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Pesticide toxicity assessment using an electrochemical biosensor with *Pseudomonas putida* and a bioluminescence inhibition assay with *Vibrio fischeri*

Received: 5 December 2001 / Revised: 11 February 2002 / Accepted: 11 April 2002 / Published online: 4 July 2002
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Abstract Two different toxicity tests, an electrochemical biosensor Cellsense and a bioluminescence inhibition assay ToxAlert were performed in order to establish and compare the acute toxicity responses of different types of raw and spiked water for a selected group of pesticides. The selected compounds were endosulfan, chlorfenvinphos, dimethoate, fenamiphos, ametryn, deltamethrin and α -cypermethrin; all of them are used in large quantities for agricultural purposes. In the first step, the study of the toxicity responses for each individual pesticide with Milli-Q water was carried out. Next, the toxic responses of different mixtures of these pesticides in different water matrices, i.e., Milli-Q water, surface water, groundwater and wastewater were studied in order to evaluate (i) device advantages and limitations for the toxicity evaluation of real environmental samples, (ii) antagonistic or synergistic effects and (iii) the influence of the water matrices. The survey of pesticides in real samples was carried out using a combined method involving both chemical analysis and toxicity bioassays. Chemical analysis involved the use of solid-phase micro-extraction (SPME) followed by gas chromatography with electron capture detection (GC/ECD) or thermoionic specific detection (GC/TSD) with mass spectrometric confirmation (GC/MS).

Introduction

Tons of pesticides are produced and used every year for control of pests, and in agriculture and horticulture. Wastewater from greenhouses and runoff from agricultural land can reach and contaminate rivers, lakes and groundwater.

Pesticides and other organic pollutants have been detected in receiving bodies of water, at $\mu\text{g/L}$ levels. However, one of the limitations of chemical analysis is that when used alone, it does not provide an entire response of the effects organic pollutants may have on the environment. Therefore, its use in conjunction with techniques that can measure biological effects, such as toxicity tests, is highly recommended [1,2] in order to establish risk assessment practices. The present paper reports on a combined method using toxicity tests and chemical analysis, in order to evaluate the occurrence and aquatic toxic impact of a selected group of pesticides of different chemical families. This protocol has been applied to different types of water to evaluate the performance of both toxicological and analytical methods.

The compounds studied were organochlorine, organophosphorus, a triazine, and pyrethroid pesticides, all of them of widespread use in many countries. The pesticides fenamiphos, chlorfenvinphos and endosulfan are very toxic to mammals and are classified by the Environmental Protection Agency (EPA) as restricted use pesticides (RUP) or class I, whereas dimethoate, deltamethrin and cypermethrin are moderately toxic to mammals, i.e. EPA toxicity class II. Ametryn is an unrestricted pesticide, toxicity class III, that means slightly toxic [3]. It is relatively non-toxic to mammals and fish [4] but highly toxic to crustaceans and mollusks [5]. From the selected compounds, chlorfenvinphos and endosulfan are priority pollutants included in the new Framework Directive on Pollution of the European Union, and in 1984 endosulfan was classified as a hazardous chemical by the World Health Organization (WHO) [6]. Its use as an insecticide in a wide variety of food crops including fruits, vegetables and cereals has somewhat increased recently due to decline in the use of other insecticides such as endrin. During 1999, 85 t of this compound were applied in Portugal alone. In many countries the use of endosulfan is restricted due to acute toxicity towards aquatic animals [7] and has been replaced by organophosphorus pesticides. Among the most common ones, chlorfenvinphos and dimethoate are widely used as insecticides and acaricides whereas fenamiphos is one of

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