Bull. Environ. Contam. Toxicol. (1987) 38:332-336

Bulletin of Environmental Contamination and Toxicology

Laboratory Assessment of Environmental Impact of Phthalazine

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Several approaches to the environmental safety assessment of chemicals have been reported (Daniels et al 1985; Gillette 1983; Gledhill et al. 1980; Neely 1982). The basic principles involved in predicting environmental behavior combine degradation kinetics and the partitioning/distribution of chemicals in the environment. The transport mechanisms within the environment can be modeled as partitioning/distribution which are essentially functions of the physico-chemical properties of the chemical.

Phthalazine (2,3-Benzodiazine, $C_8H_6N_2$) is a component of a specialized paper product. The major route for environmental entry of phthalazine is through land disposal of waste paper. Key physical properties include high water solubility (>5% by weight) and an apparent low vapor pressure, 0.42 mm Hg. Information available on phthalazine chemistry is consistent with behavior of heterocyclic aromatic hydrocarbons (Patel 1973).

Several laboratory test methods and QSAR estimation procedures were used to measure key environmental properties of phthalazine. This assessment examines the environmental release of phthalazine, and its partitioning and distribution in the environment. It predicts the probable fate and possible biological effects of phthalazine.

MATERIALS AND METHODS

Partition parameters, including water solubility, vapor pressure, Henry's Constant, octanol/water (Log K_{ow}), soil/water (Log K_{oc}) and fish/water (Log BCF), were estimated using QSAR systems for exposure assessment (Hunter et al. 1985) or found in the literature (Patel 1973). Distribution, in weight percent, of phthalazine

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in the environment was generated using the Neely 100-day distribution pattern in QSAR systems (Hunter et al. 1985). Soil/water partition tests were also performed using sandy loam soil samples (17% clay) having pH 5.7, CEC 23.7 meq/100 g soil and organic matter content of 2.1% (TOC 1.2%). The soil batch equilibration method followed the Organization of Economic Cooperation and Development (OECD) Test Guideline #106 (1981). Leachable concentrations of phthalazine from the paper were determined using the Extraction Procedure (EP) Toxicity Test (USEPA 1981).

Laboratory biodegradation tests were conducted using the standard biochemical oxidation demand (BOD) procedure (Standard Methods 1985) and the modified Zahn-Wellens technique, OECD Test Guideline #302B (1981). The 28-day modified Zahn-Wellens test evaluated inherent biodegradability under more favorable test conditions than those provided for in the ready biodegradation test (28-day BOD), including acclimation and high microbial concentrations. Determination of inherent biodegradability was based on percent removal (loss) of dissolved organic carbon (DOC).

The ecotoxicological properties of phthalazine were determined using a test system composed of seven short-term single-species tests. The aquatic acute effects tests were conducted using freshwater green algae (Selenastrum capricornutum), water flea (Daphnia magna) and fathead minnow (Pimephales promelas) as the test species. The plant emergence/growth effects tests were conducted using a monocotyledon species, sweet corn (Zea mays), and a dicotyledon species, tomato (Lycopersicon esculentum). These laboratory methods followed OECD Test Guidelines #201-203 and 208 (1984).

The microbial inhibitory effects tests were performed using the activated sludge respiration inhibition test (OECD Test Method #209, 1984) and the Microtox® Toxicity Analyzer System (Beckman Instruments, Inc., 1982). The activated sludge studies evaluated the reduction in respiration rate of mixed cultures of heterotrophic bacteria obtained from a municipal waste treatment plant. The Microtox® system measured the decrease in light output of luminescent bacteria (Photobacterium phosphoreum).

RESULTS AND DISCUSSION

The environmental properties of phthalazine are summarized in Table 1.

Table 1. Environmental Properties Of Phthalazine

Partitioning[1]	
Water solubility, mg/L; 25°C	>50,000
Vapor pressure, mm Hg; 25°C	0.42
Air/Water, Log H_L, atm-m^3/mole; 25°C	-5.8
Octanol/water, Log K_{OW} (Log P)	0.46
(from Schultz 1982)	0.6
Soil/water, Log K_{OC}	1.58
- measured (this work)	3.17
Bioconcentration factor, Log BCF	0.1
Distribution (%)[1]	
Air	0.04
Water	99.90
Soil	0.03
Sediment	0.03
Fate	
Ready biodegradation, 28-day BOD/COD; %	2.4
Inherent biodegradation,	
28-day DOC removal; %	22
Estimated biodegradation, $t_{1/2}$; days[1]	>100
Toxicity	
Green algae, 5-day EC_{50}; mg/L	18 (10-30)[2]
Water flea, 48-hr EC_{50}; mg/L	445 (410-490)
Fathead minnow, 96-hr LC_{50}; mg/L	100 (85-140)
Sweet corn - seed germination, 10-day EC_{50}; mg/L	>1000
- root elongation, 10-day EC_{50}; mg/L	130 (90-170)
Tomato - seed germination, 10-day EC_{50}; mg/L	500
- root elongation, 10-day EC_{50}; mg/L	100 (80-130)
Activated sludge respiration inhibition, 3-hr EC_{50}; mg/L	325 (240-470)
Microtox® Toxicity Analyzer system, 5-min EC_{50}; mg/L	18(10-45)

[1] Values were estimated (Hunter et al. 1985).

[2] Median toxicant concentrations and the 95% confidence limits (CL) were calculated using probit analysis.

Estimated water solubility of phthalazine was similar to the measured solubility (>5% by weight) reported for other dinitrogen derivatives of naphthalene (Patel 1973). Its vapor pressure at 25°C is 0.42 mm Hg, indicating a low tendency for atmospheric transport. The Extraction Procedure (EP) Toxicity Test (EPA 1981) showed that only 60 mg/L phthalazine could be leached from the paper.

The estimated log K_{oc} was reported as 1.58 which suggests a high mobility in the soil. However, the measured sorption constant (K_{oc}) of 1480 (log K_{oc} = 3.17) indicates a low soil mobility based on the EPA (1982) classification of the soil mobility potential of chemicals (Table 1). Low soil mobility is attributed to hydrogen bonding between the ring nitrogens and the soil colloidal matter which may hinder its mobility. Based on this study, it would appear that estimated Log K_{oc} from QSAR systems probably cannot be used to accurately predict phthalazine mobility.

The QSAR biodegradation half-life analysis, for multicyclic chemicals with at least two aromatic rings, predicts a half-life greater than 100 days (Table 1). Phthalazine was not classified as readily biodegradable in the 28-day BOD test (<10% BOD/COD) (Table 1). However, chemicals showing no evidence of ready biodegradation are not necessarily nonbiodegradable in the environment. Phthalazine gave a marginally positive result in the 28-day modified Zahn-Wellens test (>20% DOC removal) (Table 1). Phthalazine was considered inherently biodegradable, under the favorable test conditions employed.

Phthalazine was classified slightly toxic to the aquatic organisms with LC_{50} values ranging from 10 to 100 mg/L (NIOSH 1976). Its toxicity to terrestrial plants was considered moderate with phytotoxic effects at 100-1,000 mg/l (U.S. Army 1981). The observed reduction in the respiration rate of activated sewage sludge (3-hr EC_{50} = 325 mg/l), is well above any concentration expected to reach activated sludge treatment operations. Adverse effects to activated sludge systems appear unlikely.

Water is predicted to be the preferred medium for potential environmental transport of phthalazine even though release is largely to the land. However, levels of phthalazine expected in the site are low and sorption on soil will further reduce the concentration of phthalazine present in water. In light of the aqueous aerobic biodegradation results, biodegradation is likely to occur under favorable conditions in the environment.

Because of its relatively low toxicity, low bioaccumulation rate, and low potential for substantial quantities to enter the environment, phthalazine seems unlikely to pose a significant impact to the environment.

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Received June 7, 1986; accepted September 20, 1986