Science of the Total Environment 461–462 (2013) 282–289

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Pollution of surface waters by metalaxyl and nitrate from non-point sources

Alipio Bermúdez-Couso [a], David Fernández-Calviño [a], Manuel Ali Álvarez-Enjo [b], Jesús Simal-Gándara [c], Juan Carlos Nóvoa-Muñoz [a], Manuel Arias-Estévez [a,]*

[a] Soil and Agricultural Science Group, Plant Biology and Soil Science Department, Science Faculty, University of Vigo, Ourense Campus, 32004 Ourense, Spain
[b] Hydraulic Engineering Group, School of Civil Engineering, Canals and Ports, University of A Coruña, Elviña Campus, 15701 A Coruña, Spain
[c] Nutrition and Bromatology Group, Analytical and Food Chemistry Department, Science Faculty, University of Vigo, Ourense Campus, 32004 Ourense, Spain

HIGHLIGHTS

- Metalaxyl and nitrates showed as a high temporal and spatial variability in surface waters.
- Metalaxyl concentration is high in spring–summer seasons.
- Interaction between seasons and sampling explain the variability of nitrates and metalaxyl concentrations in waters.

ARTICLE INFO

Article history:
Received 28 December 2012
Received in revised form 8 May 2013
Accepted 9 May 2013
Available online 2 June 2013

Editor: Eddy Y. Zeng

Keywords:
Metalaxyl
Nitrate
Surface waters
Pollution
Non-point sources

ABSTRACT

The mobility of contaminants in soil is highly dependent upon the characteristics of the contaminant chemical and the properties of the soil. In order to explore these relationships, the district of A Limia (Galicia, NW Spain) was selected as the study area—a cropland devoted to growing potatoes, where the soil had been managed intensively over the last 50 years. The soil was characterised by low slopes with the water table located very close to the soil surface. Our aim was to study the influence of high and intensive crop production on the water bodies and non-point source contamination, with a particular focus on metalaxyl and nitrate. The highest concentrations of metalaxyl occurred when rainfalls were low and in zones of the study area where natural hydrology was significantly altered by numerous drainage canals. The spatial and temporal distributions of the nitrate also showed a high variability, with the interaction between seasons and sampling area being the most significant factor in explaining the levels found.

1. Introduction

The increase in pesticide application to agricultural lands during the last several decades has resulted in potential hazards to human health and the environment (Wyckhuys et al., 2013). The likelihood of contamination of surface waters depends on the crop type, the soil properties, the characteristics of the water bodies (depth and flow rate), the characteristics of the land close to the water bodies (soil use, slope, and distance from water bodies) and the climatic conditions (temperature, rainfall, moisture and wind) (Capel et al., 2001; Kreuger, 1998; Neumann et al., 2002; Ramos et al., 2000). The mobility of the pesticide in the soil is dependent on physical, chemical and biological processes, including adsorption–desorption, volatilisation, chemical and physical degradation, absorption by plants, runoff and leaching (Arias-Estévez et al., 2008; Vryzas et al., 2007). All of these processes are highly dependent on the chemical characteristics of the pesticide and the properties of the soil (Linn et al., 1993).

On land devoted to a potato crop, the use of inorganic (NPK) and organic fertilisers is very high. Due to the high irrigation rates of this crop, the pollutants present in the soils devoted to potatoes could be transported to the water bodies by drainage, runoff or spray drift (Bach et al., 2001). In areas with very low slopes, the movement of the pollutants in the soil is due mainly to drainage through the soil. Areas with intensive agriculture represent an important source of non-point pollution, in many cases due to a large nitrate concentration in the water bodies (Burkart and Feher, 1996; Núñez-Delgado et al., 1995). In areas with high relative moisture in the air and with the water table close to the soil surface, the use of large amounts of fungicides is necessary to avoid losses in crop yield.

The district of A Limia (Galicia, Northwest Spain) is a watershed where the soil has been intensively managed over the last 50 years. The cropland devoted to potatoes is found on low slopes, with the water table located very close to the soil surface. Therefore, this

* Corresponding author. Tel.: +34 988368899; fax: +34 988387001.
E-mail address: mastevez@uvigo.es (M. Arias-Estévez).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.05.023

area has a significant risk of environmental pollution that could cause problems to human health. High nitrate concentrations in water bodies can result from organic and inorganic fertilisation of agricultural lands; nitrate is quite mobile in agricultural soils because the biding capacity of nitrate to soil is very low. However, the pesticides used for the protection of crop yields can also reach water bodies. With respect to human health, The European Union Council Directive 98/83/CE on water for human use establishes a maximum limit of 50 mg L^{-1} for NO_3^-, of 0.1 μg L^{-1} for individual pesticides and 0.5 μg L^{-1} for the sum of all pesticides. Furthermore, the directives 2006/118/CE on the protection of groundwater against pollution and deterioration, and the directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources, confirm these limits.

The final goal of the E.U. Water Framework Directive 2000/60/EC is the protection of their surface water and groundwater and the conservation of habitats and species directly depending on water. To this, the knowledge of surface water chemical status and the identification of the main environmental pressures are the necessary tools for the application of measures to decrease pollution of surface waters.

In a previous study performed with metalaxyl, carbofuran, fenamiphos, metribuzin, deltametrin and folpet on experimental plots located in the same area, metalaxyl was the only pesticide detected in potatoes (peel, outer region, and core, between 15 and 22 μg kg^{-1}) and in water used for irrigation (between 22 and 33 μg L^{-1}) (López-Pérez et al., 2006) because of its high mobility. The high nitrate concentration in water bodies is typical in agricultural areas due to the high mobility of nitrate in the soil (López-Periago et al., 2002; Núñez-Delgado et al., 1997, 2002). Sustainable management of water resources requires improved understanding of pesticide management; however, pesticide monitoring programmes in rivers are limiting in spatial scope and tend to be limited to a few watersheds. The aim of this work was to study the influence of highly intensive crop production on the non-point source contamination of the water bodies, with a particular focus on metalaxyl and nitrate.

2. Experimental

2.1. Study area

The study area is located in a region called A Limia (Ourense, NW Spain; Fig. 1). Geologically, the region is dominated by an old tertiary depression (630 m above sea level) which was intermittently filled with quaternary sediments reaching a thickness up to 200 m (IGME, 1974). The sediments that filled the depression were eroded from its borders where several types of granite, schist and gneiss were the most abundant rocks. With time, the progressive infilling caused the depression to evolve towards a semi-endorreic system crossed in an E–SW orientation by the River Limia, the primary outflow point of the area that flows into the Atlantic Ocean. The River Limia shows the highest annual flow peaks in January, February, May, August and September (Gómez-Nieto, 1996). As result of the interaction between geology, geomorphology and climatology through the years, the study area has become a flat (slope <3%) and the origin of one of Spain's largest natural ponds. This wetland, called Lagoa de Antela, has an extent of 4200 ha and a water depth between 60 and 300 cm.

Today, the climatology of the study area is dominated by an Atlantic influence, although some features of the Mediterranean climate, such as continentality and severe droughts during summer, are also present. Mean annual temperature is 11 °C (5.1 °C in January and 18.4 °C in July), with total annual precipitation at 881 mm on average, irregularly distributed through the year (120 mm in January and 20 mm in July and August). The total annual rainfall in the three-year study was 639, 816 and 575 mm in the years 2009, 2010 and 2011, respectively. The soils of the area developed from sediments, showing surface horizons with coarse texture while a clay layer appears at a variable depth. Soils are generally acid (porewater pH < 6.0), even those dedicated to agriculture, rich in organic matter in those areas where hydromorphic conditions are still present but relatively poor in well drained areas (approximately 30 g kg^{-1}). The most characteristic soil types are Leptosols, Umbrisols, Camisols, Gleysols and Histosols (FAO, 1998).

From the hydrogeological point of view, the study area is characterised by two aquifers separated by clay-lignite layers. The upper section of the aquifer has a water sheet of around 100 m, a volume of renewable water of 90 hm^3 $year^{-1}$ and a transmissivity of 400–1000 m^2 day^{-1}; whereas the lower section of the aquifer reaches a water sheet of up to 130 m.

2.2. Land use

In the middle of the 20th century, a serious change in the land use took place due to agricultural intensification of the study area. A large effort of artificial drainage of the pond began with the construction of an elaborate system of ditches, secondary and main drainage canals which, in turn, flows to the River Limia. Consequently, 3243 ha of the former pond was drained and dedicated to cultivation of cereals and potato crops, primarily the latter because of the economic importance of this crop. In the study area, potato, grown in rotation with wheat, extends through 3804 ha showing a crop yield of 30 Mg ha^{-1} (IGE, 2012) that produces 90,000 Mg of potatoes annually (Fig. 1).

For the potato crops, the primary agricultural concerns in the study area are the soil water availability, fertiliser management and the effects of plant diseases. The water requirement of the potato crop and the summer droughts led to the construction of locks on the main drainage canal to maintain the water level, using the accumulated water to irrigate the crops. Consequently, the water table rose, and extensive areas were flooded during rainy periods. Because the potato crop demands a large amount of nutrients, organic (mainly chicken manure) and inorganic fertilisers (100–200 kg N ha^{-1}; 100–200 kg P_2O_5 ha^{-1}; 100–150 kg K_2O ha^{-1}) were used as pre-planting fertilisation (López-Mateo, 2007). Depending on climatic conditions, potato planting takes place between March and May, and the application of fungicides (mainly metalaxyl) begins as the potato plant begins its growing period up to 21 days before the harvest. Metalaxyl is sprayed above the plant, and the number of treatments depends on climatic conditions during the growing season. The content of metalaxyl in commercial fungicides ranges between 5 and 25%, whereas the treatment dose varies from 0.50 to 0.08% (5–0.8 kg ha^{-1}, respectively). Fig. 2 shows the planting, fertilisation and metalaxyl application to the potato crop.

2.3. Water sampling and flow measurement

Water samples were collected from the waters in HCl-pre-washed glass bottles (2.5 L volume) using a telescopic water sampler. In each sampling location, 500 mL of water were collected for an additional wash of sampling bottles, and then discarded. This procedure was made twice. Thus the bottle is now ready for the collection of the definitive water sample. The strategy of water sampling was focused in those areas that showed the highest agricultural activity, extended over a total 38 km of waterways that included the main drainage canal (also the secondary arm of the main drainage canal) and the River Limia (Fig. 1). Twenty-two sampling location (Table 1) were selected with 16 in the main drainage canals and 6 in the River Limia. Water samples were collected monthly for two years, from March 2009 to March 2011. Water samples were stored at 4 °C (≤24 h) pending analysis for metalaxyl and nitrate.

The water flow in the main drainage canal was monitored through the sampling period after measuring the water height in a Parshall flume located at the beginning of the main drainage canal (sampling location 2) that showed a 152 cm wide throat section (Wanielista et al., 1997). The relationship between precipitation and flow is