

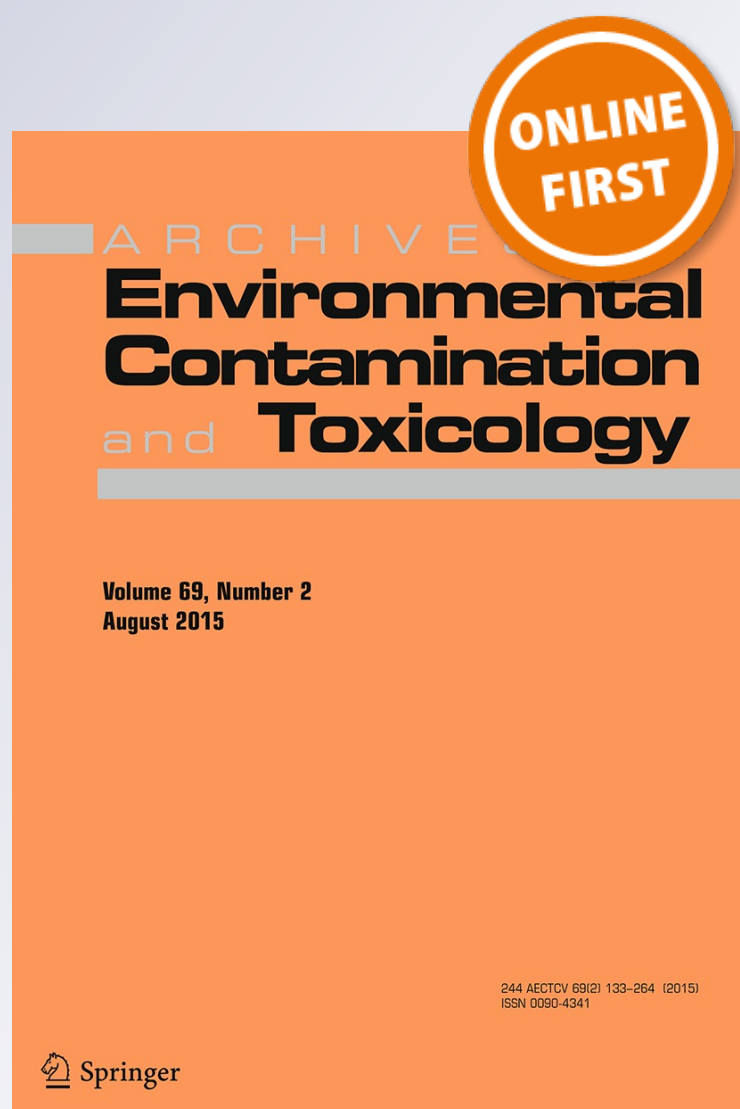
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**Archives of Environmental
Contamination and Toxicology**

ISSN 0090-4341

Arch Environ Contam Toxicol
DOI 10.1007/s00244-015-0187-y



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Toxicity Persistence of Chlorpyrifos in Runoff from Experimental Soybean Plots to the Non-target Amphipod *Hyalella curvispina*: Effect of Crop Management

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Received: 7 October 2014 / Accepted: 22 June 2015
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Abstract Toxicity persistence to the nontarget amphipod *Hyalella curvispina* in runoff events following chlorpyrifos applications to soy experimental plots was compared in conventional and no-till management. Two application scenarios were compared: an early-season application with the soil almost bare and a late-season application after the foliage had attained complete soil cover. *H. curvispina* was exposed to chlorpyrifos using two different test systems: a short-term (48 h) runoff water exposure and a long-term (10 days) soil exposure. Both commonly used crop management practices for soybean production resulted in runoff toxicity following pesticide applications and represent a toxicity risk for adjacent inland waters. Toxicity persistence was longer after the earlier than the late season application, likely because of higher volatilization and photodecomposition losses from the soy canopy than from the soil. For the early-season application, toxicity persisted longer in the no-till plots than in the conventional tillage

plots. Suspended matter was higher in the conventional treatment. Chlorpyrifos sorption to suspended matter likely contributed to the shorter persistence. For the late-season application, toxicity persisted longer in the conventional treatment. The causes remain conjectural. The soil organic carbon content was higher in the no-till treatment. Sorption to organic matter might have contributed to the shorter chlorpyrifos toxicity persistence in no-till management. Late applications are more frequent and prevail longer throughout the soy growing season. Overall, the no-till management practice seems preferably because shorter toxicity persistence in runoff represents a lower environmental risk for the adjacent inland waters.

Population growth and food consumption in developing countries have increased world food demand. Agriculture (croplands and pasture) represents the world's largest terrestrial biome (Stehle and Schulz 2015). Agricultural expansion and intensification led to a >750 % increase in pesticide production between 1955 and 2000. Non-point source contamination of streams with agrochemicals applied in agricultural production is one of the greatest stressors to stream ecosystems (Schulz 2004); runoff is an important route of entry pesticides and exposure scenario for non-target fauna (Schulz 2001). As a consequence, the highest pesticide concentrations occur as short-term exposure pulses during precipitation events, and the effect of pesticides is expected to be higher in small streams due to a close proximity to the crop (Schulz 2004). Argentina, one of the major food exporters, moved to help meet the enhanced demand by increasing agricultural production. A process of agricultural intensification is currently taking place. In 1996, the genetically modified soybean plant resistant to glyphosate was released in the Argentine

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market and was rapidly adopted by farmers. The no-till technique had long been recommended to reduce erosion soil losses. However, it was not until the soybean resistant to glyphosate became increasingly common that the practice was adopted by farmers. Several applications of the cheap and efficient glyphosate herbicide are used during the fallow period in the no-till technique. At present, soybean represents roughly half of the total harvest and cultivated area (MAGyP 2013), consisting primarily of the genetically modified variety resistant to glyphosate. Wheat and soybean varieties with a short growing period allow two harvests per year, wheat followed by soybean. Livestock has been moved to marginal areas or concentrated in feedlots. Argentina is the world's third largest transgenic soybean producer following the United States and Brazil. In South America, soy is widespread in Brazil, Argentina, Uruguay, Paraguay, and Bolivia; the crop is usually managed in the same way, often applying the no-till seeding technique, different formulations of glyphosate herbicide, and several insecticides (Bindraban et al. 2009). Pesticide consumption in Argentina increased from 6 million kilograms in 1992 (Pengue 2000) to 36 million kilograms in 2010 (CASAFE 2012). Chlorpyrifos is the most heavily used insecticide; more than 9 million kilograms were used in 2010. Chlorpyrifos is used during early soybean stages to attack soil pests, such as cutworms (*Agrotis ipsilon*, *Agrotis malefida*, *Peridroma saucia*, *Euxoa* sp) and later in the growing period to prevent attack by the borer *Epinotia aporema* (Lepidoptera, Tortricidae).

The environmental impact of such agricultural intensification remains largely unreported. Marino and Ronco (2005) determined the occurrence of insecticides in several Pampasic streams and rivers. Jergentz et al. (2004a, b) reported toxicity in streams draining intensively cultivated areas. Mugni et al. (2011) studied a first order stream draining plots cultivated under the common management practices. Toxicity was recorded in coincidence with rain events and related to pesticide applications in the adjacent crops. Some applications were followed by several toxicity pulses in relation to the succeeding rain events. In contrast, no toxicity was observed after two applications performed during dry periods in which the following rain event occurred a month after the application. It seems therefore that there is a critical time period for toxicity in runoff to be mitigated. Assessing this critical period would allow improved environmental impact assessment.

This study assesses toxicity persistence in runoff to the regionally abundant amphipod *Hyaella curvispina* in an experimental soybean crop where rain events after chlorpyrifos application were simulated by means of a sprinkler irrigation device. It was hypothesized that toxicity persistence in runoff would be different in conventional than in no-till management practices, because the soil condition is different with a conspicuous litter layer remaining over the

soil surface in the no-till technique. Two different application times were studied: an application early in the soybean growing period on bare soil, and at an intermediate stage when the soil was covered by soy foliage.

Materials and Methods

Study Site

This study was performed at the Experimental Field Station of the School of Agronomic Science at La Plata University, located 8 km southwest of La Plata city, Buenos Aires, Argentina (35°01'S, 57°59'W).

An experimental field was divided into ten plots of 8 × 30 m for the experimental crop. The irrigation equipment consisted of a perimeter pipe, which was installed surrounding every two plots, and 15 impact sprinkler heads of 9.5 mm in diameter (Senninger Inc., model 7025) mounted at a distance of 15 m apart. Simulated rainfall was applied at an intensity of 16 mm/h, with a drop diameter of 0.7–1 mm. Water was supplied from a 65-m-deep well and driven by a 60,000 L/h pump. The field had a slope of 1 %. At the lower end of each plot, a small trench was excavated in the soil and a 5-L bucket was buried in the trench to capture the runoff water.

The Agricultural Station contain Argiudol soils characterized by an A surface horizon, 30-cm deep, of grain-sized silty clay (52–64 % silt and 26–34 % clay), followed by a B horizon, 80–100-cm deep with 50–60 % clay (Mugni 2009). A composite sample of 10 mixed superficial cores taken in the experimental plots had a grain size composition of 54 % silt, 26 % clay, and 20 % sand.

Experimental Setup

Two successive soybean crops were studied during the 2009/2010 and 2010/2011 growing periods. A single chlorpyrifos application was made in each season. For the 2009/2010 growing period, the soy was sown on November 8, 2009 and the application was performed 7 weeks later on December 28, 2009 when the crop had attained soil cover, referred to hereinafter as the late-season application. For the 2010/2011 growing season, the application was made on December 1, 2010, immediately after soy was sown and the soil was bare, referred to hereinafter as the early-season application.

The ten plots were divided in two groups of five adjacent replicates for each management practice. Each group consisted of two controls and three chlorpyrifos intercalated replicates.

For conventional tillage, the preparation of the soil for the seedbed was performed with two disc harrows and one spike tooth harrow passed prior to a mouldboard plough.

After the soy harvest, the remaining stubble was chopped with a mower and incorporated into the soil with a disc harrow. The disc harrow was passed again twice during late autumn (June) and winter (August) to ensure the fallow.

For the no-till treatment, a chemical fallow was performed consisting of two glyphosate applications: the first performed in late autumn (June), and a second performed a month before seeding. This practice involves seeding in a small furrow with the soil surface remaining largely undisturbed. The soybean was seeded with 45 seeds/m² and 35 cm between furrows.

The common commercial product Terfos, consisting of 48 g of chlorpyrifos active ingredient per 100 mL of formulated product, was applied at the rate of 2 L/ha, as recommended by the manufacturers. The pesticide was applied using a tractor-mounted sprayer.

Toxicity Tests

The first simulated rain episode was produced immediately after pesticide application and was successively repeated until no mortality of *H. curvispina* exposed to runoff occurred. Each simulated rain event lasted until the runoff was sufficient to fill the collection buckets placed in the trenches and stopped soon thereafter, in order to drain the trenches and avoid further runoff. The runoff was transferred to dark bottles and immediately transported to the laboratory in coolers.

The toxicity of the runoff water to the amphipod *H. curvispina* was assessed by means of laboratory toxicity tests. Procedures were adapted from standardized protocols for the sediment toxicity test to *H. azteca* (USEPA 2000), as described by Mugni et al. (2011). Three replicates from each plot were assessed. Ten *H. curvispina* of 5–10-mm length were exposed in 100-ml beakers. Tests were performed without feeding, at 22 ± 2 °C and with the natural photoperiod, assessing mortality after 48 h of exposure. Dead individuals were removed immediately. As a validity criterion for the negative control, less than 10 % mortality was considered acceptable (USEPA 2000).

Tests of soil toxicity to *H. curvispina* were performed following sediment toxicity test protocols described for *H. azteca* (USEPA 2000). Ten *H. curvispina* measuring 5–10 mm were exposed to an amount of wet soil equivalent to 15 g dry weight in 250-ml beakers with 150 mL of laboratory reconstituted fresh water (APHA 1998), in triplicate. Mortality was assessed after a 10-day exposure. *H. curvispina* were fed *ad libitum* with algae obtained from laboratory cultures every 2 days. As a validity criterion for the negative control, less than 20 % mortality was considered acceptable (USEPA 2000).

H. curvispina were originally collected from an uncontaminated stream, 25 km south of La Plata. They

were later reared in the laboratory for several weeks in large plastic beakers filled with stream water that was gradually changed to unchlorinated tap water. The surface water was covered by the macrophyte *Lemna sp. H. curvispina* fed on the periphytic community of the *Lemna* rizosphere and was further supplemented with fresh lettuce leaves.

Physical and Chemical Analysis

Weather conditions (solar radiation, air humidity, and temperature) were recorded at an automatic meteorological station (Davis Instruments station, Groweather Industrial model), located about 300 m from the experimental plots. Soil temperature and moisture were measured with Decagon ETC and Echo20/ec5 sensors, respectively, stuck 10-cm deep in the soil and recorded every 60 min with a Decagon model Em5b datalogger device.

Soil organic carbon in each plot was measured following the Walkley and Black method (Jackson 1982) at the end of the first growing period.

Temperature, conductivity (Hanna Instruments 8733), and pH (Orion 250 A) in the runoff water were measured in situ throughout the experiment.

Runoff water samples were passed through C18 columns (Agilent, solid phase extraction) and frozen until pesticide analysis. Extracts were eluted from the C18 columns with 5 mL of hexane followed by 5 mL of dichloromethane. The sample extracts were injected into a GC-ECD (Carlo Erba, 6,000), equipped with a HP5 column, 15 m and 0.53 ID, N₂ carrier, ramp, and detector temperatures: 190–250 °C and 320 °C, respectively. The solvents used for pesticide analysis were from J.T. Baker. Standards used for calibration were Accustandard®. The chlorpyrifos detection limit was 0.01 µg/L.

Statistical Analysis

Toxicity persistence was assessed by estimating the 50 % lethal time (LT₅₀) in each application replicate. Mortality data in each runoff event following pesticide application were used to estimate the LT₅₀ by means of a two-parameter log-logistic model. Slope and LT₅₀ (inflection point of the exposure-response curve) of each fitted curve were compared. All statistical analysis was performed using the drc (Analysis of Dose-Response Curves) package in R (Ritz and Streibig 2005). The significance level for all the applied tests was 0.05.

Suspended matter and chlorpyrifos concentrations at successive simulated rain events were fitted to exponential functions by a non linear estimation. Differences among treatments were assessed by means of or analysis of variance/covariance (ANOVA/ANCOVA).

Results

Table 1 summarizes the environmental variables measured since each application until runoff toxicity ceased. Measured variables did not show significant differences between applications (t test, solar radiation $p < 0.18$; wind speed $p < 0.51$; air temperature $p < 0.97$; soil temperature $p < 0.52$).

Soil organic carbon at the end of the growing period was significantly higher in the no-till (2.2 %) than in the conventional (1.8 %) management practice (t test, $p < 0.05$).

Conductivity and pH in the runoff water of the simulated rain events did not show significant differences between treatments: range 8.2–8.5 and 702–808 $\mu\text{S}/\text{cm}$, respectively. Suspended matter in runoff after the early application was significantly higher in the conventional than the no-till treatment (ANCOVA, $p < 0.014$; Table 2). Suspended matter in each successive runoff event decreased with time since application fitting to exponential functions (no-tillage: $r = -0.98$, $p = 0.02$; conventional: $r = -0.91$, $p = 0.01$).

Toxicity Persistence After the Early Season Application

The chlorpyrifos concentrations in successive runoff events after the early season application did not show significant differences between treatments (ANCOVA, $p = 0.39$) and decreased with time following an exponential function

Table 1 Mean values of the environmental variables measured since each application until runoff toxicity ceased, following the early and late applications

	Solar radiation (Watt/m ²)	Wind speed (Km/h)	Air temperature (°C)	Soil temperature (°C)
Early-season application	5466	5.88	19.3	18.8
Late-season application	4795	6.34	19.2	18.4

Table 2 Mean suspended matter content (g/L) in successive runoff events after the early application ($n = 5$)

Days since application	No-till	Conventional seed
0	3.05 \pm 2.30	7.80 \pm 2.00
20	1.32 \pm 1.13	3.14 \pm 1.76
27	0.72 \pm 0.50	2.56 \pm 1.77
34	0.34 \pm 0.21	1.16 \pm 0.36
41	0.48 \pm 0.25	1.55 \pm 1.01
48	0.56 \pm 0.49	1.67 \pm 0.96

($r = -0.86$, $p = 5 \times 10^{-6}$; Table 3). Chlorpyrifos concentration in runoff from the control plots fell below the detection limit.

Hyalella curvispina mortality in successive runoff events following the early season application ceased 48 days after application (Fig. 1). Forty-one days after application, mortality was significantly higher in the no-till (93 %) than in the conventional treatment (30 %, t test, $p < 0.05$). Mortality in the runoff of the control plots were always below 10 %. The calculated LT_{50} was 44.5 days (95 % confident limit 43.7–45.3) for the no-till treatments and 38.8 days (37.6–39.9) for the conventional seeding treatment. Estimated LT_{50} s were significantly different ($p < 0.01$).

Chlorpyrifos toxicity to *H. Curvispina* in successive runoff events following the early application is shown in Fig. 2. Toxicity to *H. curvispina* was significantly higher in runoff from the no-till plots ($p < 0.01$).

Estimated chlorpyrifos LC_{50} to *H. curvispina* in standardized laboratory assays using moderately hard synthetic water expositions was 0.4 $\mu\text{g}/\text{L}$ (unpublished data).

Soil toxicity remained high (76–78 %) until 41 days after application, without significant differences between treatments (Fig. 1). Mortality in soil exposures in the control plots remained always below the 20 % acceptable limit (USEPA 2000).

Toxicity After the Late Application

Chlorpyrifos concentration in runoff (Table 4) fell below the detection limit 2 weeks after the late application, whereas in the early application chlorpyrifos was still detected 41 days after application (Table 3). No significant differences between treatments were observed (ANCOVA, $p = 0.3$). Chlorpyrifos concentration in runoff from the control plots fell below the detection limit.

Runoff toxicity to *H. curvispina* after the late-season application ceased 23 days after the application (Fig. 3), whereas in the early-season application toxicity ceased after 48 days (Fig. 1). Mortality in the runoff of the control plots was always <10 %. The calculated LT_{50} was 15.6 days (95.5 % confidence limit 14.6–16.5 days) for the no-till treatments and 21.6 days (confidence limit 20.2–22.9 days) for the conventional treatments. Differences were statistically significant ($p < 0.01$). The LT_{50} for the conventional treatment was significantly shorter in the late than the early-season application (ANOVA, $p = 0.0006$).

Chlorpyrifos toxicity to *H. Curvispina* in successive runoff events following the late application is shown in Fig. 4. Most measured concentrations produced either 0 or 100 % mortality. Only one sampling resulted in intermediate mortalities. Such limitation in the available data

Table 3 Chlorpyrifos concentrations ($\mu\text{g/L}$) in runoff water in successive simulated rain events following chlorpyrifos early application in conventional and no-tillage treatments

Days since application	No-till			Conventional		
20	1.4	3.1	1.7	2.9	0.9	0.2
34	0.1	0.12	0.13	0.14	0.08	0.09
41	0.3	0.08	<0.01	<0.01	<0.01	0.04
48	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

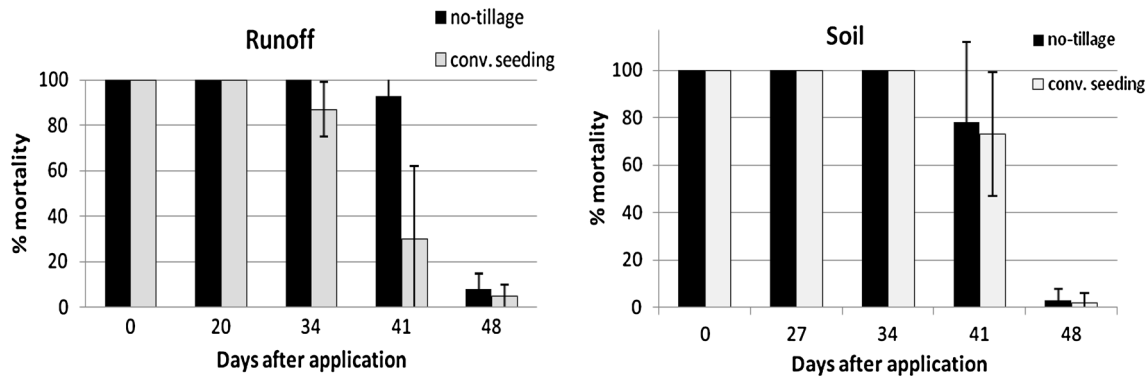


Fig. 1 Toxicity to *Hyalella curvispina* in runoff water and soil in successive simulated rain events following the early chlorpyrifos application ($n = 3$)

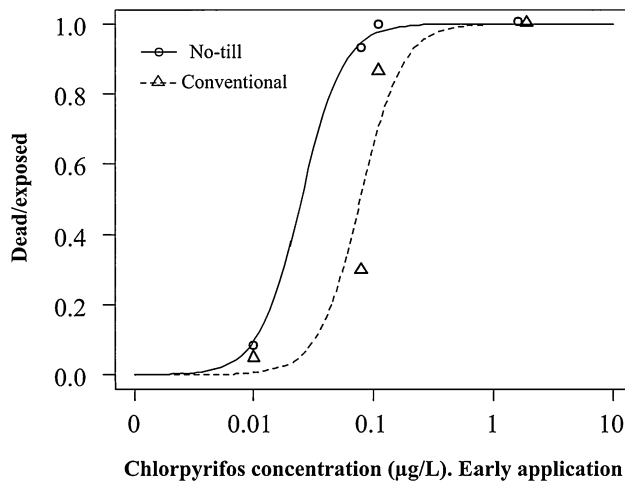


Fig. 2 Chlorpyrifos toxicity to *Hyalella curvispina* in runoff water from successive simulated rain events following the early chlorpyrifos application ($n = 3$)

Table 4 Chlorpyrifos concentrations ($\mu\text{g/L}$) in runoff water in successive simulated rain events following the late chlorpyrifos application in conventional and no-till treatments

Days since application	No-till			Conventional		
0	1.4	3.0	3.0	3.5	7.8	2.7
7	0.5	1.3	0.03	0.9	0.3	0.02
14	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

prevents estimation of significant differences between treatments.

Soil toxicity to *H. curvispina* was reduced to 15–30 % mortality 21 days after application (Fig. 3), whereas in the early application mortality remained at 70–75 % 41 days after application. No significant differences between treatments were observed. Mortality in soil exposures from the control plots remained always below the 20 % acceptable limit (USEPA 2000).

Discussion

Differences Between Application Timings

Application time influenced the persistence of toxicity in runoff: toxicity persisted longer after the early (Fig. 1) than the late (Fig. 2) application. Because measured environmental variables after each application were not significantly different (Table 1), they are not the cause of the observed differences in toxicity persistence. The applied chlorpyrifos settled on the soil surface in the early application and on the soy foliage in the late application. Being highly hydrophobic, chlorpyrifos absorbs to both soil and foliage. After the late application, a fraction of the pesticide washed out from the canopy was retained by the soil, explaining the observed soil toxicity in the first two sampling events (Fig. 3). Juraske et al. (2008) reviewed the reported degradation half lives of pesticides on plant and

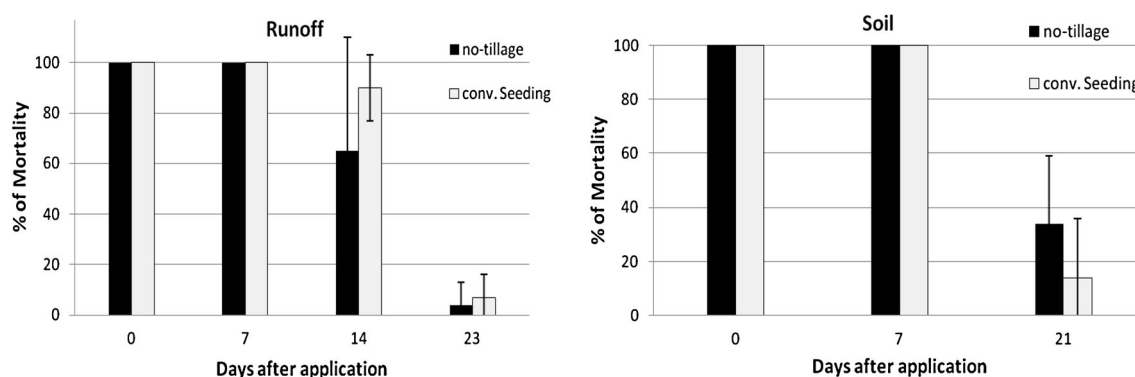


Fig. 3 Toxicity to *Hyalella curvispina* in runoff water and soil in successive simulated rain events following the late chlorpyrifos application ($n = 3$)

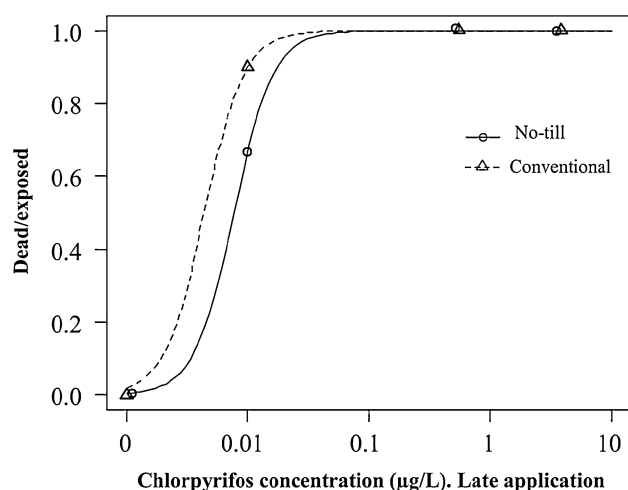


Fig. 4 Chlorpyrifos toxicity to *Hyalella curvispina* in runoff water in successive simulated rain events following the late chlorpyrifos application ($n = 3$)

soil surfaces and concluded that degradation was four times faster on plant surfaces. Volatilization, photodegradation, and plant uptake contributed to this pattern. Rude1 (1997) measured volatility on soil and plant surfaces for methyl parathion, endosulfan, fenpropimorph, lindane, and trifluralin in a wind tunnel. Pesticide volatility on plant surfaces was higher by factors of 5–13 than the respective volatility on soil surfaces. Kennedy et al. (2001) reported that the half-life of total endosulfan in foliage was about five times shorter than in soil. Meikle and Kurihara (1983) assayed an experimental approach to simulate chlorpyrifos loss rates from leaf surface measuring photodecomposition on and volatilization from an inert surface at 25 °C. Measured half lives were 3.2 and 0.3 days, respectively. Reported chlorpyrifos soil half lives are higher. Racke et al. (1990) reviewed literature data on chlorpyrifos dissipation determined in the laboratory ranging 10–120 days and measured half lives of 10–20 days in four different soils in laboratory

incubations. Chlorpyrifos dissipation ranged 7–15 days in four different soils incubated under green house conditions (Diaz-Diaz et al. 1995) and was reported as 10 days in citrus orchard soils under field conditions in a Mediterranean clay loam soil (Valencia, Spain, Redondo et al. 1997). Results in the present study are consistent with reported evidence in the literature suggesting that runoff and soil toxicity persistence was shorter in the late season application because of faster pesticide dissipation from the soy canopy.

Differences Between Conventional and No-Tillage Treatments

In the early-season application, toxicity persistence was longer in the no-till runoff (Fig. 1). Apparently higher chlorpyrifos concentrations in the no-till runoff were not statistically significant (Table 3). Chlorpyrifos sorption to the higher suspended matter content in the conventional tillage runoff might cause decreased chlorpyrifos bioavailability, as suggested by the lower toxicity of the conventional tillage treatment in the dose-response relationships (Table 2; Fig. 2). Yang et al. (2006a) studied the effect of suspended matter on the toxicity of four widely used pyrethroids (bifenthrin, cypermethrin, permethrin, and esfenvalerate) to *Ceriodaphnia dubia*. They assessed the LC_{50} of *C. dubia* in suspensions from four different sources: three bottom stream and one strawberry field furrow with concentrations of 0, 25, 50, 100, and 200 mg/L suspended matter. In all assays, LC_{50} values consistently increased with increasing suspended matter. The LC_{50} s in the 200 mg/L suspended matter were 2.5–13 times greater than those measured in sediment-free controls. Yang et al. (2006b) assessed *Daphnia magna* bioaccumulation of bifenthrin and permethrin in water samples containing suspended matter from different source sediments. Uptake of [^{14}C] bifenthrin and [^{14}C] permethrin by *D. magna* after 24-h exposure

consistently decreased with increasing levels of suspended solids in the range of 0–200 mg/L. The authors suggest that pyrethroids adsorbed on suspended matter were largely unavailable to water-column invertebrates.

Schulz and Liess (2001) compared the sublethal effects of aqueous phase and sediment-associated, short-term exposure of the caddisfly *Limnephilus lunatus* to the pyrethroid insecticide fenvalerate. Several toxicity assessment endpoints were assessed during a long observation period (240 days) following exposure: emergence success, emergence pattern, dry weight of adults, and production of biomass. Four different fenvalerate concentrations 0.001, 0.01, 0.1, and 1 µg/L were compared to the same amount of insecticide previously adsorbed to stream sediment resuspended in deionized water to attain a concentration of 5 g/L. The effects of exposure to fenvalerate were weaker for all the endpoints studied when it was associated with suspended particles. Thomas et al. (2008) showed that the toxicity of deltamethrin to the cladoceran *Ceriodaphnia dubia* and the freshwater shrimp *Paratya australiensis* was higher in Sydney tap water than in the Namoi river water with 25–30 mg/L suspended matter.

Although different alternative explanations are plausible, present evidence is consistent with the literature and suggests that chlorpyrifos sorption to suspended matter might have caused the observed shorter toxicity persistence in runoff from conventional than no-till management in the early application.

In the late application, by contrast, toxicity persistence in runoff was significantly longer in the conventional than in the no-till management practice. The causes of such differences remain conjectural. Because chlorpyrifos concentrations in successive runoff events were not significantly different between treatments, differential toxicity might be related to bioavailability. Soil organic matter was higher in the no-till treatment and the soil surface was covered by a conspicuous litter layer. It seems plausible that higher chlorpyrifos sorption to organic matter in the no-till treatment caused the observed shorter persistence. Bejarano et al. (2005a) found that natural dissolved organic matter (DOM) obtained from a salt marsh sediment significantly reduced the acute toxicity of chlorpyrifos to the estuarine copepod *Amphiascus tenuiremis* relative to copepods exposed in DOM-free seawater. Chronic exposures to chlorpyrifos caused reduced reproductive success of *A. tenuiremis*. DOM, however, mitigated the reproductive failure. Bejarano et al. (2005b) reported that natural forms of DOM, at environmentally realistic organic carbon concentrations, reduced chlorpyrifos uptake and bioconcentration in the bivalve *Mercenaria mercenaria*. Present results are consistent with reported evidence from the literature suggesting that chlorpyrifos sorption to the soil and litter organic matter might have caused the shorter persistence of toxicity in the no-till managerial practice in the late applications.

Conclusions

Commonly used crop management practices for soybean production resulted in runoff toxicity following pesticide applications and represent a toxicity risk for adjacent, nontarget inland water communities.

Toxicity persistence varies between application times during the soy growing period. Toxicity persistence in runoff remained longer after earlier applications performed over the almost bare soil than the later applications when the soy foliage covered the soil. Early applications performed over the bare soil should therefore be discouraged.

Toxicity persistence in runoff from the early applications was longer in the no-till than in the conventional management. By contrast, in the late application, toxicity persistence in runoff was shorter in the no-till management. The late application performed in the present study represent the most frequent condition and prevails longer throughout the soy growing season. Therefore, the no-till management practice seems preferable because shorter toxicity persistence in runoff represents a lower environmental risk for the adjacent inland waters.

Acknowledgments The authors thank the reviewers and the editor for their valuable comments. The authors thank the Argentine National Scientific and Technical Research Council (CONICET) and the National Agency for Scientific and Technological Promotion (ANPCYT) for their financial support.

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