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Pesticides in the rivers and streams of two river basins in northern Greece

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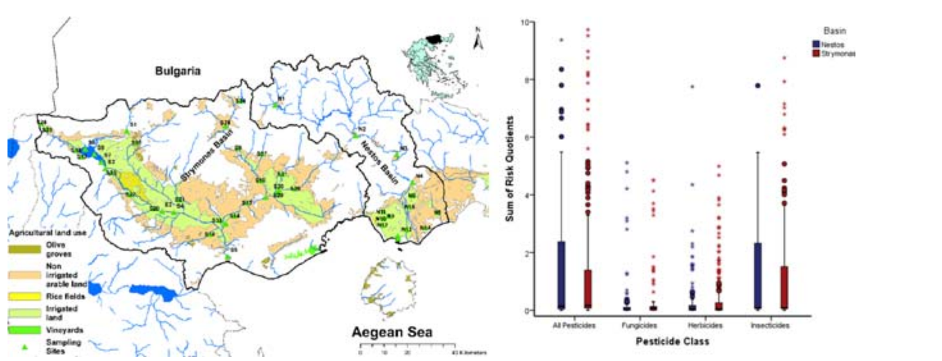
HIGHLIGHTS

- A monitoring study for 302 pesticides was conducted in two river basins.
- Chrorpyrifos was the most frequently detected pesticide in both basins.
- Alphamethrin and chlorpyrifos often exceeded Environmental Quality Standards.
- Insecticides were mostly responsible for the ecotoxicological risk.

GRAPHICAL ABSTRACT



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ABSTRACT

The pollution caused by pesticides, and their ecotoxicological implications were investigated in water samples from the Strymonas and Nestos river basins (Northern Greece). Chlorpyrifos was the most frequently detected pesticide in both basins (42 and 37% in the Strymonas and Nestos basins, respectively), followed by fluometuron and terbuthylazine (25 and 12%, Strymonas), and bentazone and boscalid (24 and 10%, Nestos). The Annual Average and the Maximum Allowable Concentration of Environmental Quality Standards set in European Union Directives were exceeded in several cases by alphamethrin and chlorpyrifos. Risk Quotient assessment revealed significant ecological risk towards the aquatic organisms in over 20% of the water samples. Insecticides (mostly pyrethroids and organophosphosphates) contributed more in the ecotoxicological risk than herbicides and fungicides. The three main rivers in the current study (Strymonas, Aggitis, Nestos) exhibited similar sum of RQs indicating that aquatic life in all three of them was at the same risk level. However, the sums of RQs were higher in the various streams monitored than the three rivers.

1. Introduction

Modern agriculture relies heavily on the use of pesticides and their use is increasing constantly. In the European Union (EU) countries only, >995,000 t of active ingredients were sold in 2014 (Eurostat, 2016). Moreover, in the EU 437 active substances belonging to the pesticide classes of insecticides, herbicides, fungicides, nematicides and acaricides are authorized for use in various crops (EU-Pesticides database,

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2017) and many more historical-use pesticides are no longer approved (EU, 2002).

Pesticides can enter surface waters after their designated application to the crops mainly via surface runoff, drainage, and spray drift (Reichenberger et al., 2007). The presence of pesticides in rivers, lakes and streams is well documented in several studies throughout the world (Ccanccapa et al., 2016a; Hapke et al., 2016; Lefrancq et al., 2017; Novic et al., 2017; Papadakis et al., 2015a) and so is the associated risk to the aquatic organisms whose habitat and communities are affected by them (Liess and Von Der Ohe, 2005; Szöcs et al., 2017; Malaj et al., 2014; Rasmussen et al., 2012).

To protect the surface- and ground-waters from further deterioration and to protect the aquatic environment, the EU has issued the Directive 2000/60/EC (European Community, 2000) prompting every member to achieve 'good ecological status' in the surface waters by 2015. Subsequently, Directive 2008/105/EC (The European Parliament and the Council of the European Union, 2008) and Directive 2013/39/EU (The European Parlament and the Council of the European Union, 2013) set Environmental Quality Standards (EQS) for priority substances and certain other pollutants (including 21 pesticides) that member states should apply to the surface waters. However, recent monitoring studies in many European countries (Cruzeiro et al., 2016a; Ccanccapa et al., 2016b; Schreiner et al., 2016) have ascertained that the risk for the aquatic environment is not only still present, but sometimes underestimated due to the inability of the current monitoring schemes to address all the challenges that need to be faced e.g. grab-samples vs passive samplers (Novic et al., 2017), event-triggered sampling vs fixed intervals (Stehle et al., 2013), number of screened pesticides (Moschet et al., 2014) and the inherent difficulties of the environmental risk assessment and the extrapolation from laboratory tests for single compounds in single species, to pesticide mixtures in actual, diverse ecosystems (Rohr et al., 2016; Van den Brink, 2013).

Strymonas and Nestos are two major transboundary rivers in Northern Greece. They originate from Bulgaria (Mount Vitosha and Mount Rila, respectively) and they both discharge in the Aegean Sea. The two basins feature several sites of great ecological significance protected by the Ramsar Convention on Wetlands (artificial lake Kerkini, Nestos Delta) and/or included in the Natura 2000 network e.g. artificial lake Kerkini, Strymonas delta, Nestos delta, Nestos gorge, are few of them (Ramsar Convention, 2017; Natura 2000 Network, 2017). The Strymonas basin is mostly a plain of intense agricultural production, whereas the Nestos basin is mostly mountainous, with agricultural production limited to the approximately 440 km^2 estuarine plain. It is therefore important to assess the impact of agricultural pesticides in the two basins on the quality of the surface waters.

Monitoring studies in the two basins have been conducted before. However, their results were from a limited number of samples and/or for a few pesticide classes (Golfinopoulos et al., 2003; Lekkas et al., 2003, 2004; Litskas et al., 2012; Papadakis et al., 2015b; Terzopoulou and Voutsa, 2016). Moreover, the focus was on Strymonas and Nestos rivers (and sometimes to the main tributaries) not considering the numerous headwater streams. The environmental quality of headwater streams can be seriously impaired by the presence of pesticides (Szöcs et al., 2017).

The aims of the present study were to (i) monitor the concentration of 302 active substances, transformation products and synthesis by-products in the surface waters (rivers and streams) of the Strymonas and Nestos basins over a two-year period, (ii) evaluate the quality of their surface waters, (iii) estimate the contribution of each pesticide (or pesticide class) to the risk towards the aquatic organisms in the two river basins.

2. Materials and methods

2.1. Reagents and chemicals

The pesticide standards were purchased from the following companies: Dr. Ehrenstorfer (Augsburg, Germany), Riedel de Häen (Seelze, Germany), ChemService (West Chester, PA, USA), Neochema (Bodenheim, Germany) and Promochem (Wesel, Germany). Hexane for gas chromatography, methanol and water of LC-MS grade were from Merck (Darmstadt, Germany). Ammonium acetate of mass spectrometry grade was purchased 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. Pesticide stock and working standard solutions were prepared and stored according to Papadakis et al. (2015a).

2.2. Area of study

The present study was conducted in the region of Macedonia, Northern Greece and specifically in the river basins of Strymonas (GR06) and Nestos (GR07) (40.52–41.31 N, 22.90–24.53E). The Greek part of the Strymonas river basin covers an area of approximately 5990 km^2 (16,747 km^2 total area in Bulgaria, Greece, FYROM and Serbia) (Doulgeris et al., 2012). The Strymonas river has a length of 390 km of which only the last 118 km are in Greece. It discharges in the Aegean Sea (Strymonikos bay). Aggitis is its main tributary and it discharges into Strymonas 18 km upstream its estuaries. Lake Kerkini is an artificial lake constructed between 1933 and 1936 for the protection against floods caused by the Strymonas river (Doulgeris et al., 2012). Nesto's springs are situated in the Rila mountain of Bulgaria. The river basin covers an area of approximately 5479 km^2 of which 2000 km^2 are situated in Greece. The river has a length of 243 km (130 km in Greece) and discharges in the Aegean Sea (Boskidis et al., 2012). The major crops in the Strymonas basin are cereals (83,777 ha), corn (36,233 ha), and cotton (18,421 ha). Other important crops include sugar beets, rice, potatoes, grapevines and tobacco. Corn (12,275 ha), cereals (3656 ha), vegetables (2100 ha) and rice (1900 ha) are mostly cultivated in the Nestos river basin.

The climate of the mountainous areas of both basins is continental with hard winters and hot summers, whereas in the plains the climate is typically Mediterranean. Mean annual precipitation for the years 2011–2012 were 469 and 546 mm for Strymonas and Nestos basins, respectively. Air temperature reached up to 39 °C during the summer months in both basins whereas the lowest temperatures recorded were −8 °C in the plains and −18 in the mountainous areas of the Strymonas basin.

2.3. Monitoring network and sampling frequency

A monitoring network covering the surface waters of both basins was established for a period of little over two years (September 2010–November 2012) (Fig. 1). The sampling sites were distributed in the river basins considering the agricultural land use (major crops in each area), year-round water flow and ease of access. Thirty-four sampling points were selected in the Strymonas basin: five sampling points (S1-S5) in Strymonas river, 3 in lake Kerkini (S6-S8), seven in Aggitis river (S9-S15), and nineteen sampling points in various streams (S16-S34). Initially, only five sampling points were selected in the Nestos river basin: four sampling points in the Nestos river (N1-N4) and one sampling point in a stream (N5). Subsequently, and due to the absence of other water bodies in the south part of the basin where the main agricultural production takes place, we included 10 riparian drainage canals (N6-N15) in the monitoring network.

Water samples were collected monthly from September 2010 to November 2012, from the Strymonas and Nestos rivers. In the Kerkini lake, water samples were collected bi-annually, starting from autumn 2010 and ending in Spring 2012. As for the Aggitis river, the tributaries and the riparian drainage canals, monthly samplings were carried out in 2011 and 2012 from May to October. Water samples were also collected in January–March-December 2011, and March–November 2012. Whenever possible, additional samples were collected from all sampling sites.