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Persistence of selected pesticides and their phenolic transformation products in natural waters using off-line liquid solid extraction followed by liquid chromatographic techniques

M. Castillo[a], R. Domingues[b], M.F. Alpendurada[b], D. Barceló[b,*]

[a]*Department of Environmental Chemistry, CID-CSIC, c/ Jordi Girona 18-26, 08034 Barcelona, Spain*
[b]*Laboratory of Hydrology, Faculty of Pharmacy, University of Porto, Rua Anibal Cunha, 164, 4050 Porto, Portugal*

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Abstract

The degradation of three organophosphorus pesticides with phenolic type structure (fenitrothion, ethyl-parathion, methyl-parathion) and pentachlorophenol in natural waters from Porto (Portugal) was studied. Three different types of natural waters (river water, estuarine water and ground water) were spiked with ethyl-parathion, methyl-parathion, fenitrothion and pentachlorophenol at 40 μg/l level and were exposed outdoor to ambient sunlight and temperature in natural conditions at the Faculty of Pharmacy of Porto during a period up to 7 weeks. Water samples were placed in 1 l Pyrex flasks, properly closed. The samples were exposed day and night at these conditions during May and June 1996, the outside temperature being 22°C with 5.5 h of sunlight exposition per day on average during the period studied. In order to monitor the degradation process, 100 ml of water was preconcentrated periodically by means of liquid solid extraction (LSE) using the polymeric sorbent Lichrolut EN from Merck (Darmstadt, Germany) and the extract was determined by liquid chromatography with diode array detection (LC-DAD). The use of LC coupled with mass spectrometry detection (LC-APcI-MS) permitted the unequivocal identification of various degradation products (4-nitrophenol, 3-methyl-4-nitrophenol, paraoxon ethyl, paroxon methyl, fenitrooxon and *S*-methylisomer of fenitrothion). Half-life for methyl-parathion was of 3 days in ground water and 4 days in both estuarine and river water; half-life for ethyl-parathion was of 2 days in ground and estuarine water and 3 days in river water; values of 1 day and less than 2 h were obtained for fenitrothion and pentachlorophenol, respectively, in all types of water. All transformation products resulted to be more stable than parent compounds except in ground water conditions. Half-lives of 5 and 4 days were calculated for 4-nitrophenol and paraoxon ethyl, respectively, in estuarine and river water. Values of 3 and 4 days were obtained for 3-methyl-4-nitrophenol in estuarine and river water, respectively.

1. Introduction

Organophosphorus (OP) pesticides are widely used in agriculture for crop production and fruit tree treatment. They are replacing the persistent organochlorine pesticides because OP pesticides are less toxic and easily degradable [1]. Transformation of OP in the environment takes place by conversion of the phosphorothioate (P=S) group to their oxon (P=O) analogues. These oxo compounds are of concern because they are the activated forms of the OP pesticides with a considerably stronger inhibition of acetylcholinester-

*Corresponding author. Permanent address: Department of Environmental Chemistry, CID-CSIC, c/ Jordi Girona 18-26, 08034 Barcelona, Spain. Fax: +34 3 204 5904.

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