

## Evaluation of the Pesticide Contamination of Groundwater Sampled over Two Years from a Vulnerable Zone in Portugal

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A monitoring program of pesticides was implemented in the “ZV1” vulnerable zone (Directive 91/676/EEC) in Portugal, in order to assess the impact of intensive horticulture practices on groundwater contamination. The monitoring network comprised 23 sampling points sampled every 3 months during a 2-year period. Forty-two pesticides belonging to varied chemical families, including current pesticides, persistent organic pollutants (POPs), and degradation products, were analyzed by solid-phase microextraction (SPME) and gas chromatography with electron-capture detection-thermoionic specific detection (GC-ECD-TSD) or mass spectrometry (GC-MS). Statistical treatment was performed by descriptive analysis followed by chemometric multivariate analysis. The latter included cluster analysis, linear discriminant analysis, and factor analysis. Twenty-two pesticides were quantitated, 20 pesticides were not detected, and metalaxyl, benalaxyl, quinalphos, pirimicarb, and prometryn were only qualitatively detected. The most frequently detected pesticides (% of samples analyzed) were lindane (53%), pendimethalin (49%), endosulfan sulfate (44%), and endosulfan (38%) while those that most frequently exceeded the  $0.1 \mu\text{g L}^{-1}$  European Union (EU) limit were pendimethalin (13%), endosulfan (12%), endosulfan sulfate (11%), and atrazine (9%). 45% of the samples exceeded the EU limit for individual pesticides while 27% exceeded the limit set to the sum of pesticides ( $0.5 \mu\text{g L}^{-1}$ ). Principal component analysis revealed five principal components that were attributed to environmental/agrochemical managing factors. The broad range of pesticides investigated combined with the intensive character of the local agriculture contributed to the diversity of pesticides that were detected. However, the frequency of pesticides above the EU regulatory limit is comparable to that found in the literature concerning different Portuguese and European regions.

**KEYWORDS:** Environmental monitoring; vulnerable; groundwater; pesticides; lindane; endosulfan; pendimethalin; multivariate analysis

### 1. INTRODUCTION

Pesticide regulation falls within two approaches: exhaustive study of new candidate pesticides regulated under the European Union (EU) Directive 91/414/EEC, which advocates that pesticides shall not be found as water contaminants under normal usage practices, and monitoring studies, as a means to disclose the present contamination status and assess the impact of newly implemented measures. In Europe, monitoring groundwaters has received somewhat less attention compared to surface waters, and comprehensive monitoring surveys are urgently necessary

(1). The quality of groundwater, as far as the pesticides content is concerned, has been traditionally assessed in the European Union in respect to the 98/83/EC Directive, which establishes the quality criteria of water intended for human consumption, since this is one of the most sensitive uses of groundwater (2, 3). Recently, a specific regulation has been introduced addressing the groundwater quality (4). Besides the limit set for individual pesticides at  $0.1 \mu\text{g L}^{-1}$  ( $0.03 \mu\text{g L}^{-1}$  for cyclodienes, except endosulfan), we shall call special attention also to the limit set for the sum of pesticides ( $0.5 \mu\text{g L}^{-1}$ ) in intensively cultivated areas, because of the large number of pesticides that may coexist.

Pesticide contamination of groundwater might be anticipated when the mitigation capacity of the soil system is exceeded, especially when enhanced productivity agriculture is carried out on hydrogeologically vulnerable soils. The agriculture developed in the Mediterranean region has a strong reliance on pesticides

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