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Pesticide impact study in the peri-urban horticultural area of Gran La Plata, Argentina

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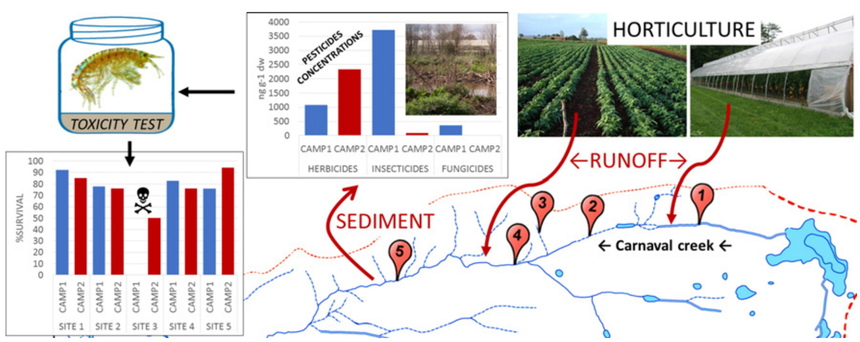
HIGHLIGHTS

- Herbicides and insecticides were detected in all the bottom-sediment samples analyzed.
- Glyphosate was detected in a watercourse near a horticultural production area.
- Lethal and sublethal effects were observed in bioassays using *Hyalella curvispina*.
- The observed toxicity was associated mainly with insecticides.
- Pesticides from horticultural production impact aquatic environments.

GRAPHICAL ABSTRACT



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ABSTRACT

Vegetable production systems are characterized by intense pesticide use, yet the effects on the surrounding environment are largely unknown and need to be studied. Given this knowledge gap, the objective of this work is to determine the impact of horticulture on a representative watercourse by conducting an integrated study of the occurrence and concentration of pesticides in bottom sediments and their relation to lethal and sublethal effects on benthic fauna. Two sampling campaigns were conducted during seasons of low and high pesticide application in five sites along the Carnaval creek, located in the peri-urban area of La Plata City (Buenos Aires, Argentina). The samples were tested for 36 pesticide compounds by GC–MS and LC-MS, and whole-sediment laboratory toxicity tests were performed using the native amphipod *Hyalella curvispina*. The results showed a general but variable distribution in the concentrations detected along the stream. For each sampling campaign (first/second), the total pesticide loads, measured as the sum of herbicides, insecticides and fungicides, were 1080/2329, 3715/88, and 367/5 ng g^{-1} dw, respectively. Lethal and sublethal effects were observed in both sampling campaigns. In order to correlate both sets of results, data were assessed by multivariate analysis, including principal component analysis. The observed toxicity was considered to be mainly due to insecticides; thus, horticultural practices have an impact on nearby watercourses and can potentially endanger the benthic fauna. This is the first study in Argentina to assess the impact of pesticides on aquatic environments close to horticultural production areas.

1. Introduction

The extensive monoculture of grains and oilseeds (maize, wheat, and soybeans) is the main agricultural activity in Argentina

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(Leguizamón, 2013). As a consequence, the number of pests attacking those crops is limited and the compounds used to control them are few (mainly glyphosate, chlorpyriphos, and cypermethrin). In contrast, horticultural production is significantly more diverse in terms of both plant species and associated pests. Production units are often small and heavily cultivated, requiring a wider range of pesticides (DP, 2015). In the Argentine pesticide market, herbicides (glyphosate, 2,4-D, atrazine) account for 86.8% of total sales, while insecticides (cypermethrin, chlorpyriphos, lambda-cyhalothrin) account for 6.2%, and fungicides (epoxiconazole, tebuconazole, metconazole) account for only 2.7% (PwC, 2014). Although this represents the sum of pesticides in extensive agriculture and horticulture, the most used insecticides and fungicides are the same for both agricultural activities, and they are being more heavily used in horticulture than herbicides (DP, 2015).

In the last 20 years, the horticultural belt in the outskirts of La Plata, Buenos Aires, Argentina (Cinturón Hortícola Platense, CHP), has grown in terms of size and productivity as well as in importance in the country. The last official census shows the CHP comprises 2880 ha of vegetable production, out of which 65.6% are open fields and 34.4% are under cover (CHBA, 2006). One of the factors that has facilitated and even boosted this expansion has been the early, committed and ongoing adoption of pesticide-intensive greenhouse technology. According to a recent government report (DP, 2015), up to 168 pesticide active ingredients are applied in the CHP.

As a consequence of this kind of pesticide-intensive horticultural activity, in several regions of the world, pesticide residues can be found both in food produce (Donkor et al., 2015) and in the environment surrounding horticultural production areas (Thoma and Nicholson, 1989; Rosendahl et al., 2009; Kreuger et al., 2010; Roseth and Haarstad, 2010).

Runoff is one of the main sources of diffuse pesticide pollution in surface water bodies (Jergentz et al., 2005). This process can mobilize pesticides in the soluble phase as well as pesticides sorbed onto suspended particulate matter from soil dragged by storm water erosion (Kronvang et al., 2004). Over time, those suspended particles settle down in the bottom of water bodies. Consequently, bottom sediments constitute an important sink for these compounds (Burton and Landrum, 2003) and can thus be used as an integrated measure of pesticide input on the hydrological system (Friberg et al., 2003).

Since bottom sediments provide nutrients and habitat for a wide variety of benthic organisms, sediment quality evaluation becomes relevant for the protection of aquatic life (Paixão et al., 2011). Whole-sediment toxicity tests provide a good methodology to assess the bioavailability of pollutants to these organisms (Hintzen et al., 2009) and allow for the evaluation of interaction effects resulting from the complex mixture of components in sediments (Peluso et al., 2013a, 2013b). In this sense, amphipods are model species for this type of toxicity bioassay (USEPA, 2000). *Hyalella curvispina* is a native South American species found in streams in the study area (Ronco et al., 2008) but not in areas impacted by agricultural activity (Solis et al., 2016), suggesting that it is a species sensitive to the presence of pesticides in sediments (Jergentz et al., 2005; Phillips et al., 2006).

Despite the significance of agriculture in the country, published data on pesticide occurrence in aquatic environments in the most heavily cultivated area of Argentina (Buenos Aires, Córdoba and Santa Fe Provinces) remains scarce. Most studies focus on the Buenos Aires Province (Jergentz et al., 2005; Marino and Ronco, 2005; Ronco et al., 2008;De Gerónimo et al., 2014; Hunt et al., 2016), and only some take into consideration the productive area in its entirety (Ronco et al., 2016; Etchegoyen et al., 2017). Moreover, there is no information on the impact of pesticides on water bodies associated with horticulture; and very little research has been done in other countries (Thoma and Nicholson, 1989; Kreuger et al., 2010; Roseth and Haarstad, 2010).

The objective of this work is to determine the impact of pesticides on a watercourse that flows through a highly productive horticultural zone by conducting a bottom-sediment integrated study of the occurrence and concentration of pesticides and their relation to lethal and sublethal effects on benthic fauna.

2. Materials and methods

2.1. Study area

The Carnaval creek and its tributaries (Fig. 1) constitute a suburban basin located in the La Plata area in the northeast of the Buenos Aires Province, Argentina. The basin has a surface area of 105 km^2. Its urbanization coefficient is estimated at 15% to 20%. Its main channel originates in the García Lagoon, has a length of 14.5 km and an average depth of 0.8 m, and shows high turbidity and low current velocity. In the upper and middle part of the basin, the main land-use activities are horticulture and floriculture, and to a much lesser extent, extensive crops like soybeans, maize and wheat. In the CHP, there are >1000 parcels that produce and condition vegetables for distribution and commercialization. The highest population density - along with some industries - is concentrated in the lower basin (Banda Noriega and Ruiz de Galarreta, 2002).

2.2. Sampling

Integrated sediments samples were collected during two monitoring campaigns in August 2015 (CAMP1) and January 2016 (CAMP2), following cycles of low and high pesticide use, respectively (Marino and Ronco, 2005). Sampling was performed at 5 sites along the Carnaval creek (S1–S5). At each site, sediments were collected for both chemical analysis and toxicity bioassays in 2 L containers. The sediment samples were obtained in shallow water, and the first 5 cm were taken using an Eckman grab. The samples were preserved in an ice-cold container until arrival at the laboratory (ASTM, 2002), where each sample was homogenized. A subsample of the homogenized sediment was separated in a 200 mL container for pesticide residue analysis and stored at −20 °C until the analysis. The subsample for the toxicity bioassay was preserved at 4 °C in darkness until its use (Peluso et al., 2013a, 2013b). Dry weight was measured at 105 °C until constant mass, and organic matter content was determined by calcination at 550 °C (loss on ignition) (APHA, 1998).

2.3. Chemicals and reagents

Pesticide-residual-grade dichloromethane, *n*-hexane, HPLC grade acetonitrile and methanol were all obtained from J. T. Baker (USA). The 9-fluorenylmethyl chloroformate (FMOC-Cl) for HPLC derivatization, primary-secondary amine (PSA), standards of glyphosate (99%), AMPA (98.5%), glyphosate-2-^{13}C,^{15}N (99 atom % ^{13}C, 98 atom % ^{15}N; ^{13}C,^{15}N-GLY), and atrazine-D_5 (ATZ-D_5) were acquired from Sigma Aldrich (St. Louis, MO, USA). A Sartorius Arium water purification system (Sartorius AG, Göttingen, The Netherlands) was used to obtain nanopure water in the laboratory. Sodium chloride (NaCl), anhydrous magnesium sulfate ($MgSO_4$), potassium phosphate dibasic (K_2HPO_4), and ammonium acetate (NH_4Ac) (all analytical grade) were obtained from Merck (Darmstadt, F.R. Germany). Certified standards of pesticides as 1000 ng mL^{-1} standard stock solutions in *n*-hexane were obtained from AccuStandard, Inc. (USA).

2.4. Chemical analysis

2.4.1. Extraction

One portion of 7 g of wet sediment was weighed into a 50 mL polypropylene tube. In each sample, ATZ-D_5 was added as an internal quality standard at nominal concentration at the instrumental detection of 100 ng mL^{-1}. The multiresidue *QuEChERS* method was used for pesticide extraction (Anastassiades and Lehotay, 2003), using the modification proposed by Kvíčalová et al. (2012), where 2 g of NaCl and 6 g of anhydrous $MgSO_4$ were used for extraction without buffer media. To the spiked