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Pesticides in the surface waters of Lake Vistonis Basin, Greece: Occurrence and environmental risk assessment

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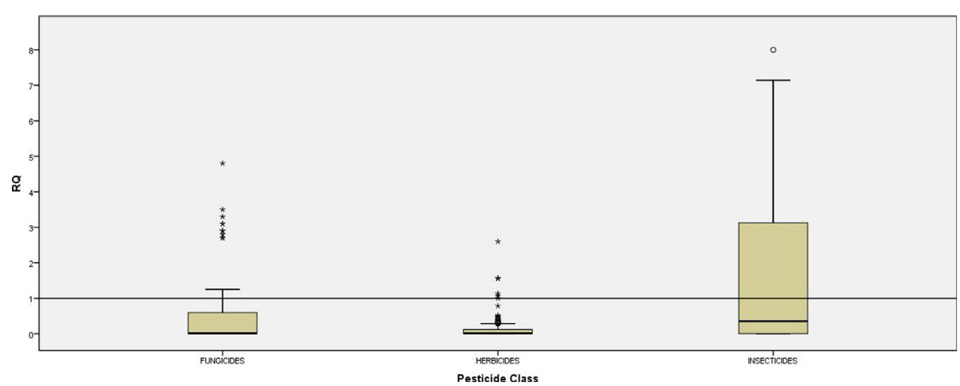
HIGHLIGHTS

- Fluometuron was the most frequently detected pesticide followed by chlorpyrifos
- Prometryn was found in drainage canals suggesting a recent use
- Lambda–cyhalothrin and alphamethrin were detected in Lake Vistonis
- Alphamethrin was responsible for the majority of the EQS exceedances
- Insecticides were often responsible for the ecotoxicological risk

GRAPHICAL ABSTRACT



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ABSTRACT

A study was undertaken for the evaluation of the pesticide pollution caused by the agricultural activities in the basin of Lake Vistonis, Greece during the years 2010–2012. Water samples were collected from Lake Vistonis, four major rivers and various small streams and agriculture drainage canals. The concentration of 302 compounds was determined after solid-phase extraction of the water samples and subsequent LC-MS/MS and GC-MS/MS analysis of the extracts. Overall, herbicides were the most frequently detected pesticides (57%), followed by insecticides (28%) and fungicides (14%). In Lake Vistonis 11 pesticides were detected. Specifically, fluometuron was detected in the 75% of the samples (maximum concentration 0.088 μg/L) whereas lambda–cyhalothrin was detected in all the samples of spring 2011 and alphamethrin in all the samples of spring 2012 (maximum concentration 0.041 and 0.168 μg/L, respectively). In the rivers and drainage canals 68 pesticides were detected. Specifically, fluometuron was detected in the 53% of the samples (maximum concentration 317.6 μg/L) followed by chlorpyrifos and prometryn (16 and 13% of the samples respectively). An environmental risk assessment was performed by employing the Risk Quotient (RQ) method. The risk assessment revealed that at least one pesticide concentration led to a RQ > 1 in 20% of the samples. In Lake Vistonis, alphamethrin and lambda–cyhalothrin concentrations resulted in RQ > 1, whereas in the other water bodies this was mainly the

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result of chlorpyrifos–methyl and alphamethrin exposure. In contrast, herbicide and fungicide concentrations contributed substantially less to environmental risks.

1. Introduction

Numerous monitoring studies throughout the world have demonstrated the potential of pesticides to contaminate surface and ground waters (Cerejeira et al., 2003; Clark and Goolsby, 2000; Götz et al., 1998; Kimbrough and Litke, 1996; Kreuger, 1998; Mogensen and Spliid, 1995). Pesticides enter the surface waters primarily via surface runoff, spay drift and drainage. The amount lost from the agriculture fields and transported to surface waters depends on several factors, including soil characteristics, topography, weather (especially heavy rainfall events), agricultural management practices and the physicochemical properties of the pesticides (Larson et al., 1995; Schulz, 2001).

Management of water resources is of great importance in the EU countries. According to the Water Framework Directive 2000/60/EC (EEC, 2000), all member countries should achieve good status of their surface waters by 2015. The good chemical status of the surface waters is assessed by taking into account the list of 33 priority compounds (including several pesticides) included in the Directive 2008/105/EC (EEC, 2008) and comparing the results of the monitoring studies with the respective Environmental Quality Standards (EQS) of those priority compounds. Directive 2013/39/EU (EEC, 2013) has recently extended the list of priority pollutants.

The ecological impact of a pesticide that is discharged in the environment depends both on the exposure level, which is usually referred to as Predicted Environmental Concentration (PEC), and the ecotoxicological effects as those are usually represented by the Predicted No Effect Concentration (PNEC) (Palma et al., 2014). The latter is derived by selecting the most sensitive biotest (representing the most sensitive trophic level) and applying an appropriated assessment factor (AF) (Backhaus and Faust, 2012). The use of the Risk Quotient (RQ) e.g. the ratio between the PEC and the NOEC (No Observed Effect Concentration) has been used for the initial (tier 1) ecotoxicological risk assessment in various water bodies (Palma et al., 2014; Thomatou et al., 2013; Vryzas et al., 2009).

Most of the monitoring studies that have been published recently deal with only a limited number of pesticides (usually <50) (Karaouzas et al., 2011; Köch-Schulmeyer et al., 2012; Masiá et al., 2013; Palma et al., 2014). Recently, Moschet et al. (2014) reported on the importance of incorporating as many pesticides as possible in the target list of any monitoring study since otherwise the risk to surface waters can substantially be underestimated, especially when pesticide mixtures are taken into consideration. Moreover, there is a need to identify river-basin specific pollutants in addition to those listed in the European Directives (EEC, 2008, 2013) so that basin managers can introduce them in the monitoring schemes (Guillén et al., 2012).

Lake Vistonis is a shallow coastal lagoon in Northeastern Greece. It is an important biotope for many bird species and fish and it is protected by the Ramsar Convention and included in the Natura 2000 Network along with adjacent lake Ismaris and several small lagoons. The lake's basin includes several small rives, lagoons and streams. Despite its ecological significance and although it is an area of intense agricultural production, very few studies have dealt with the presence of pesticides in the major water bodies of the area and their possible ecotoxicological effects (Golfinopoulos et al., 2003; Lekkas et al., 2004; Papadakis et al., 2015). Moreover, since the aforementioned studies took place more than fifteen years ago, there is a need for more up-to-date monitoring data.

The aims of the present study were to (i) monitor the concentration of 302 active substances and transformation products in the surface waters of the basin (ii) compare the concentration of the pesticides found in the present study with those detected a decade ago and with the EQS values of the pesticides included in the Directive 2008/105/EC, and (iii) perform an environmental risk assessment based on the RQ method.

2. Experimental

2.1. Reagents and chemicals

The pesticide standards that were used in the present study were of the highest available purity (>98%) and were purchased from various companies: Dr Ehrenstorfer (Augsburg, Germany), Riedel de Häen (Seelze, Germany), ChemService (West Chester, PA, USA), Neochema (Bodenheim, Germany) and Promochem (Wesel, Germany). Methanol and water of LC-MS grade and hexane for gas chromatography were purchased from Merck (Darmstadt, Germany). Ammonium acetate of mass spectrometry grade was from Sigma Aldrich (St Louis, MO, USA). Methanol and ethyl acetate (Pesticide grade) were from Chem-Lab (Zedelgem, Belgium). Lichrolut EN cartridges (200 mg) were purchased from Merck.

Individual pesticide stock solutions (1 mg/mL) were prepared in either methanol (for LC-MS/MS analysis) or ethyl acetate (for GC-MS/MS analysis) and stored in the freezer at −23 °C in aluminum/Teflon-lined capped vials. Working standard solutions containing all analytes were also prepared in either methanol (0.005, 0.01, 0.025, 0.05, 0.1 and 0.25 μg/mL) or ethyl acetate (0.1, 0.25, 0.5, 1, 1.25, 2.5 μg/mL) and stored at −23 °C.

2.2. Area of study

The present study was conducted primarily in the basin of Lake Vistonis which is situated in Thrace (Northeastern Greece, 40.97–41.12 N, 24.97–25.36E). Lake Vistonis has a surface area of approximately 45 km^2 and a catchment area of 1350 km^2. It is connected to the sea by three tidal canals (Markou et al., 2007). The adjacent lake Ismaris and the estuaries of the river Lissos were also included in the study due to their ecological significance (as already mentioned in the Section 1: Introduction). The total area of the present study was approximately 3509 km^2. The main rivers of the area are Kosynthos (52 km length; catchment area of 247 km^2), Kompsatos (68 km length; catchment area of 567 km^2) and Aspropotamos (28 km length; catchment area 158 km^2), which discharge in Lake Vistonis (Delimani and Xeidakis, 2003), and Lissos (45 km length; catchment area of 1475 km^2) which discharges in the Aegean Sea (Gikas et al., 2013). The soils of the area are classified as either Entisols or Inceptisols, and most of them (50.1%) have a high content of clay. The major crops of the area are wheat (28,000 ha), cotton (25,000 ha), corn (5200 ha), tobacco (5500 ha), fodder crops (5000 ha), oilseed crops (1150 ha) and to a lesser extent potatoes, vegetables, vines and trees (Hellenic Statistical Authority, 2015).

2.3. Monitoring network and sampling frequency

In order to assess the various sources of pesticide contamination on a basin scale a monitoring network was established (Fig. 1 and Supplementary data).

2.3.1. Lake Vistonis

Three sampling locations were selected in Lake Vistonis (VIS1, VIS2, VIS3). From each location water samples were collected from the surface of the lake and 0.5 m above the bottom of the lake. Four sampling campaigns were conducted: October 2010, May 2011, October 2011 and April 2012.