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Pesticide monitoring and ecotoxicological risk assessment in surface water bodies and sediments of a tropical agro-ecosystem☆

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ABSTRACT

A pesticide monitoring study including 80 and 60 active ingredients (in surface waters and sediments, respectively) was carried out in a river basin in Costa Rica during 2007–2012. A special emphasis was given on the exceptional ecological conditions of the tropical agro-ecosystem and the pesticide application strategies in order to establish a reliable monitoring network. A total of 135 water samples and 129 sediment samples were collected and analyzed. Long-term aquatic ecotoxicological risk assessment based on risk quotient in three trophic levels was conducted. Short-term risk assessment was used to calculate the toxic unit and prioritization of sampling sites was conducted by the sum of toxic units in both aquatic and sediment compartments. Dimethoate (61.2 μg/L), propanil (30.6 μg/L), diuron (22.8 μg/L) and terbutryn (4.8 μg/L) were detected at the highest concentrations in water samples. Carbendazim and endosulfan were the most frequently detected pesticides in water and sediment samples, respectively. Triazophos (491 μg/kg), cypermethrin (71.5 μg/kg), permethrin (47.8 μg/kg), terbutryn (38.7 μg/kg), chlorpyrifos (18.2 μg/kg) and diuron (11.75 μg/kg) were detected at the highest concentrations in sediment samples. The pesticides carbendazim, diuron, endosulfan, epoxyconazole, propanil, triazophos and terbutryn showed non-acceptable risk even when a conservative scenario was considered. Sum TU_{site} higher than 1 was found for one and two sampling sites in water and sediment compartments, respectively, suggesting high acute toxicity for the ecosystem.
Main finding of the work: Exceptional ecological conditions of the tropical agro-ecosystem affect the fate of pesticides in water and sediment environment differently than the temperate one.

1. Introduction

The agricultural sector represents one of the main economic activities in Costa Rica. By the year 2014 it represented 8.6% of the GDP (together with forestry and fisheries) (SEPSA, 2015) and agricultural products accounted for 23.3% of all the country exportations (Alonso and Jiménez, 2015). The intensive agricultural activities combined with excessive use of pesticides has significantly impacted the surface water bodies and sediments through run-off, leaching, and spray drift (Dalton et al., 2014; McKnight et al., 2015). Factors such as land use and pesticide application pattern, rainfall intensity and irrigation strategy, soil type, landscape and field slope, pesticide mobility, adsorption, absorption, solubility and Log K_{ow}, physical, chemical and biological processes are crucial for the environmental fate and persistence of pesticides in surface water bodies, their accumulation in sediments and bioaccumulation, and impact in water and sediment-related biota (Sabatier et al., 2014).

According to the Phytosanitary Protection Law N° 7664 of Costa Rica, the management and registration process of pesticides used in agricultural crops is responsibility of the Phytosanitary Service, affiliated to the Ministry of Agriculture and Livestock (SFE-MAG) (La

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Gaceta Official Newspaper, 1997). The Regulation 33495 "Registration, use and control of formulated synthetic pesticides, active ingredient technical grade, and related substances for agricultural use", establishes the requirements for the registration of the agricultural synthetic products (La Gaceta Official Newspaper, 2007a). The distribution of pesticides at national level comprises three main sectors: importation, local formulation and exportation. Between 2008 and 2012, 8019.9 ton a.i. (average) of pesticide formulations were imported and 4807.6 ton a.i. (average) were formulated in Costa Rica. However, the total of the above amount was not used in the country, as 2173.7 ton a.i. (average) was exported, with a total of 10653.8 ton a.i. (average) of pesticide formulations kept to be used in the country per year. Overall, the official annual average application of pesticides in the country is 14.7 kg a.i./ha (SFE, 2017).

Management of pesticide residues in water bodies in Costa Rica is established by three main regulations: Decree N° 33903-MINAE-S (surface waters) (La Gaceta Official Newspaper, 2007b), Decree N° 33601-MINAE-S (residual waters) (La Gaceta Official Newspaper, 2007c), and Decree N° 38924-S (drinking waters) (La Gaceta Official Newspaper, 2015). Maximum permissible levels of individual pesticides in water samples were established in the last version of the regulation only for drinking waters dating from year 2015; previously, these regulations referred only to the control of the total concentrations of organochlorine, organophosphate and carbamate pesticides for surface waters. In addition, there is not legislation for the maximum residue levels of pesticides in soils and sediments.

Several monitoring studies on surface water and sediments have been conducted in Costa Rica, focused in the agricultural areas of the Caribbean lowlands and coast (Castillo et al., 2000; Echeverría-Sáenz et al., 2012; REPCar, 2011); nonetheless, some reports describe the presence of pesticides in environmental samples and biota from other regions such as the northwestern, central and Pacific areas (Daly et al., 2007; Rainwater et al., 2007; Rizo-Patrón and Trama, 2008; Standley and Sweeney, 1995; Rasmussen et al., 2016). Reports in the rest of Central America are scarce, and include pesticide monitoring in surface and ground water in Guatemala (Knedel et al., 1999), coastal lagoons (Carvalho et al., 1999) and lakes (Calero et al., 1992) in Nicaragua, and water, sediments and agricultural production systems in Honduras (Kammerbauer and Moncada, 1998; Meyer, 1999).

The Tempisque river basin comprises the largest basin in Costa Rica, where La Mula micro-catchment is located. It contains the protected wetlands of Palo Verde National Park, included in the List of Wetlands of International Importance according to the Ramsar Convention since 1991 (Rizo-Patrón and Trama, 2008). At La Mula micro-catchment an important part of the land is employed for the production of rice and sugar cane. These crops do not represent the highest exportation products in Costa Rica, nonetheless they constitute productive sectors with a high level of support to other economic sectors (Jiménez and Alonso, 2016). The impact of these productive activities on surrounding environments has been seldom described and represents a critical concern in a country highly devoted to environmental conservation.

Due to the threat risk that pesticides pose on the ecosystems, there is an urgent need to intensify the environmental monitoring data and ecotoxicological risk assessment. Moreover, the tropical conditions and the exceptional biodiversity found in Costa Rica impose the need for ecosystem protective actions. Most post registration pesticide risk assessment studies are conducted on water samples through toxic unit (TU) and risk quotient (RQ) approaches (Ginebreda et al., 2014; Kuzmanovic et al., 2016; Papadakis et al., 2015; Tsaboula et al., 2016). However, higher pesticide concentrations can be found on sediments acting as reservoirs of xenobiotics within the aquatic environment (Masiá et al., 2013). Thus, pesticide risk assessment on sediments should be conducted complementary to the one performed on water samples (Ccanccapa et al., 2016; EU, 2013; De Castro-Català et al., 2016; Roig et al., 2015).

The aims of this study were to (i) monitor the concentration of up to 80 and 60 selected pesticides in surface waters and sediments, respectively, at different sites of La Mula micro-catchment, Costa Rica (6-year monitoring data); (ii) correlate the pesticides found with the agricultural-environmental-physicochemical factors affecting the fate of pesticides; (iii) compare the findings of the present study with previously published data in similar exceptional ecological conditions; (iv) perform an aquatic ecotoxicological risk assessment in three trophic levels (algae, daphnid and fish) based on the RQ and TU method; and (v) extrapolate the concentrations found in sediments to pore water and conduct an ecotoxicological risk assessment.

2. Materials and methods

2.1. Area of study

La Mula creek micro-catchment is located in the department of Bagaces, Guanacaste province, Costa Rica (10°30′36.91″N, 85°18′11.77″W), within the Tempisque river basin, the largest basin in Costa Rica (Fig. 1). The total cultivated area of the rice and sugar cane crops in the department of Bagaces was 6563 ha in 2008 (SEPSA, 2010) and 4267 ha in 2008 (Chaves-Solera and Chavarría-Soto, 2013), respectively. La Mula micro-catchment comprises a total area of 4700 ha, mostly used for agricultural activities; in 2010 the area contained approximately 2400 ha cultivated with rice and sugar cane crops, 720 ha dedicated to cattle raising, 1550 ha covered by forest and 30 ha employed in aquaculture. The micro-catchment is located near the wetlands of Palo Verde National Park, and covers an area of transition of humid tropical forest to tropical dry forest according to the Holdridge life zone system (Holdridge, 1967). Even though Costa Rica is located in the tropical region, and counts with two well defined seasons (dry and rainy), due to the irregular topography the country is divided in three different weather regions. La Mula micro-catchment belongs to the Pacific Tropical Region with an average annual rainfall of 1800 mm distributed in 97 rainy days, with an average temperature of 28 °C (22 °C min – 33 °C max); however, in other areas in the country the average rainfall could be more than 4000 mm (Solano and Villalobos, 2001). The information concerning the monthly and annual precipitation and monthly maximum and minimum temperatures in the area are shown in Fig. S1 (Supplementary Material).

Before 2003 the area was mostly devoted to the cultivation of rice; however, due to the increase in sugar cane prices and lower rice prices, the area shifted to sugar cane production during the period 2003–2008. Problems in sugar cane production plus a recovery in the prices of rice, resulted in a return to rice production as the main crop in the area since 2009. All these changes in the profile of agricultural production were coincident with differential pesticide use patterns. Table S1 shows the registered pesticides for both rice and sugar cane crops in Costa Rica during the period of study; Table S2 and Table S3 present the available information on the rice and sugar cane cultivated area, nominal application rates of the detected pesticides and unauthorized pesticides in Bagaces, Costa Rica.

2.2. Monitoring network and sampling

Monitoring campaigns were performed from 2007 to 2012, in order to evaluate the pesticide concentrations on surface waters