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Residues of 1-Naphthol in Soil and Water Samples In and Around Bhopal, India

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Carbaryl, a methyl carbamate insecticide, is known for its wide application and low mammalian toxicity (Carpenter et al. 1961, Benson et al.1967 Robens 1969, Dikshith et al. 1976, Dikshith and Raizada 1983 and Barik 1984). The use of carbaryl in tropical agriculture is of recent origin and the degradation pattern of carbaryl in tropical environment is, thus very scanty (Matsumura 1985). The present report therefore deals with the residues of 1-naphthol present in soil and water samples collected in and around Bhopal, India where carbaryl was commercially produced on large scale for more than a decade.

MATERIALS AND METHODS

Analytical standard for 1-naphthol was obtained from U.S.E.P.A.Pesticides and Industrial Chemicals Repository (MD-8), Research Triangle Park,N.C. USA. All solvents used in extraction and cleanup processes were of A.R. grade and distilled in all glass-still prior to use. Silica gel (Glindia Ltd.) activated charcoal (E.Merck India Ltd.) and sodium sulfate (Sarabhai Chemicals Bombay) used in this experiment were of high purity.

Sixty two samples of soil, surface and ground waters (Ponds, well and handpumps) were obtained from different locations in and around Bhopal, India. Each sample of soil in replicates of ten was weighed (50 g) in 250 mL Erlenmyer flask and mixed thoroughly for 3 min with 150 mL dichloromethane A.R. grade (Sisco Laboratories, Bombay), shaken for 30 min and filtered with suction through Buchner funnel. The Erlenmyer flask was washed with 25 mL dichloromethane and filtered through Buchner funnel. The filtrate was transferred to 1L separatory funnel. 450 mL water containing 4% sodium sulfate (w/v) was added to the separatory funnel and shaken vigorously for 30 min. The organic layer was filtered through 30g anhydrous sodium sulfate under high pressure. Extraction was carried out successfully with 3 x 150 mL portions of dichloromethane and filtered as above. The combined extract was concentrated to a volume of 1 mL with vaccum rotary evaporator at 35°C, dissolved in 25 mL distilled acetonitrile (Spectrochem Pvt.Ltd. Bombay) and washed with 4% sodium sulfate. It was extracted again with 3 x 10 mL portion of dichloromethane. The combined dichloromethane extract was concentrated to 1 mL volume, The mixed phase column was dry packed with 1 x 5 cm bed of anhydrous sodium sulfate at the bottom followed by 1 x 10 cm bed of

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silica gel. 1 x 10 cm of activated charcoal and approximately 1 x 5 cm bed of sodium sulfate at the top. The concentrated extract was then applied to the pre-washed chromatography column and elluted with 40 mL dichloromethane. The fractions containing 1-naphthol were collected, concentrated and transferred to 2 mL volmetric flask and made to a volume of 2 mL in dichloromethane. Analysis was carried out using CHEMTECH series 3865 chromatograph equipped with a FID detector. A stainless steel column (2 m x 3 mm i.d), packed with 3% SE-30 on chromosorb WHP 100/120 mesh was used. Operation temperatures were 170, 225 and 225°C for column, injector and detector respectively. Purified nitrogen gas passing through silica gel and molecular seives was used as carrier gas at a flow rate of 30 ml/min. Hydrogen at a flow rate of 30 mL/min and air at a flow rate of 300 mL/min were used.The analytical procedure for water samples was same as above except the sample volume being 1L.

Procedural blanks, consisting of all reagents and glass ware used during the analysis were periodically determined to check the cross contamination. Since no compound that interferred with 1-naphthol was detected, the sample volumes were not corrected for procedural blanks. Recovery studies with fortified samples have indicated that overall recovery value exceeded 95%. Results were not adjusted for percent recovery. Identification and quantification were accomplished using a known amount of external standard (Ambrus et al. 1981).

RESULTS AND DISCUSSION

The concentration of 1-naphthol in soil and water samples are summarized in Table 1. Presence of 1-naphthol was found in all the samples subjected to GLC analysis. Water samples of wells had the minimal residual contents (0.012 ppm) and varied between 0.002 to 0.024 ppm range. Water samples obtained from handpumps also showed an appreciable level of 1-naphthol (mean concentration of 0.026 ppm) and the range was found to be 0.017 to 0.048 ppm, while water samples obtained from the ponds showed higher residual contents, pond 1 (0.083 ppm), pond 2 (0.042 ppm) and pond 3 (0.079 ppm) and varied between 0.036 to 0.088 ppm.

The soil samples obtained from ponds however showed an alarming levels of 1-naphthol which ranged between 0.153 to 0.656 ppm. The mean concentration in soil samples from pond 1 (0.446 ppm) was found to be the highest followed by pond 3 (0.365 ppm) and pond 2 (0.279 ppm) respectively. It is interesting to note that the trend of 1-naphthol residues in pond water and pond soil samples have the same pattern (Table 1). The presence of 1-naphthol in soil and water samples from Bhopal may have been associated with the commercial production of carbaryl. It may have accumulated in soil and water as carbaryl and leached through soil, transmigrated to different adjoining areas and finally degraded to 1-naphthol and other metabolites. Metabolism of carbaryl in soil and water is well studied and reported by several authors (Boush and Matsumura 1967, Bolag and Lin 1971, 1971a, Rodriguez and Borough 1977, Ambrus et al.1981). Carbaryl is an unstable compound and breaksdown to 1-naphthol and to unidentified metabolites which are water soluble (Sikka et al. 1975, Ambrus 1984).

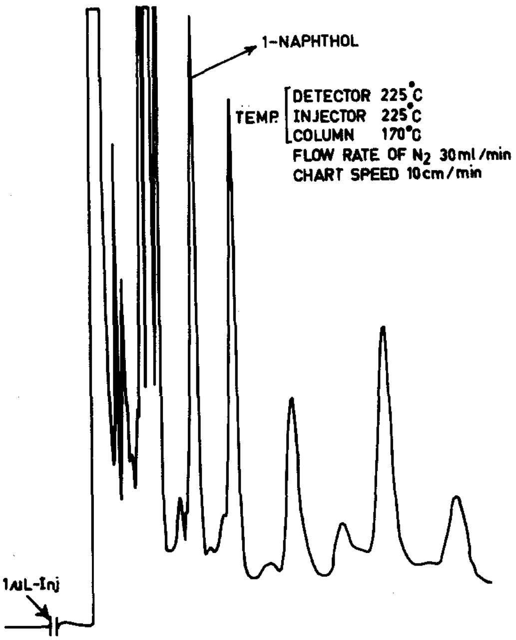

Figure 1 Characteristic chromatogram of 1-naphthol in soil/water samples

Table 1. Residues of 1-naphthol in samples of water and soil from Bhopal, India.

	Sample source	Mean concentration* (ppm)	Concentration Range (ppm)
Water	Wells	0.012	0.002-0.024
	Hand-pumps	0.026	0.017-0.048
	Pond-1	0.083	0.075-0.098
	Pond-2	0.042	0.036-0.048
	Pond-3	0.079	0.068-0.081
Soil	Pond -1	0.466	0.250-0.656
	Pond-2	0.279	0.153-0.598
	Pond-3	0.365	0.250-0.508

* Values indicate the mean of ten replicates each.

In adquatic environment carbaryl is known to degrade to 1-naphthol, 1,4-naphthoquinone and 2-hydroxy-1,4-naphthoquinone and other products (Sud et al. 1972, Şzeto et al. 1979, Osman and Belal 1980), as we too have found unidentified peaks besides 1-naphthol (Fig.1). Further the patterns of carbaryl degradation into other metabolites (besides 1-naphthol) in water and soil of Bhopal seems to follow similar metabolic phenomenon. More studies are in progress to quantitate the specific metabolite or all possible metabolites of carbaryl present in water and soil samples collected from Bhopal.

Many reports have appeared on the clinical and toxicological effects of methyl isocyanate (one of the starting materials needed for the production of carbaryl) on the population exposed to the accidental release in Bhopal, India (Misra et al. 1988 and Saxena et al. 1988, Gupta et al. 1988, Rastogi et al. 1988 and Srivastava et al. 1988). Health effects due to presence of 1-naphthol in water and soil samples in and around Bhopal is unknown and therefore needs elaborative study. As the present study is based on a limited number of samples of water and soil only and may not be representative of 1-naphthol concentrations at other locations in Bhopal. In view of the complex nature of water and soil system of several tropical environments including Bhopal and the modulating factors operating therein, there is a great need for more monitoring data to determine the concentration variation of 1-naphthol and other metabolites in the environment of Bhopal, India.

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