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A pesticide monitoring survey in rivers and lakes of northern Greece and its human and ecotoxicological risk assessment

Emmaluel N. Papadakis [a], Zisis Vryzas [b,*], Athena Kotopoulou [a], Katerina Kintzikoglou [a], Konstantinos C. Makris [c], Euphemia Papadopoulou-Mourkidou [a]

[a] *Aristotle University, School of Agriculture, Pesticide Science Laboratory, P.O. Box 1678, 54006 Thessaloniki, Greece*
[b] *Democritus University of Thrace, Laboratory of Agricultural Pharmacology and Ecotoxicology, 193 Pantazidou Street, 68200 Orestias, Greece*
[c] *Cyprus International Institute for Environmental and Public Health in association with Harvard School of Public Health, Cyprus University of Technology, Limassol, Cyprus*

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ABSTRACT

A pesticide monitoring study covering the main rivers and lakes of Northern Greece (Macedonia, Thrace and Thessaly) was undertaken. A total of 416 samples were collected over a 1.5-year sampling period (September 1999– February 2001) from six rivers and ten lakes. The water samples were analyzed with an off-line solid phase extraction technique coupled with a gas chromatography ion trap mass spectrometer using an analytical method for 147 pesticides and their metabolites, including organochlorines, organophosphates, triazines, chloroacetanilides, pyrethroids, carbamates, phthalimides and other pesticides (herbicides, insecticides and fungicides). Based on the pesticide survey results, a human health carcinogenic and non-carcinogenic risk assessment was conducted for adults and children. Ecotoxicological risk assessment was also conducted using default endpoint values and the risk quotient method. Results showed that the herbicides metolachlor, prometryn, alachlor and molinate, were the most frequently detected pesticides (29%, 12.5%, 12.5% and 10%, respectively). They also exhibited the highest concentration values, often exceeding 1 μg/L. Chlorpyrifos ethyl was the most frequently detected insecticide (7%). Seasonal variations in measured pesticide concentrations were observed in all rivers and lakes. The highest concentrations were recorded during May–June period, right after pesticide application. Concentrations of six pesticides were above the maximum allowable limit of 0.1 μg/L set for drinking water. Alachlor, atrazine and a-HCH showed unacceptable carcinogenic risk estimates (4.5E-06, 4.6E-06 and 1.3E-04, respectively). Annual average concentrations of chlorpyriphos ethyl (0.031 μgL), dicofol (0.01 μg/L), dieldrin (0.02 μg/L) and endosulfan a (0.065 μg/L) exceeded the EU environmental quality standards. The risk quotient estimates for the insecticides chorpyrifos ethyl, diazinon and parathion methyl and herbicide prometryn were above acceptable risk values. The coupling of monitoring data to probabilistic human and ecotoxicological risk estimates could find use by Greek regulatory authorities, proposing effective pollution management schemes.

1. Introduction

Numerous monitoring studies throughout the world have demonstrated the potential of pesticides to contaminate surface and ground waters (Readman et al., 1993; Mogensen and Spliid, 1995; Kimbrough and Litke, 1996; Kreuger, 1998; Götz et al., 1998; Clark and Goolsby, 2000; Lacorte et al., 2001; Cerejeira et al., 2003). Pesticides are primarily transported downstream from the agricultural fields to surface waters through surface runoff. The amount of applied pesticides lost from the fields and transported to surface waters depends on several factors, including soil physicochemical properties, topography, weather (especially sudden rainfall incidents), agricultural management practices and the chemical properties of each pesticide (Larson et al., 1995; Schulz, 2001). Generally, the pesticide residues that are detected in the water bodies are closely related to the agricultural practices of the nearby areas.

The European policy demands an improvement of chemical and ecological status in surface and groundwater bodies by 2015 (ECC, 2000). In addition, environmental quality standards of the priority substances (including 18 pesticides and metabolites) have been designated (ECC, 2013). Pesticides may pose risk to human health and wildlife and various approaches have been proposed for the assessment of the respective risks. The traditional assessment

* Corresponding author. Tel./fax: +30 2552041120,
E-mail address: zvryzas@agro.duth.gr (Z. Vryzas).

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method is to directly compare the actual measured concentrations with the permissible limits (e.g. 0.1 μg/L for each pesticide and 0.5 μg/L for the sum of them in each sample, established for the drinking water in Europe or the environmental quality standards proposed by the directive 2013/39/EC). The concept of toxicity-exposure ratio or risk quotient that is expressed as the ratio between the measured (instead of predicted) concentrations to predicted no-effect concentrations is widely accepted. Predicted no-effect concentrations are usually calculated on the basis of critical concentrations, e.g. EC50, LC50, and NOEC (Palma et al., 2004, 2014; Verro et al., 2009).

Although a number of studies dealt with the presence of pesticides in the rivers and lakes of Northern Greece (Golfinopoulos et al., 2003; Lekkas et al., 2003; Albanis et al., 1998; Lekkas et al., 2004; Kotrikla et al., 2006), the target list of the selected pesticides was rather small (< 40) and/or the sampling frequency was low (once per season). The aim of this study was to monitor 147 pesticides and metabolites in the major surface water bodies (6 rivers and 10 lakes) of Northern Greece. Moreover, the pesticide monitoring scheme results were incorporated into probabilistic human health and ecotoxicological risk assessment exercises.

2. Materials and methods

2.1. Survey area

The survey was conducted in the regions of Macedonia, Thrace and Thessaly, all situated in Northern Greece. These regions constitute the main cultivation areas of Greece. In Macedonia, the main crops were cereal grains, rice, corn, sugar beets and cotton, while in some areas there were also fruit tree orchards and vineyards. In the region of Thrace, the dominant crops were corn, cotton, sugarbeet and sunflower. In the region of Thessaly, the major crops were cotton, corn, grains and sugar beets (Damalas et al., 2008; Vryzas et al., 2009).

The main rivers of the aforementioned areas were selected in this monitoring study (Fig. 1): Aliakmonas (AL), Axios (AX), Loudias (LO), Nestos (NE), Pinios (PI), and Strymonas (ST). Axios river originates from FYROM, while Nestos and Strymonas rivers originate from Bulgaria. The number and geographic location of the sampling points were decided upon consideration of the total length of each river and the types of crops cultivated in each river's basin. Thus, six sampling points were selected for Aliakmonas, four for Pinios, three for Axios, Nestos and Strymonas and finally, a single point for Loudias (Fig. 1). Samples were collected 0.5 m below the water surface.

Ten lakes were also included in this monitoring study: Large Prespa (LP), Small Prespa (SP), Kastoria (KA), Vegoritida (VE), Petron (PE), Zazari (ZA), Volvi (VO), Koronia (KO), Doirani (DO) and Vistonida (VI). Four sampling sites were chosen for Vistonida and Volvi, three for Vegoritida, two for Kastoria, and one for Large Prespa, Small Prespa, Petron, Zazari, Doirani and Koronia (Fig. 1). For each sampling site, two water samples were collected, one sample being 1 m below the water surface and another sample 0,5–1 m above the bottom of the lake.

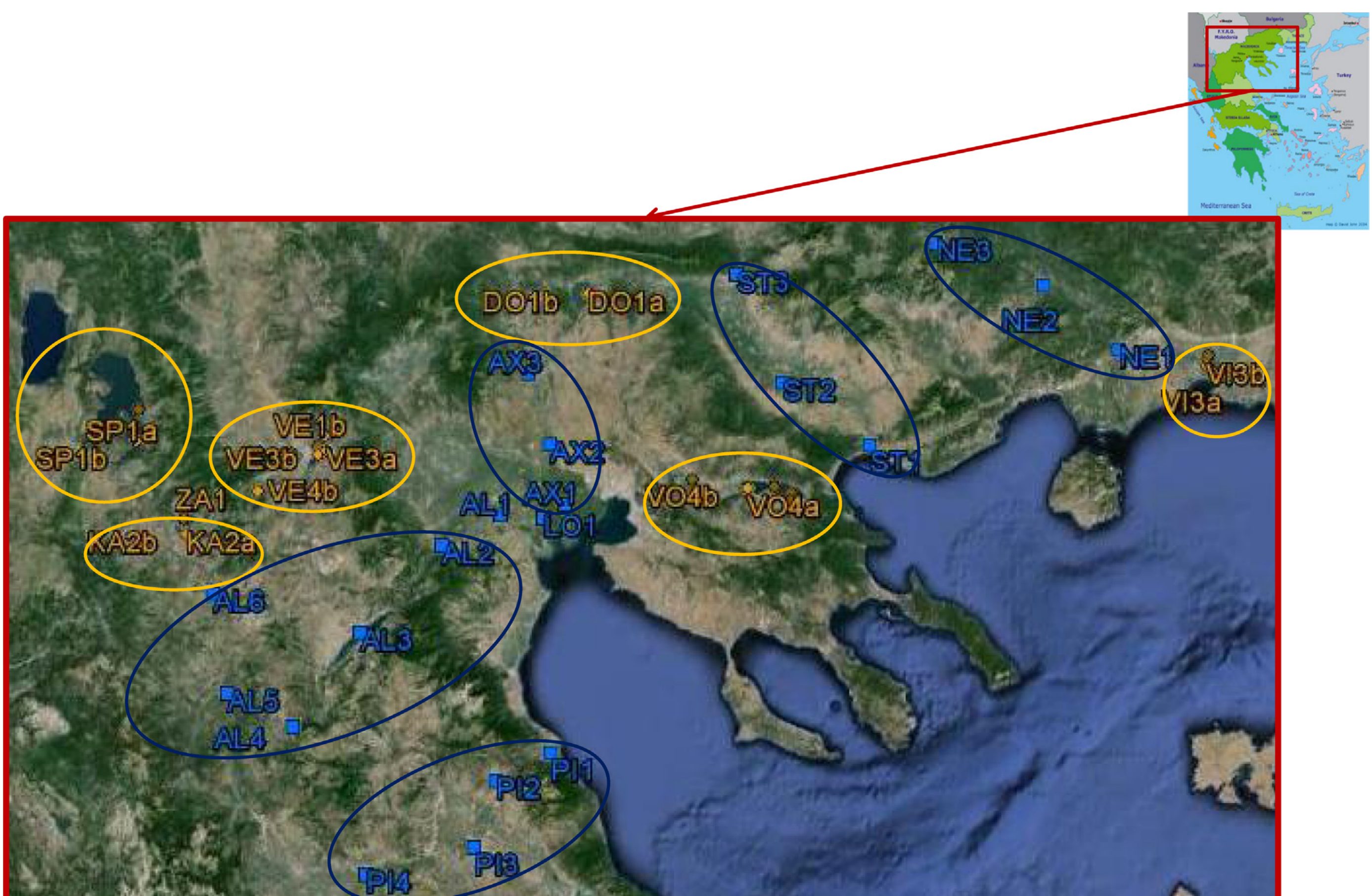

Fig. 1. River's (blue frame) and Lake's (yellow frame) sampling sites. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)