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Biodegradation of Carbaryl in Simulated Aquatic Environment

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Until recently, an insecticide has always been designed from the economic point of view which demanded that the insecticide should possess a combined broad-spectrum of insecticidal activity with extended persistence in the environment. However, this combination is now regarded as undesirable, and broad-spectrum activity has to be combined with limited persistence (BROOK 1976). To meet such a new demand, the carbamate insecticides were thus developed and among which carbaryl (1-naphthyl-N-methylcarbamate) was by far the most widely used carbamate insecticide, as evidenced by the 55 million pounds manufactured by Union Carbide in 1971 (KUHR & DOROUGH 1976).

With its low mammalian toxicity and short half-life in the environment, carbaryl has become one of the most popular insecticides for the control of approximately 160 harmful insect species at home, in the garden, orchard and vegetable farming practice. The half-life of carbaryl in the environment ranged from 1.7 to 5.8 days in river water (EICHELBERGER & LICHTENBERG 1971; STANLEY & TRIAL 1980), 3 to 4 days on plant foliage (KUHR & DOROUGH 1976) and 8 to 9 days in soils (JOHNSON & STANSBURY 1965). The very short half-life of carbaryl in the environment is particularly desirable as this would reduce the possibility of inducing the development of pesticide-resistant insects. However, recent public concerns regarding the safety of using carbaryl for the control of gypsy moths have caused the New Jersey Department of Environmental Protection to suspend the use of this insecticide. After some extensive studies, the carbaryl was again approved for general use earlier this year (ANON 1981) indicating the complexities involved in the assessment of the environmental behaviour of an insecticide. The objective of this study was to assess the biodegradability of carbaryl in simulated aquatic environment; factors affecting the degradation rates were also discussed.

MATERIALS AND METHODS

Reagents and Growth Medium. Organic solvents were glass distilled as supplied by Caledon Laboratories Ltd. and the carbaryl was obtained from Aldrich Chemicals, Inc., Milwaukee, WI. The basic growth mediim contained the following ingredients: (g L^{-1}): K_2HPO_4, 2.6; KH_2PO_4, 1.9; $(NH_4)_2SO_4$, 1.0; $MgSO_4.7H_2O$, 0.05; $FeSO_4.7H_2O$,

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0.01; $CuSO_4.5H_2O$, 0.01; $CoSO_4.6H_2O$, 0.001, $MnSO_4.4H_2O$, 0.001, sodium ligninsulfonate, 0.05; carbaryl, 20 mg; distilled water 1 L. Final pH of the medium was 6.8 and the medium was not sterilized.

Experimental Design. Due to the many variables involved, it was impractical to study the biodegradation of carbaryl in all natural environments. Consequently degradation studies were conducted in the modified cyclone fermentors (LIU & FOX 1980) under controlled laboratory conditions which were environmentally relevant such as aeration and anoxia. Because abiotic degradation processes such as hydrolysis and photolysis sometimes occurred during biological degradation, control fermentors with microbial inhibitors were also included to allow for correction for such processes. Six fermentors were used: three were operated under aerobic conditions and three others under anaerobic environments. Under each of these two basic conditions, carbaryl was simultaneously subjected to metabolic (carbaryl as sole carbon and energy source), co-metabolic (with the more easily biodegradable glucose and peptone at the concentration of 1 g L^{-1} each) and abiotic degradations in separate fermentors. The abiotic system was accomplished by using microbial inhibitors as follows: $HgCl_2$, 100 ppm; KCN and NaN_3 at 5 m moles L^{-1} each. The fermentors were operated at 20°C with a steady supply of air (aerobic) and nitrogen (anaerobic) at 20 mL min-1. The concentration of carbaryl used was 20 ppm with the mineral medium described above as the growth broth.

Inoculum. In order to obtain a more representative environmental sample, the standard inoculum was made from the folowing procedure: one gram each of lake sediment and silt loam were added to 100 mL of fresh domestic activated sludge. The mixture was vigorously shaken for 0.5 min and allowed to stand at room temperature for ten min. Two mL of the supernatant were used as the inoculum for each 1 L of medium in the degradation study.

Extraction and Analysis. At various time intervals, 5 mL of culture broth were withdrawn from the fermentors and acidified to pH 2 prior to extraction with 2 mL of $CHCl_3$. The chloroform extract was washed once with an equal volume of 0.1 M K_2CO_3 and the washed $CHCl_3$ extract was allowed to react with 2 mL of 10% methanolic KOH overnight at room temperature (20 ± 1°C). Two mL of water were then added and the aqueous phase washed with 5 mL of benzene, followed by addition of 2 mL of water. The combined aqueous phase was acidified to pH 2 and extracted with 1 mL of $CHCl_3$. This $CHCl_3$ extract was analyzed on a gas chromatograph equipped with dual FID. This instrument was interfaced with a Spectra Physics SP4000 chromatography data system to facilitate calculations. The dual 180 cm x 2 mm i.d. stainless steel columns contained 10% OV-1 on 80/100 mesh Chromosorb W (AW-DMCS). The injection port and the detector were at 250°C while the oven was programmed from 150-220°C at 8°C min^{-1}. The carrier gas was nitrogen at a flow rate of 30 mL min^{-1}.

Measurement of Biodegradation Rate. Carbaryl biodegradation was measured in terms of primary degradation, i.e., by following the disappearance of carbaryl from the fermentor broth after correction from loss due to abiotic processes. Rate constants (k) were determined from the assumed first-order process in which

$$-\frac{dc_s}{dt} = kt \quad \text{(integrated form: } \ln C_s^o/Cs = -kt$$

where C_s = concentration of carbaryl and the superscript "o" refers to time zero. The half-lives were determined form the expression $t_{\frac{1}{2}} = 0.693/k$.

RESULTS AND DISCUSSION

The stability of carbaryl in aqueous solution was known to be pH dependent (LAMBERTON & CLAEYS 1970), a growth medium with strongly buffering capacity was, therefore, used in the present investigation. Routine examination of the fermentor broth was also conducted and in no case a shift of greater than 0.2 pH unit was observed in any fermentor at the termination of the experiments. In addition, the efficiency of the microbial inhibitors in the control fermentors was also checked by the plate count technique and no viable microorganisms were detected. The fairly rapid decrease of carbaryl concentrations in all fermentors (Figure 1), including the controls, suggested the inherent instability of this insecticide in the aquatic environment. This observation agreed with the literature data that carbaryl was the most labile carbamate insecticide in an aquatic milieu (KUHR & DOURGH 1976).

Table 1 shows the degradation rates of carbaryl under the variously environmental conditions of the experiment. Apparently, abiotic degradation was one of the major processes responsible for the destruction of carbaryl in the fermentors. In addition, oxygenation enhanced such abiotic degradation rate ($t_{\frac{1}{2}}$ = 8.3 days) when compared with an anoxic environment ($t_{\frac{1}{2}}$ = 15.3 days). The results implied that even the abiotic degradation of carbaryl was susceptible to conditions of oxygenation in the aquatic environment. Since the concentrations of dissolved oxygen in a body of water vary with seasons and locality, precise prediction of the environmental behaviour of a labile chemical such as carbaryl in a natural aquatic

TABLE 1. Degradation rates of carbaryl

	Aerobic			Anaerobic		
	Control	Meta.	Co-meta.	Control	Meta.	Co-meta.
k x $10^{-3}h^{-1}$	3.5	4.3	7.7	1.9	5.0	6.9
$t_{\frac{1}{2}}$ (days)	8.3	6.8	3.8	15.3	5.8	4.2
r	0.996	0.999	0.988	0.993	0.990	0.951
n	7	7	7	7	7	7

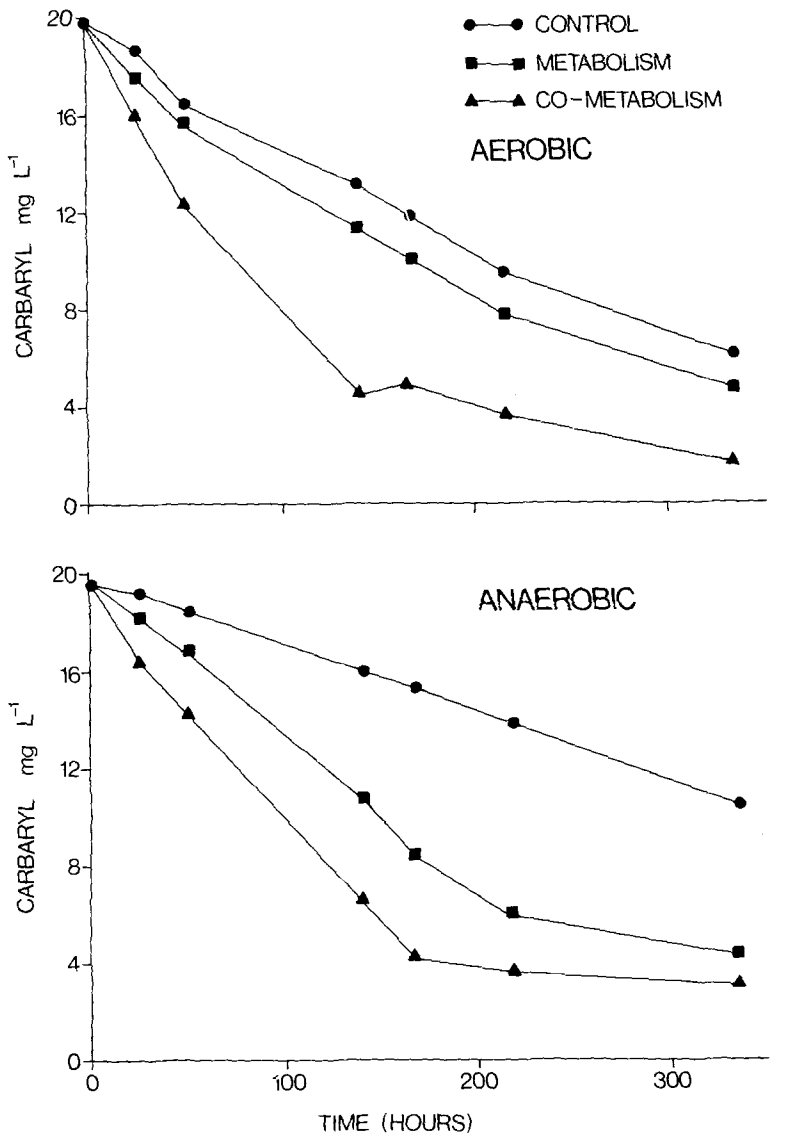

Figure 1. Degradation of carbaryl in fermentors.

environment would be difficult. In the absence of organic nutrients (metabolism), carbaryl exhibited a half-life of 6.8 and 5.8 days in the aerobic and anaerobic fermentors respectively. Addition of exogenous organic nutrients (co-metabolism) could significantly shorten its half-life to the respective 3.8 days (aerobic) and 4.2 days (anaerobic). Such results were not surprising as organic nutrients would encourage the rapid development of bacterial populations in the co-metabolism fermentors. Various micoorganisms including a Flavobacterium have demonstrated their ability to degrade carbaryl (KUHR & DOROUGH 1976). Literature data on cabaryl's half-life in aquatic environments varied from 1.3 days in fish aquarium (KANAZAWA 1975), 1.7 days in river water (EICHELBERGER & LICHTENBERG 1971) to 5.8 days in mountain streams (STANLEY & TRIAL 1980). In view of the complexity involved in the assessment of a chemical's stability, our results could be considered in agreement qualitatively with those literature data cited above. The difference between our results and their data may be at least partially explained by the fact that we used the rigidly controlled fermentor system while natural river water or field approach was employed in their studies. In some cases the pH effect on carbaryl's stabilty was apparently not appreciated (STANLEY & TRIAL 1980). For example, the pH of the river water used in one experiment changed from 7.3 to 8.0 during the eight-week period (EICHELBERGER & LICHTENBERG 1971). Such a change of pH during the test could affect the final results. ALY and EL-DIB (1971) studied the hydrolysis of carbaryl and reported that the half-life of this insecticide changed from 10.5 days at pH 7, to 1.8 days at pH 8. Nevertheless, the roles of aerobic and anaerobic environments as well as the organic nutrient availability in determining the stability of carbaryl are clearly demonstrated in the present study.

The biodegradability of carbaryl is presented in Table 2 and the results indicated that metabolism process played an insignificant part in degrading this insecticide ($t_{\frac{1}{2}}$ = 54 days) at an aerobic situation; the biodegradation rate was greatly acceletated ($t_{\frac{1}{2}}$ = 7.6 days) in the presence of co-metabolites (glucose and peptone). A similar effect was also noted under anaerobic conditions though the change was not as dramatic ($t_{\frac{1}{2}}$ from 11.6 to 6.1 days).

TABLE 2. Biodegradation rates of carbaryl*

	Aerobic		Anaerobic	
	Metabolism	Co-metabolism	Metabolism	Co-metabolism
k x $10^{-3}h^{-1}$	0.53	3.8	2.5	4.7
$t_{\frac{1}{2}}$ (days)	54	7.6	11.6	6.1
r	0.946	0.995	0.995	0.998
n	5	4	6	5

* corrected for abiotic degradation

In conclusion, the present study indicates that abiotic degradation is a major process for the degradation of carbaryl in a clean aquatic environment such as the mountain stream where the organic nutrients are limited. In a polluted river, both the abiotic and biotic degradation processes play an equal role in destroying the carbaryl. The river or lake sediment normally has a higher bacterial population and a richer organic nutrient content, but with less dissolved oxygen; the degradation of carbaryl in sediment is likely to proceed via the biodegradation route. Finally, we wish to emphasize here that our laboratory system does not pretend to be a natural aquatic ecosystem. It does, however, provide a convenient tool for investigating the complex degradation processes involved in the degradation of a chemical in the aquatic environment.

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