

IDENTIFICATION OF CARBOFURAN AND METHIOCARB AND THEIR TRANSFORMATION PRODUCTS IN ESTUARINE WATERS BY ON-LINE SOLID PHASE EXTRACTION LIQUID CHROMATOGRAPHY—MASS SPECTROMETRY

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The degradation of the carbamate insecticides carbofuran and methiocarb in distilled and natural waters was determined. Degradation studies were carried out both under a xenon arc irradiation and natural sunlight at pesticide concentrations of 50–100 µg/L. 50–100 mL water sample were preconcentrated using automated on-line solid phase extraction (SPE) followed by liquid chromatography (LC), UV detection or post column fluorescence detection (EPA method 531.1 for carbamate insecticides). Structure identification was carried out by on-line SPE-LC-MS either with thermospray and/or high flow pneumatically assisted electrospray interfaces. Half-lives varying between 4–12.5 days for carbofuran and methiocarb were determined under natural sunlight exposure, being chemical hydrolysis the major degradation pathway. When using xenon arc lamp irradiation both pesticides degraded very rapidly with half-lives varying from 0.3–1.7 hours. The various degradation products identified were: methiocarb sulfoxide, 4-methylthio-3, 5-dimethylphenol, 3-hydroxy-7-carbofuranphenol and 2-hydroxy-3-(2-methylprop-1-enyl)-phenyl-*N*-methylcarbamate.

KEY WORDS: Carbofuran, methiocarb, degradation products, photochemical degradation, solid phase extraction, liquid chromatography-mass spectrometry.

INTRODUCTION

Carbofuran (2,3-dihydro-2, 2-dimethyl-7-benzofuranyl methylcarbamate) and methiocarb (4-methylthio-3, 5-xylyl methylcarbamate) are both broad spectrum insecticides belonging to the *N*-methyl carbamate group. Carbofuran is used in rice culture, where it is applied in the form of granule¹. Carbofuran was detected in surveys of

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