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Pesticide residue concentration in soil following conventional and Low-Input Crop Management in a Mediterranean agro-ecosystem, in Central Greece

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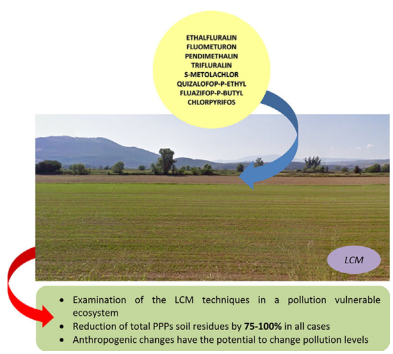
HIGHLIGHTS

- Effect of Low Input Crop Management (LCM) in a vulnerable to pollution ecosystem.
- LCM resulted in herbicide residues reduction in the range of 75 and 100% in all cases.
- Conventional practices resulted in increased herbicide residues up to 18%.
- Anthropogenic changes have the potential to change pollution levels.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study was focused on the comparative evaluation of pesticide residues, determined in soil samples from Kopaida region, Greece before and after the implementation of Low-Input Crop Management (LCM) protocols. LCM has been suggested as an environmental friendly plant protection approach to be applied on crops growing in vulnerable to pollution ecosystems, with special focus on the site specific problems. In the case of the specific pilot area, the vulnerability was mainly related to the pollution of water bodies from agrochemicals attributed to diffuse pollution primarily from herbicides and secondarily from insecticides. A total of sixty-six soil samples, were collected and analyzed during a three-year monitoring study and the results of the determined pesticide residues were considered for the impact evaluation of applied plant protection methodology.

The LCM was developed and applied in the main crops growing in the pilot area i.e. cotton, maize and industrial tomato. Herbicides active ingredients such as ethalfluralin, trifluralin, pendimethalin, S-metolachlor and fluometuron were detected in most samples at various concentrations. Ethalfluralin, which was the active ingredient present in the majority of the samples ranged from 0.01 $\mu g\ g^{-1}$ to 0.26 $\mu g\ g^{-1}$ soil dry weight. However, the amount of herbicides measured after the implementation of LCM for two cropping periods, was reduced by more than 75% in all cases.

The method of analysis was based on the simultaneous extraction of the target compounds by mechanical shaking, followed by liquid chromatography mass spectrometric and gas chromatography electron capture (LC–MS/MS and GC–ECD) analysis.

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1. Introduction

The distinctive feature of pesticides is their widespread application on soil or over field crops and hence their deliberate release in the environment (Vega et al., 2005; Goncalves et al., 2006). Furthermore, the potential environmental contamination from pesticides is raising concerns for the public and regulatory bodies (Liu et al., 2010) since it may constitute one of the most hazardous groups of contaminants to human health, fauna and the environment in general (Vega et al., 2005). The lessons learned from the widespread contamination of the aquatic and soil ecosystems have forced the adoption of restrictive legislative measures to protect the environment against pollution (Vega et al., 2005). As a result of the increasing public awareness, soil quality has become a key issue in political agendas (Louis et al., 2014; EEC, 2002, 2006). Soil contamination by pesticides is addressed within the European Union in the context of the recently adopted Regulation 1107/2009/EC (EEC, 2009) as well as in the former Directive 91/414/EEC (EEC, 1991), which regulates the authorization of pesticide placement on the market. Furthermore, the European Commission has published a guidance document to regulatory authorities in Member States and to the industry on how to evaluate the environmental fate and behavior of pesticides for the decision making process (EEC, 2000).

In addition to the above legislative framework for the control of pesticide properties, the use of pesticides and field practices to be followed are addressed by the Sustainable Use Directive (128/2009/EC) (EEC, 2009) where the application of Integrated Pest Management (IPM) as well as the use of low input or pesticide-free crop farming is among the priorities. In the reformed Common Agricultural Policy among the new legal proposals is “greening” and its link to direct payment. To strengthen the environmental sustainability of agriculture and enhance the efforts of farmers, the Commission is proposing to spend 30% of direct payments specifically for the improved use of natural resources and preservation of environmental reservoirs such as soil (www.EC.europa.eu/agriculture).

Soil is the main and first recipient of the applied pesticides, thus representing a source from which residues can be released to the atmosphere, surface and ground water as well as to living organisms (Goncalves and Alpendurada, 2005; Xia and Leidy, 2002). Soil is a complex and dynamic living system that occupies much of the earth's surface and it is composed of organic matter, minerals and organisms (Vig et al., 2008). Soil characteristics vary continuously in terms of climate, parent materials, living organisms and management that are provided to the crops.

The behavior of pesticides in soil is governed by a variety of complex physical, chemical and dynamic biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, run-off and leaching. These processes directly control the transport of pesticides within the soil and their transfer from the soil to water, air and food. The relative importance of these processes varies with the chemical nature of the pesticides and the properties of the soil, but two processes stand out: degradation and sorption (Arias-Estevez et al., 2008). Pesticides with low water solubility and moderate to high hydrophobicity used to be strongly absorbed to soil particles (Liu et al., 2010).

Soil must be considered as relatively static and of limited human control, hence the application of precautionary measures has higher potential benefits compared to costly remediation acts (Goncalves et al., 2006). The European Commission (EC) realizes that preservation of soil quality is crucial for long term sustainability. In this regard, stronger emphasis should be given to research, among which monitoring has a key role, in order to provide both an information basis and impact assessment of the implemented measures (Goncalves et al., 2006; Papamichail et al., 2002).

The present study was focused in one of the most intensively cultivated areas in Greece, surrounded by a complex aquatic system, in Kopaida region, seventy kilometers north-west from the capital of Greece, producing a variety of crops. However in the pilot project carried out in the area three crops were considered, namely, cotton, maize and industrial tomato. A three-year monitoring work was carried out intended to assess the pollution levels by pesticides and to apply specifically-designed farming practices in order to protect this vulnerable ecosystem.

Cotton (*Gossypium hirsutum L.*) cultivation constitutes one of the most dominant crops grown in Kopaida plain as well as in the project pilot area. The crop protection needs of the cotton grown in the specific area are primarily related to the control of perennial weed nutsedge grass (*Cyperus rotundus*) which is extremely widespread in the area and secondly to the entomological problems such as the cotton bollworm (*Helicoverpa armigera*). For the control of the abovementioned problems, pesticide usage is a significant and integral component in Greek cotton production crops (Papamichail et al., 2002).

Soil is plowed in autumn and left during winter to crumble. In January and February, a cultivator is used to break large clods and control weeds. Seedbed preparation is completed by the end of March and cotton is usually sown in April (Stathakos et al., 2006). Cotton growth is significantly affected by weed competition. Yields reduction depends on weed species, density and distribution, as well as on the soil's properties (Stathakos et al., 2006). Herbicides have become an important tool for crop protection and are often applied several times during one cropping season (Vig et al., 2008). Their use cannot be neglected due to the enormous benefits in agricultural outputs. On the other hand, it has been reported that herbicides are lost from agricultural fields and aquatic sediments to surface-and groundwater by run-off and leaching (Sun et al., 2012; Konstantinou et al., 2006). Herbicides run-off and leaching are recognized as serious environmental problems and a primary source for surface and groundwater pollution (Carter, 2000). Thus, the monitoring of herbicide residues especially in agricultural ecosystems where their use is intensive is of crucial importance for the evaluation of health status of the environment.

In that case, the chemical analysis of soil samples for the determination of the background concentration levels of herbicides in soil before the implementation of LCM was of highly importance. For this purpose, a multi-residue method was fully validated and applied to the collected samples. The complexity of soil matrices and the wide range of physicochemical properties of the pesticides of interest in combination with the potentially low amounts of pesticide residues and/or metabolites present in the soil make the sample preparation for the extraction of the potential pollutants one of the most critical steps of the analytical procedure (Diez et al., 2006; Schreck et al., 2008).

For the identification and quantification of the pollutants in the soil extracts, GC–MS/MS and LC–MS/MS are the most frequently used instrumentation (Pose-Juan et al., 2014). The use of GC–MS/MS and LC–MS/MS is, at present, the most versatile and sensitive method for pesticide residue analysis due to the high sensitivity and selectivity, especially when used in the single ion monitoring (SIM) mode (Vega et al., 2005; Tadeo et al., 2000). For pesticides belonging to the same chemical group, multi-residue methods can be applied (Kremer et al., 2004).

The aim of the present study was to monitor quantitatively and qualitatively the pesticide residues in soil from three different crops crowing in the pilot area of Kopaida plain which is considered to be of high vulnerability to pollution. Furthermore the study aims at the identification of potential environmental improvement especially in soil quality following the implementation of the LCM protocols in cotton crops of the pilot area during two cropping periods. The priority pesticide active ingredients, as it results from the record keeping, consist of herbicides and insecticides. Significant increase in the chlorpyrifos containing insecticides use has been reported in years 2010 and 2011 due to the outbreak of cotton bollworm (*H. armigera*).