In biological samples the principal metabolic pathways involve hydrolysis and N-demethylation (both on the ring and the carbamate moiety).

The persistence of aminocarb in river water (under laboratory conditions) has been studied by Eichelberger and Lichtenberg (4). They reported that 60% of the parent compound still remained after one week and traces were detectable after three weeks. Sundaram *et al.* (5) studied the persistence of aminocarb in pond and stream water after a forest spray and reported no trace after 32 days. In another study Sundaram and Hopewell (6) investigated the disappearance of aminocarb from forest soil and foliage under environmental conditions and found no detectable amounts left after approximately one month.

It is still not known whether the disappearance of the chemical is caused mainly by dilution, by degradation (chemical or biological), or by dispersion throughout the ecosystem (absorption by sediments, living microorganisms, plants, etc.). In terms of chemical degradation the parameters that contribute directly to the disappearance of aminocarb in environmental water are also unknown. The chemical dissipates quickly under environmental conditions and it is claimed (2) that hydrolysis is an important degradation pathway but contrary to studies with biological substrates, very few degradation products other than the hydrolysis product have ever been reported in water.

Thus the main object of this study was to determine the effects of various physical and chemical parameters on the rate of degradation of aminocarb. Hopefully, the information so obtained would shed some light on some of the processes primarily responsible for the chemical degradation of aminocarb in water.

EXPERIMENTAL PART

I. Materials and apparatus

1. *Chemicals, reagents and solvents* Aminocarb was obtained free of charge as an analytical standard from Chemagro Ltd, Mississauga, Ont.

Standard solutions were prepared 1000 mg/L in methylene chloride (pesticide grade). Solutions were kept refrigerated in amber bottles and were stable for at least three months.

Amberlite XAD-4 resin was obtained from BDH Laboratory Reagents, Toronto, Ontario. The XAD columns were prepared as usual (7).

2. *Apparatus* A Tracor Model 560 gas chromatograph (GC) equipped with a thermionic nitrogen-phosphorous detector (TRACOR 702) was used. The glass column was 1.2 m × 4 mm I.D. and contained 3% OV-17 on CHROMOSORB W, 60–80 MESH, AW-DMCS.

II. Methods

1. *General procedure for the recovery of Aminocarb from water* One litre of water containing aminocarb, was passed through a glass column (30 cm × 1.9 cm I.D.) containing 12 cm of Amberlite XAD-4 resin. The column was then eluted with 3 × 30 mL of ethyl acetate. The eluate was dried by filtering through a Whatman no. 2, containing anhydrous sodium sulfate, and evaporated to 1.0 mL for gas chromatographic analysis.

2. *Procedures for kinetic studies*

i) Degradation of aminocarb in water (control) under standard conditions (pH 7.0).

The water was doubly distilled and de-ionized. A buffer was prepared by mixing 50 mL of a 0.2 M solution of KH_2PO_4 with 29.54 mL of a 0.2 M solution of NaOH and diluting to 250 mL (8). To one litre of this buffer, 100 mg of aminocarb were added. The container was wrapped with aluminum foil and kept in the dark at 25°C unless otherwise stated. Aliquots (100 mL or 50 mL) were removed periodically and passed through an XAD-4 column as described above. The eluate was dried and diluted to 100 mL with ethyl acetate ready for the GC analysis.

ii) Degradation of aminocarb in water at various pH values.

In these experiments the pH was set to 6.0, 7.5 and 8.0 by the addition of 5.64 mL, 41.04 and 40.85 mL of 0.2 M NaOH, respectively to separate solutions containing 50 mL of 0.2 M KH_2PO_4 and dilution to 1L.

Before extraction with the resin the pH of each aliquot was adjusted to 7.0 with either HCl or NaOH (0.1 M). All other conditions were standard (see Section 2(i)).

iii) Degradation of aminocarb at various temperatures.

In these experiments the samples were kept at 4, 10, 20 and 30°C, respectively. All other conditions were standard (see Section 2(i)).

iv) Degradation of aminocarb in oxygenated water.

In these experiments compressed air was bubbled slowly but continuously through the water. Evaporation was nullified by saturation of the compressed air with control water. All other conditions were standard (see Section 2(i)).

v) Degradation of aminocarb in saline water.

In these experiments sodium chloride (5 ppm) was added to the sample. All other conditions were standard (see Section 2(i)).

vi) Degradation of aminocarb in the presence of other metallic ions.

In these experiments either cupric nitrate or ferric nitrate was added to the sample such that the final concentration was 0.02 or 0.1 ppm, respectively. All other conditions were standard (see Section 2(i)).

vii) Degradation of aminocarb in environmental water.

The water was taken in Hall's Creek, a tributary to the Petticodiac River passing through Moncton, N.B. Values for water quality are given in Table I. The water was filtered to remove larger particles but it remained turbid. All other conditions were standard (see Section 2(i)).

viii) Degradation of aminocarb in the presence of sunlight.

The samples were subjected to sunlight outdoors. The samples were brought indoors and kept in the dark when the sun was out.

TABLE I[a]

Water quality parameters (Hall's Creek)[b]

Parameter	*Value*
pH	6.52
Conductivity	275 micromhos
Nitrate-nitrite	9.20 mg/L
Alkalinity	22.09 mg/L
Acidity	62.35 mg/L
Total Organic Carbon (TOC)	13.1 mg/L
Total Inorganic Carbon (TIC)	13.5 mg/L
Sulphate	8.72 mg/L
Chloride	13.8 mg/L
Chemical Oxygen Demand (COD)	10.0 mg/L
Cobalt	2.94 mg/L
Copper	0.14 mg/L
Iron	2.25 mg/L
Lead	N.D.
Nickel	0.71 mg/L
Cadmium	0.13 mg/L
Zinc	0.26 mg/L

[a] Courtesy of F. Cyr (U. de Moncton).
[b] Sampling was done September 23, 1982.

Thus the total time (h) of sunlight exposure could be measured. These experiments were done in May 1981 and the average temperature outdoors was 10–15°C. All other conditions were standard (see Section 2(i)).

RESULTS AND DISCUSSION

I. Statistical evaluation of the methods

1. *Method of recovery and quantitation* A choice had to be made at first upon the method to be used for the recovery of aminocarb from water. Aminocarb may be extracted from water using ethly acetate (9) or dichloromethane (10) but liquid-liquid partition is not suitable for some derivatives.

In previous studies (11,12) we had obtained over 90% recovery for aminocarb and several derivatives in water using Amberlite XAD resins. Brun and MacDonald (9) and Sundaram *et al.* (13) had also obtained excellent recoveries using XAD-2. Since we were also interested in the degradation products of aminocarb in water we opted for a recovery method using Amberlite XAD-4. We chose this particular resin because it was readily available in our laboratory and also because it provided better recoveries with derivatives of aminocarb (12).

In the present project a total of 47 experiments (not all included in this article) were done under a variety of experimental conditions such as different pH values, changes in temperature, etc.... The average % Recovery calculated from the data at "time zero" becomes 96%±4.9% with values ranging between 84% and 108%. This information is really indicative of the reliability to be expected in the recovery of aminocarb from water under operational conditions, using Amberlite XAD-4 and subsequent quantitation by gas chromatography using a Nitrogen-Phosphorous Detector (NPD).

2. *Method for estimating half-lives* In this study the half-life of aminocarb for a particular degradation reaction was obtained by extrapolating the time corresponding to 50% recovery on a curve of % recoveries versus time. The best fit for such a curve was obtained through visual inspection of the plotted experimental data. Such a procedure is subject to human error but our statistical evaluation of the method reveals that the error is within acceptable levels.

There are at least two ways of obtaining half-lives by visual inspection of degradation curves: (i) by averaging half-lives obtained from individual plots in a series of degradation studies or (ii) by averaging the percentage recoveries at each extraction time, plotting an "average curve" from which the average half-life can be obtained. The data in Table II illustrate the results when both methods are used. In the first instance four half-lives were obtained from four respective curves, from which an average half-life of 343 h±3.0% may be calculated. In the second instance an average half-life of 342 h was derived from the graph of the averaged data. Coefficients of variation were calculated for each set of % recoveries at a particular time from which an average coefficient of variation of 3.3% was obtained. There is obvious agreement between the two approaches in estimating half-lives but the second approach is usually preferable because only one graph needs to be plotted as shown in Figure 1.

TABLE II

Half-life of aminocarb in reference water: Reproducibility study

Time (*h*)		% *Recovery*[a]						
	Exp. No.	1	2	3	4	Average	Standard Deviation	Coefficient of variation
T_0		105	96	100	98	100	3.9	3.9
4		103	94	100	97	99	3.9	3.9
10		98	96	98	93	96	2.4	2.5
24		96	94	97	94	95	1.5	1.6
30		93	92	93	91	92	1.2	1.3
54		91	90	92	86	90	2.4	2.7
78		86	87	89	81	86	3.5	4.1
102		82	85	84	84	84	1.3	1.5
174		78	66	77	76	74	5.7	7.7
232		67	63	65	63	65	2.0	3.1
315		52	53	54	51	53	1.4	2.6
450		48	43	46	—	46	2.1	4.6
480		46	42	45	40	43	2.8	6.5
	half-life (h)	351	335	352	332	342	2.6	3.3%
	Average half-life from individual curves	343±3.0%				Average half-life from average curve	Average Standard Deviation	Average Coefficient of Variation

[a] Experiments 1-4 were done simultaneously.

II. Determination of the half-lives of aminocarb in water

The purpose of measuring half-lives was to evaluate the effects of various parameters on the rate of degradation of aminocarb in water. One parameter which was expected to be important was pH. Table III gives the half-life of aminocarb at pH 7.0 (Ref. to Table II) and the half-lives at the other pH values obtained by plotting individual curves for each experiment. The agreement between each experiment is obvious. In terms of pH the results show that aminocarb is more stable in slightly acid medium than it is under slightly basic conditions. This was expected since other workers (14) have shown that in general, carbamates are hydrolysed under basic conditions.

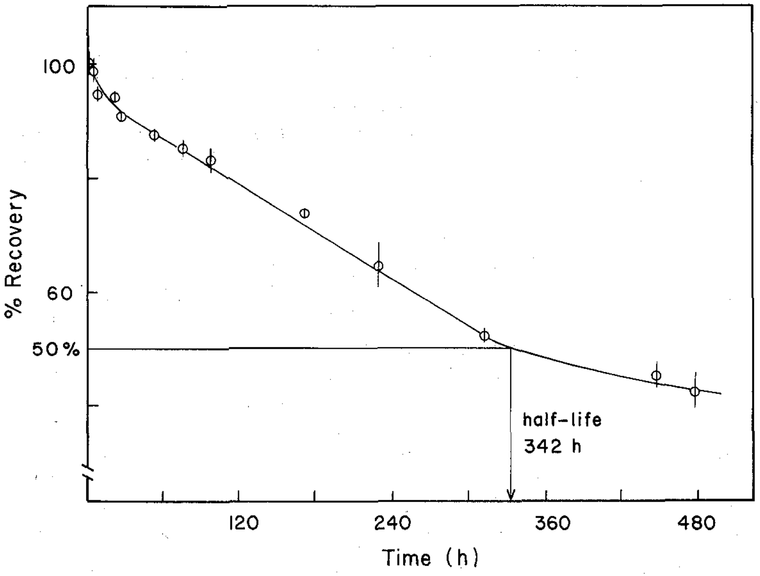

FIGURE 1 Half-life of aminocarb in reference water (standard conditions) obtained from curves of averaged data.

TABLE III

Effect of pH on the half-life of aminocarb in water

pH	*Average half-life* (*h*)		
	Experiment no.		Average half-life (h)
	1	2	
6.0	414	414	414
7.0	(Ref. to Table II)		342
7.5	236	240	238
8.0	147	148	148

Another parameter which could possibly increase the rate degradation of aminocarb in the environment is temperature. In a series of experiments the percentage recoveries at various temperatures were measured at fixed times. Duplicate extractions were done for each temperature after 100 h and 300 h, respectively.

The data are presented in Table IV. The trend seems to be faster degradation at higher temperature as evident from the extractions at 100 h and more so at 300 h (see also Figure 2). The data for the control at 25°C (see Table II) are in agreement with those in Table IV showing reproducibility between replicate experiments.

TABLE IV

Degradation of aminocarb in reference water:
Effect of temperature

% Recoveries	*Temperature (°C)*				
after	4	10	20	25	30
100 h	94,101	97,96	88,87	85,82	76,71
after 102 h (replicate experiment)	—	—	—	84[a]	—
300 h	93,92	90,93	62,59	54,48	46,44
after 315 h (replicate experiment)	—	—	—	53[a]	—

[a] Average of 4 experiments run concurrently (see Table II).

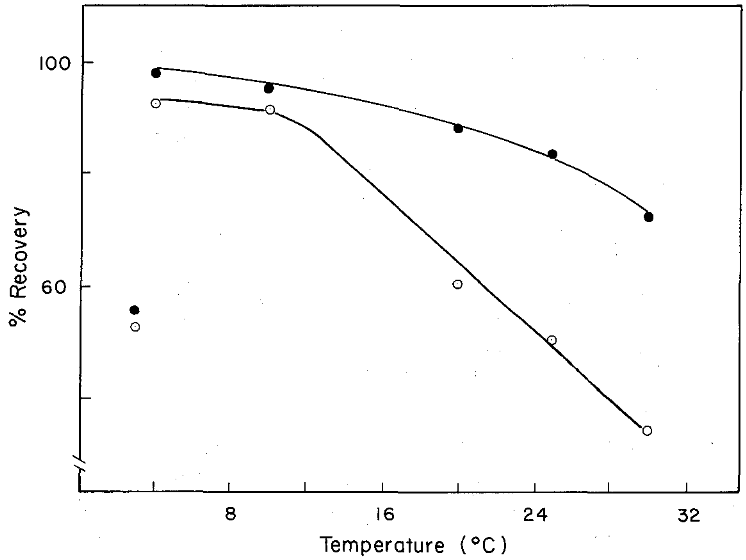

FIGURE 2 Effect of temperature on the half-line of aminocarb in water. ●—100 h; ○ 300 h.

Another parameter studied was the effect of excess oxygen. This element is usually present in parts per million in natural water reasonably free from oxygen-demanding wastes. In our experiments compressed air was bubbled continuously to saturate the solution which was kept at constant volume. The results for duplicate experiments and a control are given in Table V. Since duplicate experiments were performed, the % recoveries were averaged at each particular time and an average curve was plotted. The average half-life obtained was 258 h, significantly less than the half-life of the control at 336 h. Thus oxygen seems to have a positive effect on the degradation of aminocarb in water. It is important to note that the half-life of the control, 336 h is within experimental error as predicted by the statistical evaluation 342 h ± 3.3% reported earlier (see Table II).

TABLE V

Degradation of aminocarb in water

Time (h)	% *Recovery*[a]			
	Control	Presence of Oxygen	Presence of NaCl	Presence of Sunlight
T_0	98	98	96	92 (0)[b]
24	90	94	90	83 (7)
99	—	70	86	66 (14)
192	81	64	80	57 (23)
240	65	54	64	57 (23)
312	54	45	55	48 (33)
408	44	35	46	42 (33)
Average half-life (h)	336	258	330	279

[a] Each % recovery is the average of duplicate experiments.
[b] Values in brackets indicate total hours of sunlight exposure.

Another parameter studied was salinity. Water was spiked with 5 ppm of NaCl (a concentration to be expected near estuaries). The average recoveries for duplicate experiments are given in Table V along with those of the control. A half-life of 330 h in presence of NaCl as compared with 336 h for the control indicates no significant effect since the variation to be expected for the control is ± 11.3 h.

The effect of sunlight on the degradation of aminocarb was also studied. Samples were left outdoors when it was sunny and brought in at night or when it was cloudy. Thus Table V also gives the total amount of sunlight exposure. Experiments were done in May when the outside temperature was around 15°C. The data for duplicate experiments yield a half-life of 279 h which has to be considered significant as compared with the control at 336 h. Also the fact that the temperature was much less than 25°C strengthens the belief that sunlight increases the degradation of aminocarb in water.

Metallic ions are common components in natural water. A previous study (15) with fenitrothion [0,0-dimethyl-0-(3-methyl-4-nitrophenol)phosphorothioate] had shown a catalytic effect of metallic-ions such as Fe^{3+} and Cu^{2+} on the rate of hydrolysis of this insecticide. In this study cupric nitrate (0.02 ppm) and ferric nitrate (0.1 ppm) were added to aminocarb in water at pH 7.0. The data are presented in Table VI. With copper the average half-life was determined to be 348 h as compared with 348 h for the control run simultaneously. For ferric ions, the half-life was 342 h. Thus it seems clear that at the above concentrations which represent environmental conditions, those metal ions have no effect on the rate of degradation of aminocarb in water.

TABLE VI

Degradation of aminocarb in reference water: Effect of metallic ions

Time (h)		*% Recovery*	
	Control	Presence of Fe^{3+} (0.1 ppm)	Presence of Cu^{2+} (0.02 ppm)
T_0	90	90	98
23	89	93	96
72	88	75	90
144	—	72	77
192	—	73	77
216	69	62	64
264	63	57	58
312	53	54	59
363	45	44	49
459	42	44	39
Average half-life	348	342	348

TABLE VII

Degradation of aminocarb in environmental water

Time (h)	*% Recovery* Experiment no. 1	 2	 Average	 3
T_0	98	92	95	—
4	—	—	—	98
10	—	—	—	89
24	104	100	102	83
30	—	—	—	86
54	89	80	85	87
99	71	73	72	—
168	62	63	63	66
267	57	57	57	53
291	—	—	—	51
315	43	40	42	46
408	—	—	—	39
459	37	37	37	39
Average half-life			279	276

Note: Experiments 1 and 2 were duplicates; Experiment no. 3 was a replicate.

Duplicate experiments and one replicate (done at a later date) were done with environmental water (Table VII). The average half-life obtained with the duplicate experiments was 279 h while 276 h was obtained with a replicate showing good agreement. The results indicate a significant increase in the rate of degradation as compared with the control (336 h see Table V). This increase in the rate of degradation was suspected considering that this environmental water contained untreated sewage and thus was very contaminated in terms of microorganisms and other things.

CONCLUSION

Thus, a series of parameters were investigated to determine whether or not they could contribute significantly to the degradation of aminocarb in natural water. These parameters were pH, temperature, oxygen, salinity, sunlight, metallic ions (Cu^{2+} and Fe^{3+}) and environmental water. Parameters such as pH, oxygen, temperature, and sunlight were shown to have a positive effect on the degradation. Environmental water also caused an accelerated degradation.

Thus, under controlled conditions the statistical half-life of aminocarb in water was found to be $342\,h \pm 11.3$ or approximately 14 days. It is expected that under environmental conditions where many additional chemicals are present and other factors such as evaporation, dilution and dispersion in the ecosystem are important, the half-life of aminocarb should be further reduced. In fact some experiments suggest a rapid disappearance (two to three days) of aminocarb in environmental water at pH 6.5 (3).

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