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Insecticide toxicity to *Hyalella curvispina* in runoff and stream water within a soybean farm (Buenos Aires, Argentina)

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ABSTRACT

Toxicity to the locally dominant amphipod *Hyalella curvispina* was assessed in a first-order stream running through a cultivated farm. Cypermethrin, chlorpyrifos, endosulfan and glyphosate were sprayed throughout the studied period. Toxicity was assayed under controlled laboratory conditions with runoff and stream water samples taken from the field under steady state and flood conditions. Ephemeral toxicity pulses were observed as a consequence of farm pesticide applications. After pesticide application, runoff water showed 100% mortality to *H. curvispina* for 1 month, but no mortality thereafter. Toxicity persistence was shortest in stream water, intermediate in stream sediments and longest in soil samples. Runoff had a more important toxicity effect than the exposure to direct aerial fumigation. The regional environmental features determining fast toxicity dissipation are discussed.

1. Introduction

Population growth and food consumption in developing countries have increased world food demand. Argentina, a major food exporter, moved to help meet this demand by increasing agricultural production. A process of agricultural intensification is currently taking place. Increased production has been due more to enhanced productivity (231% in the last decades) than to the increase in the area under agricultural crop production (36%, CASAFE, 2008). For a long time farmers had concentrated on a mixed system of livestock and crops, mainly wheat and corn. Soybean was not a traditional crop. Genetically modified soybean, resistant to glyphosate, was released on the market in 1996, and was immediately adopted by farmers, together with the no-tillage management practice. Several applications of the cheap and efficient glyphosate herbicide are needed in order to implement the no-tillage technique. Wheat varieties with a short growing period allowed two harvests per year: wheat followed by soybean. Livestock were moved to marginal areas or concentrated in feedlots. At present, soybean represents roughly one-half both of the total harvest and of the cultivated area in Argentina (50 million tons and 15 million ha, respectively). Almost all of it belongs to the genetically modified soybean resistant to glyphosate, with Argentina being the third largest transgenic producer of soybean after the United States and Brazil.

Pesticide consumption increased from 6 to 18 million kilograms in the 1992–1997 period (Pengue, 2000) and thereafter continued to increase at lower rates. Cypermethrin, chlorpyrifos and endosulfan are the insecticides most frequently used. Cypermethrin represents more than half of the total insecticide consumption. Cypermethrin is usually sprayed twice during the soybean growing period. When the crop reaches a certain size, airplane applications are commonly used to avoid the crop damage caused by terrestrial vehicles. The application of pesticide mixtures is also a common practice. When glyphosate is to be applied, farmers usually add also cypermethrin in the belief that the residual action will prevent insect infestations and thus save the cost of gasoline by avoiding a later application. The opposite combination is also common: when cypermethrin applications are needed, glyphosate is often added, to prevent further weed proliferation. These agricultural practices represent an environmental risk for surface waters.

Schulz (2004) pointed to the numerous reports concerning the toxicity of different insecticides following single-species exposures tested in laboratory, and emphasized the need for studies performed in natural environments to assess the impact of farming practices in different basins. Marino and Ronco (2005) detected pesticides in rivers running through the main agricultural districts in the Argentine Pampa. Jergentz et al. (2004a, 2004b) showed the occurrence of toxicity pulses in streams draining intensively cultivated basins. Jergentz et al. (2005) detected cypermethrin, chlorpyrifos and endosulfan in a first-order stream originating in a plot sown to soybean in the main soybean district of Argentina.

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In the present study, we hypothesized that pesticide applications in Argentina have adverse effects for the locally abundant amphipod *Hyalella curvispina* produced by runoff-mediated pulses of acute toxicity occurring after pesticide applications. This hypothesis was tested in a first-order stream on a typical farm where the farmer gave advance notice of each application, reporting date, pesticide and dose applied. Toxicity persistence in the runoff events following applications was assessed.

2. Materials and methods

The first-order Sauce stream was studied. It is located roughly 15 km southwest of La Plata city, Buenos Aires, Argentina (35°01S, 57°59W). The stream goes through a private farm of 110 ha containing two cultivated plots. In a steady-state condition it has a 2–6 m wide riparian strip, 2–3 m wide, 10–20 cm deep, with a 10–20 l/s discharge. The basin, comprising 1800 ha almost completely under cultivation, contains Argiudol soils characterized by an A surface horizon, 30 cm deep. Grain-size was silty clay (58–64% silt and 26–34% clay) and 4.5% organic matter, followed by a B horizon, 80–100 cm deep, with 50–60% clay (Mugni, 2009).

The study was performed over the course of the 2005–2007 growing periods. In the first (2005–2006), soybean was grown on one of the plots, and wheat followed by soybean on the other plot. In the second growing period (2006–2007) corn was grown on both plots.

Stream water under steady state and flood conditions, runoff water, sediment and soil samples were taken after each pesticide application throughout the 2 successive growing periods (October–March). An effort was made to perform a sampling after each runoff event following application until mortality ceased in the exposures. Stream water was sampled immediately after application at three sites in the cultivated plots. An upstream site was included for control purposes (Fig. 1). Three runoff samplers were installed at the edge of each cultivated plot, in erosion rills, to collect runoff water during rain events. Control runoff samplers were installed on a nearby uncultivated plot. Runoff samplers consisted of 3 l glass bottles buried in the soil up to their necks, adjacent to the stream (Schulz et al., 1998). Passive sampling devices were installed at three sites within the stream and at one control site upstream from the cultivated plots to sample stream water during flood-peaks induced by rain events. The samplers were similar to those described by Schulz (2001). Bottles (0.5 l) with two holes 5 mm in diameter in the lid were attached to sticks, with the opening about 10 cm higher than the water surface during steady flow condition. After rain events, water samples from the runoff and flood samplers were obtained and immediately transported in dark and cooled boxes to the laboratory for exposure assays and analytical determinations.

Precipitation was measured at a Field Experimental Station located 7 km from the study site.

2.1. Toxicity tests

The locally abundant and often dominant amphipod *H. curvispina* was chosen for toxicity assessment. The amphipod *H. curvispina* was originally obtained from an uncontaminated stream. It was later reared in the laboratory in large plastic beakers filled with stream water. Beakers were replenished with dechlorinated tap water to compensate for evaporation losses. Water composition in the beakers remained within the wide variation range observed in the stream. The surface water was covered with the macrophyte *Lemna* sp. *H. curvispina* fed on the periphytic community of the *Lemna* rhizosphere. In addition, a food supplement was added twice a week that included a mixture of fresh lettuce leaves and dried algae.

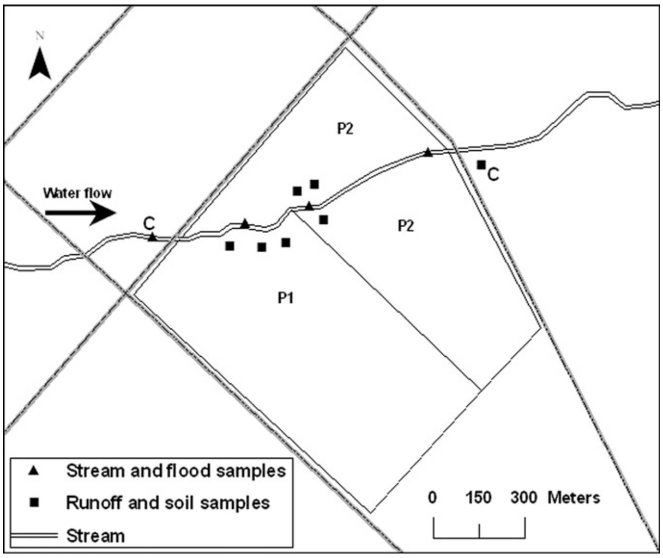

Fig. 1. Studied stream and cultivated plots (P1 and P2). C stands for controls.

Laboratory toxicity tests with *H. curvispina* were performed in water samples taken from the field following USEPA (U.S. Environmental Protection Agency) (2000). Ten *H. curvispina* with a length of 10–15 mm were exposed to 100 ml stream and runoff water in 250 ml beakers, in triplicate. Tests were performed without feeding, at 22 ± 2 °C, and natural photoperiod. Mortality was assessed after 48 h of exposure to the water samples. As a validity criterion, less than 10% mortality was considered equivalent to no effect (USEPA (U.S. Environmental Protection Agency), 2000). Stream controls were performed with samples from an upstream site. Runoff controls were made with runoff water samples taken from an adjacent uncultivated plot turned over to cattle, where pesticides were not applied. Reference tests with copper sulfate ($SO_4Cu \cdot 5H_2O$) from Merck® were performed as a positive control.

Soil and stream sediments toxicity tests to *H. curvispina* were performed following USEPA (U.S. Environmental Protection Agency) (2000). Ten *H. curvispina* measuring 10–15 mm were exposed to an amount of soil or wet sediment equivalent to 50 g dry weight, and 150 ml of reconstituted fresh water (APHA, 1998) in 250 ml beakers, in triplicate. Mortality was assessed after a 10 day exposure. *H. curvispina* was fed with algae obtained from cultures every two days. Controls were made with soil samples taken from the same uncultivated plot where runoff controls were taken. Mortalities lower than 20% in soil and sediment exposures were considered as no effect (USEPA (U.S. Environmental Protection Agency), 2000).

2.2. Chemical analysis of samples

Dissolved oxygen and temperature (YSI 51B) and pH (Orion 250A) in the stream water were measured *in situ*.

Water samples were immediately filtered through Whatman GF/C filters, and carried in cool dark boxes to the laboratory. Na^+ (flame photometry) and HCO_3^- (Gran titration) were determined following APHA (1998). Suspended matter (SM) was determined as the weight difference after filtration through the Whatman GF/C filters. The filters were heated to 550 °C for 2 h prior to use. Total Organic Carbon (TOC) in unfiltered water samples was measured according to Golterman et al. (1978). Textural soil and sediment analyses were performed according to Day (1965). Soil or sediment organic matter (OM) was determined by weight loss after ignition (Dean, 1974).

Pesticide in water was determined after a liquid–liquid extraction in NaCl saturated water enriched with methylene chloride, at $pH < 4$, followed by roto-evaporation (vacuum: 600 mmHg; bath temperature 40 °C) and a solvent change to *n*-hexane, in order to reach a final concentration factor of 1000 (Díaz-Báez et al., 2000).

Pesticides in sediments were extracted from wet samples in a solid:liquid sonication system (50 g:50 ml *n*-hexane; 1 h stirring; and repeated twice with 25 ml of the same solvent), filtered and taken to a final volume of 0.5 ml with nitrogen flow (USEPA (U.S. Environmental Protection Agency), 1986, method 3550).

Pesticides were analyzed by GC-ECD (Carlo Erba, 6,000), equipped with an HP5 column, 15 m and 0.53 ID, N_2 carrier, ramp and detector temperatures of 190–250 and 320 °C, respectively (Marino and Ronco, 2005). Recovery was tested by spiking environmental samples with known concentrations of the assayed pesticides. Sample storage at −20 °C was also tested to assess the holding time of the tested pesticides. Solvents used were J.T. Baker for pesticide analysis. Standards of cypermethrin, endosulfan and chlorpyrifos were provided by SENASA (Argentine National Farm Food Sanitation and Quality Service). Detection limits in water samples were 0.025 μg/l for cypermethrin and 0.01 μg/l for endosulfan and chlorpyrifos, and in sediment samples 1 μg/kg d.w. for all insecticides.

2.3. Statistical analysis

The Kruskal–Wallis non-parametric ANOVA by ranks test (KW) was used because the data did not fit the requirement of normality and homoscedasticity even after transformation. In cases where significant differences were detected, the comparison of means was used to determine differences between means by the method of multiple comparison between means.

3. Results

The stream water was alkaline, sodium and bicarbonate being the dominant ions (Table 1). The apparently lower ionic concentrations in runoff water compared to stream water were not statistically significant. By contrast, suspended matter was significantly higher in runoff than in stream water in a steady stage and flood condition ($p=0.0038$ and 0.0045, respectively). TOC in stream water averaged 14.4 mg/l throughout the period studied, ranging from 10.8 to 18.2 mg/l.

The texture of the stream surface sediments was: 22% clay, 67% silt and 11% sand, its organic matter content being 12%.

On January 5, 2006, a mixture of 100 ml/ha cypermethrin, 1 l/ha chlorpyrifos and 4 l/ha glyphosate was applied with a tractor in a small part of the first plot comprising 4 ha, adjacent to the stream. On January 6–8 small precipitations (14 mm) did not result in a runoff event. On January 9, a 65 mm rain produced a runoff event. Exposure tests of the runoff water from the plot where the application had taken place showed 100% *H. curvispina* mortality (Table 2) while the other runoff samples, including controls (Fig. 1), showed mortalities below threshold levels, with no contamination effect (USEPA (U.S. Environmental Protection Agency), 2000).

On January 22, an aerial application was performed with a mixture of 150 ml/ha cypermethrin and 800 ml/ha endosulfan in the first plot. A few rains of small intensity, below 16 mm/day, did not produce runoff events, until a month later, on February 22, a rain event of 130 mm, attaining a peak intensity of 65 mm/h, produced a runoff event. Toxicity tests performed with runoff water showed no mortality (Table 2).

On March 3, a rain of 47 mm produced a runoff event. The following day, runoff and stream water samples from sites adjacent to the studied plots showed mortalities below threshold levels, with no contamination effect (USEPA (U.S. Environmental Protection Agency), 2000). However, the water sample taken upstream of the studied plots showed 100% mortality and reached 17 of chlorpyrifos and 38 μg/l of endosulfan (Table 3). On March 6, an aerial application of 150 cypermethrin and 700 ml/ha endosulfan was performed on the second plot containing soybean grown after wheat. At that time the water stage height was rather low and stream flow was almost imperceptible. The following day two stream water samples had chlorpyrifos concentrations of 0.014 and 0.044 μg/L, and these were associated with 6% and 30% mortality to *H. curvispina*, respectively. The concentration of chlorpyrifos in bottom sediments on that day was 12 μg/kg. However, the applied pesticides in the soybean field remained below detection levels in both water and stream sediments. Chlorpyrifos measurements, not applied in the studied plots but previously detected in upstream water, indicate that the detected toxicity was coming from the upstream basin. On March 15 and 16 intermittent rains amounted 38 mm and resulted in a runoff and flood event. The following day, 11 days after fumigation, runoff and flood samples attained 100% mortality, being significantly lower in stream water samples (40%), while mortalities in the controls remained below threshold levels showing no contamination effect (USEPA (U.S. Environmental Protection Agency), 2000). A high cypermethrin concentration was measured in the runoff sample of the plot where pesticide had been applied (92 μg/l). Chlorpyrifos was detected in the flood water sample while cypermethrin and endosulfan remained below detection levels. On March 21, 15 days after the application, significant differences were found between water and soil samples: stream water exposures fell below threshold values showing no concentration effect while soil exposures remained with 100% mortality. On March 24, 18 days after application, significant differences were measured in water, sediments and soil samples: no mortality was detected in stream water, 30% was determined in stream sediments, while it remained at 100% in the soil.

In the 2006–2007 growing period corn was sown on both plots. A mixture containing 150 ml/ha cypermethrin, 2.5 atrazine, 2 acetochlor, 1.5 glyphosate and 180 ml/ha dicamba was applied

Table 1
Mean (±SE) water quality parameters measured throughout the studied period in runoff and stream water under steady state and flood conditions. *N* denotes the total number of samples analyzed.

	N	pH	Susp. matter (mg/l)	HCO_3^- (mg/l)	Na^+ (mg/l)
Stream	25	7.7	86 ± 23	71 ± 40	22 ± 15
Flood	15	7.8	148 ± 60	65 ± 31	17 ± 12
Runoff	15	7.3	529 ± 491	48 ± 15	13 ± 5

Table 2
Percentage of mortality of *H. curvispina* exposed to runoff water after pesticide applications in the field.

Application date	Sampling date	Period since application (days)	Pesticide applied	Applic. form	Rain (mm)	% Mortality in runoff
05.01.06	09.01.06	4	Cyp+chlorp	Tractor	65	100
22.01.06	22.02.06	30	Cyp+endosul	Aerial	130	0
06.03.06	16.03.06	10	Cyp+endosul	Aerial	38	100
08–15.10.06	11.11.06	33–26	Cyp+herbicides	Tractor	32	0

Table 3
Percentage of mortality in *H. curvispina* exposures of field samples before and after the aerial application of cypermethrin and endosulfan performed on March 6.

Date	**Sample type**	**Cypermethrin (μg/l)**	**Endosulfan (μg/l)**	**Chlorpyrifos (μg/l)**	**% Mort.**
04.03.06	Upstream water	nd	38	17	100
07.03.06	Stream water	nd	nd	0.01–0.04	6–30
17.03.06	Runoff water	92	–	nd	100
17.03.06	Flood water	nd	–	0.11	100
17.03.06	Stream water	–	–	–	40
21.03.06	Stream water	nd	nd	nd	10
21.03.06	Soil	–	–	–	100
24.03.06	Stream water	–	–	–	0
24.03.06	Soil	–	–	–	100
24.03.06	Stream sediments	–	–	–	30

nd = not detectable.
– = not analyzed.

simultaneously with the seed on October 8 and 15 on plots 1 and 2. On November 11, roughly a month after the applications, a 32 mm rain produced a runoff flood event. Exposures of stream, flood and runoff water samples did not induce *H. curvispina* mortality. On November 28, 43 days after pesticide application on the studied plots, stream water exposures did not show mortality, while soil exposures caused 100% mortality, the differences being statistically significant.

4. Discussion

Pesticide application in the studied farm resulted in toxicity pulses in the adjacent runoff and stream waters. However, not all the applications performed on the field resulted in a runoff toxicity pulse. The present results suggest that the time period between the application and the next rain producing a runoff event is one of the main factors determining the occurrence of a runoff toxicity pulse. There is a critical persistence period of roughly 1 month as of the application in which runoff contains toxicity. Toxicity persistence in the soil is longer. On two occasions soils showing toxicity produced runoff events without toxicity. The higher suspended matter content in the runoff water compared to the stream water shows the contribution of soil-originated particles transported by erosion. Since the runoff did not show toxicity, the amount of insecticide transported together with the runoff particulate matter must represent a modest portion of the total soil pool. Moreover, since microbial degradation is an important pesticide soil fate, it seems likely that the proportion of available insecticide in the runoff particles decreases with time following application. Direct aerial fumigation in the small headwater streams seems the worst toxicity scenario, because the pesticide is applied directly above the stream with the same load as over the crop and the applications are often performed in coincidence with steady-state conditions. However, in the aerial application of cypermethrin and endosulfan performed on the studied farm on March 6, the small detected toxicity in the stream water the following day was caused by chlorpyrifos, not applied in the studied plot but coming from the upstream basin (Table 3). By contrast, the following runoff event produced 11 days after the application contained high toxicity and huge amounts of the applied cypermethrin. It follows that under the present management practice and regional environmental conditions runoff is a more important toxicity source than either the drift or the aerial application, and that toxicity pulses are always ephemeral, independent of stream conditions.

Our results are consistent with previous studies performed in the field, or in outdoor mesocosms, showing fast pesticide dissipation rates. Crossland et al. (1982) reported that cypermethrin concentrations in stream waters adjacent to vineyards decreased from 0.4 to 1.7 μg/l after spraying to undetectable values (<0.1 μg/l) a few hours later, and cypermethrin concentrations in pond water adjacent to potatoes and sugar beet decreased from 6 to 23 μg/l after application to undetectable values in 13 out of 14 surface water samples tested the following day. Mazanti et al. (2003) reported a 70–75% chlorpyrifos disappearance during the 6 h following experimental application in outdoor mesocosms. Farmer et al. (1995) observed fast cypermethrin dissipation in outdoor mesocosms, decreasing to 13% of the initial nominal concentration 24 h after the application.

Several environmental factors contribute to the observed short toxicity persistence. Hydrophobic pesticides are known to be extensively adsorbed on both inorganic and biological surfaces. Maund et al. (2002) reported that 98% of added cypermethrin was adsorbed by the sediments within the first 2 h of incubation in laboratory water–sediment systems. In the present study toxicity persistence was shortest in water, intermediate in sediments and largest in soil. Half-life values in soils depend on moisture, microbial activity, clay and organic content, and temperature (Odenkirchen and Eisler, 1988). The major routes by which pesticide is lost are chemical hydrolysis, clay-catalyzed hydrolysis, microbial degradation and volatilization. Hydrolysis strongly increases with pH for chlorpyrifos (Odenkirchen and Eisler, 1988; Bondarenko and Gan, 2004) and cypermethrin (Laskowski, 2002). The high alkalinity prevailing in the stream water (Table 1) enhanced hydrolysis in the water itself, and probably in superficial sediments. Photolysis and volatilization also represent important losses (Meikle and Kurihara, 1983). Since the stream is extremely shallow both processes probably contributed to the fast dissipation observed.

Both floating and emergent macrophytes were common in the studied stream. *Lemna* sp. was the dominant form among the former, *Sagitaria* sp. and *Scirpus californicus* among the latter. Macrophytes decrease water velocity favouring suspended matter settlement together with the associated contaminants (Wharton et al., 2006). Macrophytes are known to uptake pesticides. Di Marzio et al. (2005) showed that *Vallisneria spiralis* uptake endosulfan from contaminated sediments under laboratory exposure. Mugni (2009) showed that cypermethrin toxicity decreased faster in laboratory containers with the surface water completely covered by *Lemna* sp., than in containers with a free water surface. The assayed biomass, attaining 100 g dw/m^2, was similar to the amounts often sampled in the field. Miglioranza et al. (2004) reported the presence of several pesticides including endosulfan in *S. californicus* growing in a shallow lake surrounded by farms in Buenos Aires. Concentrations were higher in the affluent than in the effluent and in the roots than in rhizomes and shoots. Concentrations were also lower in the rhizosphere than in sediments without roots, suggesting that root metabolism enhanced degradation. Emergent macrophytes attain high biomass and coverage. *S. californicus* typically attains 3 kg dw/m^2 in the region's environments (Villar et al., 1996).

The present results are consistent with previous studies in the same region (Jergentz et al., 2004a, 2004b, 2005) and elsewhere, performed over a wide range of different cultures and environments (Crossland et al., 1982; Wan et al., 1995; Schulz, 2001, 2004; Capri et al., 2005). Cooper et al. (2004) simulated a runoff event in a vegetated channel. After 24 h, 86% of the added esfenvalerate was recovered in the vegetation, against 14% retained by the sediments, while water concentrations fell below detection limits. Moore et al. (2001) reported that 61% of the atrazine and 87% of lambda cialothrin applied to vegetated channels were recovered in the vegetation in the following hour. Beketov Mikhail and Liess (2008) studied the temporal dynamic and spatial cross-channel variability of thiacloprid in outdoor stream mesocosms. They showed that insecticide concentrations in the macrophyte-dominated section of the channel were 20–60% lower than those in the non-vegetated section.

5. Conclusion

The present management practices commonly utilized in Argentina produced toxicity pulses for *H. curvispina*. Toxicity is introduced in the streams by the runoff events following routine pesticide application. The time period between pesticide application and the first runoff producing rain was critical. Runoff events occurring a month after application did not produce toxicity. *H. curvispina* is a widespread organism very common in the region's environments. The concentrations of cypermethrin and chlorpyrifos that are lethal for it are similar to other values reported in the literature for *H. azteca* (Mugni, 2009), and both are among the most sensitive organisms to insecticides (Laskowski, 2002; Farmer et al., 1995). Once toxicity ceased for *H. curvispina*, further small acute effects would be expected among the resident faunal community. It is therefore concluded that current agricultural practices result in several ephemeral but acute toxicity pulses per season for the resident invertebrate fauna in the surface waters of the Pampa region.

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