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Assessment of insecticide contamination in runoff and stream water of small agricultural streams in the main soybean area of Argentina

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Abstract

The first- and second-order streams, Brown and Horqueta, respectively, which are located in the main area of soybean production in Argentina were examined for insecticide contamination caused by runoff from nearby soybean fields. The insecticides most widely used in Argentina (chlorpyrifos, cypermethrin and endosulfan) were detected in sediments, suspended particles and water. Highest concentrations in suspended particles were 318 μg/kg for endosulfan in the stream Horqueta, while 226 μg/kg chlorpyrifos and 13.2 μg/kg cypermethrin were measured in the stream Brown. In the Horqueta stream 150 and 53 μg/kg chlorpyrifos and cypermethrin were detected in runoff sediments, respectively. Whereas cypermethrin concentrations in the suspended particles were relatively low, levels in the floodwater of Brown reached 0.7 μg/l. The highest chlorpyrifos concentration in floodwater was 0.45 μg/l in Brown. However, endosulfan was not detected in the water phase. In runoff water the highest concentrations measured were 0.3 μg/l for chlorpyrifos in Horqueta and 0.49 μg/l for cypermethrin in the Brown stream. On five sampling dates during the pesticide application period in Brown stream (2002/2003) the concentration of chlorpyrifos and cypermethrin in runoff and/or floodwater exceeded the water quality criteria for freshwater mentioned in this study. In three cases this insecticide concentration was measured in stream water, indicating an acute risk to aquatic life. The acute toxicity–exposure-ratio (TER) for chlorpyrifos and cypermethrin also shows an acute risk for aquatic invertebrates in the Brown stream. In the Horqueta chlorpyrifos concentrations in the runoff exceeded the safety levels three times during the application period (2001/2002), potentially endangering the aquatic fauna. Effects on aquatic macroinvertebrates after insecticide contamination were reported in earlier studies in Horqueta stream.

Keywords: Risk assessment; Small streams; Insecticides; Runoff; Chlorpyrifos; Cypermethrin

1. Introduction

In intensively cultivated regions, streams are severely affected by the input of agrochemicals such as pesticides and nutrients, which often enter streams associated with

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soil particles as a result of erosion caused by edge of field runoff and from agricultural land (Cooper et al., 1993; Schulz, 2004). Runoff is one of the major sources of non-point pesticide contamination of streams (Wauchope, 1978). International monitoring programs such as the EU Water Framework Directive (WFD established in 2000, 2000/60/EG) may overlook the importance of non-point-source pollution in small streams. For instance, streams with a catchment area below 10 km^2 are not considered in the WFD.

Since 1997 transgenic soybeans have been planted in the province of Buenos Aires (Pengue, 2000), and the harvested area and the production of soybean is increasing. In the season 2002/2003 the USDA estimated a harvest of 33.5 million tons, an increase of 12% over the previous season. The harvested area increased by 10% to 12.5 million hectares in the same period. Soybeans are a low-cost choice compared to most other crops. The cost of production for soybean is US$ 100 per hectare versus US$ 200 per hectare for corn (FASonline, 2002). The continuous Argentine economic crises and the peso devaluation in 2001 made most farmers decide to plant soybean to deal with the uncertainties of the market. The comparatively low investment required for soybean production lowers the risk for farmers in an unstable economy. In the main Argentine soybean area the farmers use the direct seeding technique (minimal interference with the soil/no tillage) to prevent loss of the soil, because the rolling pampa is characterized by severe soil damage due to water erosion (Casas et al., 2000). In the main pesticide application period, from November to March, short and heavy rainfalls are very common in that region and cause intensive surface runoff. Together with the suspended soil, pesticides are transported to non-target compartments such as aquatic ecosystems.

With the use of transgenic soybean the pesticide market is increasing, mainly with respect to the product glyphosate for Roundup Ready® (RR) soybean. The farmers mix glyphosate with insecticide to produce a cocktail for application. Soybean is the crop accounting for the highest proportional percentage of the insecticide market. From 2000 to 2001 this proportion increased from 24% to 36% of 9 the amount of all insecticides sold (CASAFE, 2004). Cypermethrin, chlorpyrifos and endosulfan are the insecticides sold in the greatest amounts in Argentina. The market for endosulfan increased in two years (2000–2002) by 75% and cypermethrin by 160%, while the amount of sold chlorpyrifos increased slightly. As yet there have been hardly any studies dealing with levels of current pesticides in Argentine pampean streams.

The aim of this study is to characterize and assess aquatic exposure by the three most important current-use insecticides in the main soybean region of Argentina. As a route of entry into small streams, runoff was investigated here. However, spray drift from airplanes is also very common in this area with huge fields. These three insecticides are highly toxic to aquatic macroinvertebrates and fish, so it is possible that the concentrations of insecticides found in the streams may pose a risk for aquatic life. An assessment was made to compare concentration levels of in-stream insecticide with various water quality criteria based on no-effect concentrations for aquatic organisms.

2. Materials and methods

2.1. Study area

The two investigated streams are located near the villages Capitán Sarmiento (Horqueta) and Arrecifes (Brown) in the province of Buenos Aires, 150 km west of Buenos Aires. (In the following the abbreviation "Brown" and "Horqueta" is used for the Brown and the Horqueta streams, respectively.) Both streams are tributaries of the Rio Arrecifes (upstream the same river is called Rio Pergamino). They belong to the catchment area of the Rio Paraná. In the ecoregion of the rolling pampa the streams and rivers flow along small valleys, with a slow water velocity through extended sections of the streams and vegetated wetlands. The streams are located in the main soybean area of Argentina. Brown is a first-order stream with a catchment area of 70 ha. The whole catchment area is covered by a single soybean field. The characteristic parameters of the streams are given in Table 1. The hydrology of the streams can change dramatically during rainfalls. Brown reached a discharge of 0.23 m^3/s, more than 100 times greater than the average discharge, during a rainfall event of 17 mm/day lasting for 2 h. Horqueta is a second-order stream with a mean discharge of 0.15 m^3/s. After a rainfall event with 67 mm/day a peak discharge of 2.1 m^3/s was reached (14 times more than average). The catchment area consists of soybean fields around the sampling site and pasture and soybean fields upstream. Slopes of the nearby fields in the rolling pampa can reach 2–5% (Casas et al., 2000). Sites of runoff are indicated by erosion rills leading from the fields into the streams. The main application period for pesticide between November and April is characterized in this region by a few heavy rainfalls. In between there are dry periods lasting about one or two weeks.

2.2. Insecticide sampling

For the in-stream sampling of insecticides suspended particle samplers (Liess et al., 1996) and floodwater samplers (Schulz et al., 2001) were used. In the suspended particle sampler the fine suspended particles transported in the water phase of the streams were accumulated con-

Table 1
Characteristics of catchment areas and stream parameters of Brown and Horqueta about 150 km west of Buenos Aires

	Brown	Horqueta
Catchment area upstream of sample site (ha)	70	1000
Arable land in catchment (ha)	70	400
Mean slope (%) of fields adjacent to water body	1.5	3
Minimal buffer strip (m)	3	10
Average water depth (m)	0.2	0.4
Average streambed width (m)	0.5	3.5
Mean discharge (m^3/s) in low flow conditions	0.002	0.15
In-stream macrophytes coverage (%)	1	4
Oxygen content (mg/l)	9.4 ± 1.1	7.4 ± 2.5
Conductivity (μS/cm)	411 ± 60	870 ± 113
pH	8.0 ± 0.2	8.2 ± 0.4
NO_3^-–N (mg/l)	0.4 ± 0.3	1.1 ± 0.8
NO_4^+–N (mg/l)	0.02 ± 0.005	0.03 ± 0.03
Soluble reactive phosphate SRP (mg/l)	0.12 ± 0.2	0.15 ± 0.14

tinuously. The samplers consist of 3 l glass bottles firmly attached to metal stakes, were installed at each sampling site on the bottom of the streams with an inlet (opening: 10×3 mm) and an outlet pipe. They remained in the streams during the whole sampling period and were emptied and replaced once a week. The fine suspended particles of one week were used for the insecticide analysis. The suspended particles in the stream water were retained with an efficacy for the grain-size fraction below 0.02 mm averaging 50% at 0.05 m s^{-1} and 15% at 0.41 m s^{-1} flow velocity (Liess et al., 1996). In the sampling period from 22.02.01 to 07.04.01 lasting for six weeks in the Horqueta stream, six suspended particles samples were taken. In one of the six samples, endosulfan was detected. In the sampling period from 02.01.02 to 20.02.02 (eight weeks) in Horqueta eight samples were taken and in three of them chlorpyrifos were measured.

The sampling period in Brown lasted from 10.12.02 to 13.02.03. During this time nine samples of suspended particles were taken weekly. On four occasions insecticides were detected.

The floodwater samplers consisted of glass bottles, which were installed attached on sticks at each sampling side in the stream. When installing the bottles the neck were adjusted 10 cm above the water surface, so that the bottle was filled as a result of the rising water level during a runoff event. Bottles were recovered and replaced after every runoff. Three runoff events occurred during the first sampling period (22.02.01 to 07.04.01) and three events during the second sampling period (02.01.02 to 20.02.02) in Horqueta with concentrations of the investigated insecticides in the floodwater below the detection limits. In the sampling period of Brown (10.12.02 to 13.02.03) six runoff events occurred. On two rainfalls (09.01.03 and 16.01.03) with 12 and 17 mm/day, respectively, no clear runoff was observed and no floodwater and runoff sediment samples were obtained. On the 16.01.03 a sample of runoff water was recovered.

Sediment samples were taken at the bottom of the streams with a cylindrical corer. The first three centimeters of the surface layer were used for the analysis. These samples were taken additionally in Brown after the application of chlorpyrifos.

2.3. Edge of field sampling

During rainfalls and runoff events, insecticides are transported with rainwater and soil particles from the fields into the streams. Runoff samplers installed at the edge of the agricultural fields in erosion rills collected samples of sediment and water during a runoff event (Schulz et al., 1998). The samplers consist of 3 l glass bottles buried in the soil up to their necks at the edge of agricultural fields, adjacent to the surface water of the streams. After a rainfall event the samplers were removed and samples of the sediment and the water were analyzed separately. In the first sampling period of Horqueta the concentration of the investigated insecticides were below the detection limits. In the second sampling period of Horqueta in all three runoff events insecticides were detected in the water and in the sediment samples. In Brown insecticide were detectable in four runoff events in the runoff water. In the runoff sediment only on two occasions (one sample was lost) insecticides were detected.

2.4. Analytical procedures

Suspended particles, runoff sediment and bottom sediment samples were extracted twice with 50 ml methanol in an ultrasonic bath for 30 min and then passed through C18 columns (Bakerbond, solid phase extraction) and frozen until analysis. Runoff water and stream water samples were passed directly though the columns. Extracts were eluted from C18 columns with 2 ml hexane followed by 2 ml dichloromethane. The sample extracts were injected into a gas chromatograph fitted with standard electron-capture and flame photometric detectors, following methods described in Schulz et al. (2001). Detection limits were as follows: for chlorpyrifos, α- and β-endosulfan 2 μg/kg, 0.01 μg/l and α-cypermethrin 5 μg/kg, 0.05 μg/l, for sediments and water samples, respectively. Surface stream water samples were collected in bottles filled by hand for chemical analysis. Nitrate, ammonium and soluble reactive phosphorus concentrations in the stream water were determined by standard methods (APHA, 1985).

2.5. Risk assessment

In order to assess the level of insecticide contamination in pampean streams, the peak concentrations measured in water and sediment of Brown and Horqueta are compared (Table 4) with toxicity data for standard test organisms (*Daphnia magna* and *Oncorhynchus mykiss*) and water quality criteria (US EPA, 1986; CCME, 1999; Brock et al., 2000; EU 91/414/EEC). Additional LC_{50} values for scuds (Amphipoda) were included, because the amphipod species *Hyallela curvispina* appears abundantly in the streams in this region (Jergentz et al., 2004b) and they represent a group of species very sensitive to both insecticides chlorpyrifos and cypermethrin. For all the insecticides studied here this value represents the lowest concentration level. Furthermore, the toxicity–exposure-ratio (TER) was calculated with the LC_{50} of the most sensitive species (Table 4) and the peak concentration of chlorpyrifos and cypermethrin measured in floodwater in Brown. To apply the approach of Brock et al. (2000), $NOEC_{eco}$ or $LOEC_{eco}$ derived from long-term micro- or mesocosm studies were calculated. The resulting threshold levels are suggested as the most realistic water quality criteria because the calculation is based on the most complex study of the ecosystem. No data were available with which to derive quality criteria for the insecticides in sediment; therefore only a comparison with literature data was made for the sediments.

3. Results

Storm events with precipitation from 12 up to 184 mm/day produced edge-of-field runoff in the studied streams. The amount of rainfall seemed to play no major role in the intensity of insecticide contamination. No correlation was found between precipitation and contamination (not illustrated). Other factors, such as elapsed time between application and rainfall event or soil moisture, most likely do influence the concentrations found in the streams.

In runoff samples in Brown (Table 2) chlorpyrifos concentrations of 30.3 μg/kg in sediment and 0.28 μg/l in the runoff water were detected. Higher concentrations of 63 and 225.8 μg/kg were measured in the suspended particles during a period with two rainfall events of 67 and 13 mm/day, respectively. The concentrations in stream water were 0.21 and 0.45 μg/l for the same rainfall events, the latter value being even higher than the concentration in the runoff water. Bottom sediments showed nearly the same concentrations as suspended particles and lower concentrations of chlorpyrifos than the runoff sediment.

Chlorpyrifos was measured in runoff sediment of Horqueta in concentrations ranging from 15 to 150 μg/kg (Table 3). The associated runoff water samples showed concentrations from 0.07 to 0.3 μg/l. The concentrations in suspended particles (7.7 and 11 μg/kg) were much lower than those found in runoff sediment. The highest concentration of chlorpyrifos in the suspended particles (64 μg/kg) was measured in a period without rainfall, so that spray drift was probably the route of entry. Throughout the sampling period the concentrations of insecticides in the floodwater were below detection limits. Higher concentrations of 63 and 225.8 μg/kg were measured in the suspended particles during a period with two rainfall events of 67 and 13 mm/day, respectively. The concentrations in stream water were 0.21 and 0.45 μg/l for the same rainfall events, the latter value being even higher than the concentration in the runoff water. Bottom sediments showed nearly the same concentrations as suspended particles and lower concentrations of chlorpyrifos than the runoff sediment.

Cypermethrin was observed in Horqueta (Table 3) only in runoff sediments with concentrations from 13 to 53 μg/kg. The concentrations in runoff and floodwater were below the detection limits. As in the case of Horqueta, the highest concentration of cypermethrin measured in Brown (Table 2) was measured in runoff sediment, with 20.8 μg/kg being detected. In the suspended particles the concentration was slightly lower, 4.4 and 13.2 μg/kg. In runoff water concentrations from 0.1 to 0.49 μg/l were detected, and those found in stream water during runoff were even higher, 0.54 and 0.71 μg/l.

Endosulfan was found to be bonded to suspended particles or sediment in Horqueta. In Brown the insecticide was not applied during the sampling period and no residues from earlier sprayings were detectable. The highest concentration was detected in suspended particles of Horqueta, namely 318 μg/kg (Table 3), after a rainfall event of 184 mm/day on 1/3/2001. It was also present in runoff sediment, but in lower concentrations.

In Table 4 various criteria are given for evaluating the highest concentrations of the insecticides investigated here that would be safe for aquatic life in freshwater. Brock et al. (2000) calculated the $NOEC_{eco}$ (no observable effect concentration in the ecosystem) and $LOEC_{eco}$ (lowest observable effect concentration in the ecosystem) for several insecticides from (semi) field experiments. In Table 4 the $NOEC_{eco}$ for chlorpyrifos (0.1 μg/l) and the $LOEC_{eco}$ for cypermethrin ($\leqslant$0.07 μg/l, Farmer et al., 1995) were divided by 10 following the procedure in an environmental risk assessment (ERA) where 10 served as a safety factor with NOECs (EU 91/414/EEC). As a first step of an environmental risk assessment (EU 91/414/EEC) the concentration that is safe for the whole aquatic population is calculated by dividing the lowest LC_{50} by 100 to obtain the concentrations of the compound at which no effects on the organisms could be expected. As in the approach of Brock et al. (2000), the EU

Table 2
Current-use insecticide concentrations in in-stream samples (suspended particles and floodwater) and edge-of-field samples (samples of water (runoff water) and sediment (runoff sediment) before the runoff enters the stream) from Brown during the sampling period 10.12.02–13.02.03

Type of sample	Sampling date	Rain (mm/day)	α-Cypermethrin	Chlorpyrifos
In-stream sampling				
Suspended particles (μg/kg)	17.12.02	57	4.4	<3
	26.12.02	35	Sample lost	
	09.01.03	12	<3	13.3
	16.01.03	17	13.2	17.01
	16.01.03	17	<3	9.0
	23.01.03	67/13[a]	<3	63.0
	23.01.03	67/13	<3	225.8
Floodwater (μg/l)	17.12.02	57	0.16	ND
	26.12.02	35	0.71	ND
	26.12.02	35	0.54	ND
	09.01.03	12	No sample	
	16.01.03	17	No sample	
	23.01.03	67/13	0.05	0.45
	23.01.03	67/13	<0.05	0.21
Bottom sediment (μg/kg)	11.01.03	12	<3	12.8
	14.01.03	12	<3	13.5
Edge-of-field sampling				
Runoff sediment (μg/kg)	17.12.02	57	9.7	ND
	26.12.02	35	<3	<3
	09.01.03	12	No sample	
	16.01.03	17	No sample	
	23.01.03	67/13	20.8	30.3
Runoff water (μg/l)	17.12.02	57	0.16	ND
	17.12.02	57	0.1	ND
	26.12.02	35	0.49	ND
	09.01.03	12	0.13	0.09
	16.01.03	17	No sample	
	23.01.03	67/13	<0.05	0.28

Alpha-cypermethrin was applied on the 28.11.02 and chlorpyrifos had two application dates on the 09.01.03 and 10.01.03 (the application was stopped because of the rain on the 09.01.03). In samples taken after the 29.01.03 all concentration of both insecticides were below the detection limit. At the sampling on the 09.01.03 and 16.01.03 no floodwater and runoff sediment sample were obtained because of the small rainfall amount with 12 and 17 mm/day. Runoff water were obtained on the 09.01.03. On some sampling dates two independent samples were available (suspended particles 16.01.03 and 23.01.03, floodwater 26.12.02 and 23.01.03, runoff water 17.12.02) Bottom sediment samplers were taken additionally after the application with chlorpyrifos. The peak concentrations in Brown were compared with water quality criteria in Table 4.
ND = not detected.
[a] In the sampling period 16.01.03–23.01.03 two runoff events occurred.

uniform principles are based on (semi) field tests and on (eco)toxicological standard tests, whereas the EPA quality criteria for water and the CCME guideline represent national regulations for chemicals in freshwater. However, on two dates the concentrations of chlorpyrifos and on four dates the concentrations of cypermethrin in the sampling period 2003 were higher than all water quality criteria (Table 4) in runoff- and/or stream water of Brown (Table 2). In runoff water of Horqueta on three occasions in the sampling period 2001/2002 the concentration of chlorpyrifos exceeded all the above-mentioned water quality criteria (Table 3). For an exposure assessment the acute toxicity–exposure-ratio (TER) was calculated for chlorpyrifos and cypermethrin with the peak concentrations in Brown as a worst case scenario and with the LC_{50} of the most sensitive organism from Table 4 following Crane et al. (2003). A risk is indicated when the acute TER value is below 100, which is the case for chlorpyrifos (0.22) and for cypermethrin (0.13). No endosulfan 1 concentration in water was found during the sampling period. Therefore a calculation 2 of the TER was not possible.

Table 3
Current-use insecticide concentrations in in-stream samples (suspended particles) and edge-of-field samples (samples of water (runoff water) and sediment (runoff sediment) before the runoff enters the stream) in Horqueta during the sampling period 2001 and 2002

Type of sample	Sampling date	Rain (mm/day)	Chlorpyrifos	α-Cypermethrin	Endosulfan (α and β)
In-stream sampling					
Suspended particles (μg/kg)	05.03.01	184	ND	ND	318
	05.03.01	184	ND	ND	30
	08.01.02	94	7.7	ND	ND
	23.01.02	0	64	ND	ND
	29.01.02	34	11	ND	ND
	07.02.02	85	ND	ND	ND
Edge-of -field sampling					
Runoff sediment (μg/kg)	08.01.02	94	150	46	7.8
	23.01.02	0		No sample	
	29.01.02	34	43	53	ND
	07.02.02	85	15	13	ND
Runoff water (μg/l)	08.01.02	94	0.3	ND	ND
	23.01.02	0		No sample	
	29.01.02	34	0.09	ND	ND
	07.02.02	85	0.07	ND	ND

Floodwater samples were not obtained for this stream. The application dates of the insecticides were not known and only sampling dates with insecticides contents are shown. In the sampling period 2001 only one runoff event with an endosulfan input into Horqueta appeared (two independent samples were obtained). Three runoff events occurred in the sampling period 2002. In the week before the 23.01.02 no rain fell, so that there was not corresponding sample in the edge-of-field sampling.
ND = not detected.

Table 4
Measured peak concentrations of chlorpyrifos, cypermethrin and endosulfan in water and suspended particles in Brown and Horqueta as well as acute toxicity data for *Daphnia magna*, different species of scuds and the rainbow trout (*Oncorhynchusmykiss*)

	Chlorpyrifos	Cypermethrin	Endosulfan
Peak conc. in water in Brown	0.45 μg/l	0.71 μg/l	ND
Peak conc. in suspended particles Brown	225.8 μg/kg	13.2 μg/kg	ND
Peak conc. in suspended particles Horqueta	64 μg/kg	ND	318 μg/kg
Acute toxicity in standard tests (μg/l)			
Daphnia magna 48 h LC_{50}	0.6[a]	1.0[c]	62.0[f]
Scud	0.1[a]	0.09 [d]	0.43[g]
Rainbow-trout 96 h LC_{50}	7.1[b]	0.5[e]	0.3[f]
Water quality criteria (μg/l)			
Ecologically acceptable concentration based on meso/microcosm studies Brock et al. (2000)	0.01	⩽0.007	–
EU uniform principles 91/414/EEC	0.001	0.0009	0.003
US EPA Quality criteria for water (1986)	0.041[h]	–	0.056[i]
Canadian environm. quality guidelines CCME (1999)	0.0035	–	0.02
Exposure assessment in Brown			
TER acute	0.22	0.13	–

ND = not detected.
[a] 48 h LC_{50} *Daphnia magna* and *Hyalella azteca* (Moore et al., 1998).
[b] Johnson and Finley (1980).
[c] Hill (1989).
[d] 24 h LC_{50} *Gammarus pulex* (Shires, 1983).
[e] Stephenson (1982).
[f] Schoettger (1970).
[g] 96 h LC_{50} *Gammarus palustris* (Leight and van Dolah, 1999), EPA quality criteria for water.
[h] 4 days average.
[i] 24 h average.

4. Discussion

In Brown the application date of cypermethrin and chlorpyrifos were known, so that it was possible to follow the fate of the two insecticides in the edge-of-field runoff and in the aquatic environment. Cypermethrin was detectable in the suspended particles until seven weeks and in runoff sediment until eight weeks after the field application of the insecticide. In floodwater the highest and latest detectable concentration of cypermethrin were measured four weeks after the application. In runoff water the period from the application until the last detection lasted six weeks. Chlorpyrifos was detected in all investigated compartments (in stream and edge of field sample) until two weeks after the field application. It seems that physical properties influence the presence of the insecticides in the different compartments such as water and sediment. No correlation was found between the amount of rain and the insecticide concentration in the stream, as it is uncertain as to whether the sampling method collects samples that represent the peak concentration of a substance. In Brown, the stream with the smaller catchment, the concentrations in runoff water and floodwater were similar. It seems that no dilution took place and the floodwater was mainly the runoff water that came from the field. In the following the insecticide concentrations are discussed with the aim to come to a risk assessment of the single compound and to assess their impact to aquatic life.

4.1. Chlorpyrifos

In this study the highest floodwater concentration of chlorpyrifos was 0.45 μg/l and the highest concentration in the suspended particles was 225.8 μg/kg in Brown. In the sampling period 2002/2003 the concentration of chlorpyrifos in water (runoff and stream, Table 2) on two sampling dates exceeded the water quality criteria given in Table 4. In Horqueta in the sampling period 2001/2002 (Table 3) the quality criteria in Table 4 were exceeded on three sampling dates in runoff water, with a peak concentration of 0.3 μg/l, while in the stream chlorpyrifos concentrations were below the detection limit. For chlorpyrifos in Brown the peak concentration in the stream was higher than the LC_{50} for *Hyalella azteca* (Table 4) and the discrepancy between measured concentration and acceptable concentration for no effects to aquatic life varied from 11- to 450-fold higher in-stream. Horqueta has a much bigger discharge than Brown, so it appears likely that the dilution of the runoff water was much greater and hence the potentially available chlorpyrifos concentrations were much lower in the stream water. Chlorpyrifos was found bound to soil particles in high concentrations in both streams: 225.8 μg/kg in suspended particles after runoff in Brown, and 150 μg/kg in the runoff sediment in Horqueta. In Horqueta a concentration of 64 μg/kg was found in the suspended particles during a period without rain, which was most likely caused by a spraying aircraft (Jergentz et al., 2004b). A 100% mortality in in situ bioassays of *H. curvispina* and *Macrobrachium borelli* was observed during this event. In other agricultural areas even higher concentrations were found after runoff and spray drift. In a section of the Lourens River in South Africa with a small catchment size of 15–100 ha, chlorpyrifos concentrations from 0.01 to 1.3 μg/l were reported by Dabrowski et al. (2002), Moore et al. (2002) and Schulz (2001). These results correlate well with the concentration levels measured in Brown during runoff. In a larger-scale catchment of 15,000 ha, in a creek channel in California Hunt et al. (2003) measured concentrations up to 3.2 μg/l. Schulz et al. (2001) detected a concentration in suspended sediment samples of 344.2 μg/kg in the Lourens River, South Africa. The concentration in stream water of Brown was 11-fold higher than the continuous peak concentration specified by the US quality criteria for water (US EPA, 1986) and 100-fold more than the Canadian environmental quality guidelines for aquatic life in 9 freshwater (CCME, 1999). Moore et al. (1998) reported a 48-LC_{50} for *Hyalella azteca* of 0.1 μg/l (Table 4) and 0.3 μg/l for *Chironomus tentans*. Green and Chandler (1996) reported a sediment LC_{50} 96 h of 68 μg/kg for the benthic copepod *Amphiascus tenuiremis*. All in all, chlorpyrifos concentrations in stream water and sediment in Brown reached a toxic level for stream invertebrates as indicated by the TER.

4.2. Cypermethrin

The pyrethroid cypermethrin has the lowest threshold level in the EU uniform principles as well as the lowest ecological acceptable concentration based on the (semi) field studies by Brock et al. (2000) of the insecticides investigated here (Table 4). In this study the highest concentration in floodwater was detected in Brown, 0.7 μg/l. The concentrations in the floodwater were slightly higher than those in the runoff water. As discussed before, this results from the small catchment area of Brown. During a runoff event the floodwater consists mainly of runoff water and dilution could therefore be neglected. In the sampling period 2002/2003 on four sampling dates (Table 2) the cypermethrin concentration exceeded the water quality criteria (Table 4) in runoff and/or stream water. For cypermethrin the peak concentration in the stream was higher than the LC_{50} for the amphipod *Gammarus pulex* and rainbow trout (Table 4). Compared with various guidelines and freshwater criteria, the peak concentration of cypermethrin was 100- to 790-fold higher than the concentrations considered safe for aquatic organisms. Cypermethrin was detected in lower concentrations in both suspended particles and sediment than were the other two insecticides.

Of the three insecticides, cypermethrin has the highest K_{oc}-value which means that it has a tendency to be more strongly bound to soil particles. The risk for aquatic life, according to the following studies, is high in Brown. Brock et al. (2000) reported a pronounced long-term effect based on a mesocosm study by Hill (1985) employing a runoff simulation, in which a concentration of 0.16 μg/l was applied twice in a 7-day interval. In the study of Hill (1985) a severe reduction of amphipods and isopods with a recovery time of more than 48 weeks was observed. A slight effect was reported for ephemeropterans and dipterans, with a recovery time within three weeks. As a safe concentration for surface water without effects on aquatic life, Brock et al. (2000) calculated a $LOEC_{eco}$ of $\leqslant$0.07 μg/l, based on mesocosm studies of Farmer et al. (1995). Stephenson (1982) detected an EC_{50} 2 h of 0.08 μg/l with the amphipod *Gammarus pulex*. Clark et al. (1989) found sediment toxicity of cypermethrin, with mortality rates from 28% of grass shrimp and 85% of mysids following exposure to a sediment concentration of 100 μg/kg in 4 days static test systems. In a more realistic runoff scenario Maund et al. (2002) investigated the effect of cypermethrin in three aquatic sediments varying in organic carbon content (1–13%). He found LC_{50} 10 days of 3.6 to 23 μg/kg for *Hyalella azteca* and 13 to 62 μg/kg for *Chironomus tentans*. As was shown for chlorpyrifos, the cypermethrin concentrations in stream water in Brown reached toxic levels for aquatic life (TER), indicating that environmental risk is presented by both insecticides.

4.3. Endosulfan

The organochlorine insecticide endosulfan was present only in Horqueta, because it was not applied in the catchment of Brown during the sampling period. In the following the concentrations are compared with data from the literature but no assessment of the risk is made. The highest concentration of endosulfan, 318 μg/kg, was found during the present study in suspended particles from the flood sampler in Horqueta. Schulz (2001) reported total endosulfan (α, β, S) concentrations associated with suspended particles during runoff in the range of 179–12 082 μg/kg and water concentrations from 0.03 to 0.16 μg/l in the Lourens River of South Africa, which is surrounded by orchards and had a catchment size of 9200 ha. In the same river system but, in smaller catchments of 15–100 ha Dabrowski et al. (2002) detected concentrations ranging from 9.7 to 273 μg/kg in suspended particles. Following spray application, Wan et al. (1995) measured endosulfan concentrations in farm ditch sediments in Canada with a catchment size of 1–12 km^2 ranging from 5 μg/kg to 2461 μg/kg. Leonard et al. (2000) measured up to 48 μg/kg of total endosulfan in sediments of the Namoi River, Australia. Potential effects of insecticide levels reported in the present study on macroinvertebrate dynamics in the streams were shown by Leonard et al. (2000) and Jergentz et al. (2004a).

4.4. Potential risk presented by runoff in the two streams

In the sampling period 2002/2003 in Brown the safety criterions (Table 4) for chlorpyrifos and cypermethrin were exceeded on five sampling dates for runoff water. Following three of the runoff events the concentration in stream water of these insecticides was also higher than the water quality criteria. It can be assumed that there was a potential risk for aquatic life on five occasions during the application period. An acute exposure of aquatic organisms to insecticides could be assessed for a minimum of three runoff events in which insecticide concentrations were detected in-stream. The peak concentrations of insecticides in Brown were used to exemplify the first step of an ERA following the EU guidelines (91/414/EEC). In the standard FOCUS procedure predicted environmental concentrations (PEC) are calculated by computer simulation. In this study we can use real concentrations from field measurements for the toxicity–exposure-ratio (TER). The TER value indicates, according to the first tier in an environmental risk assessment procedure, a risk to aquatic life in Brown in the cases of chlorpyrifos and cypermethrin. For all the standard test species in Table 4 the TER values for chlorpyrifos and cypermethrin were below 100, the uncertainty factor for acute exposure. This means, in the procedures of an environmental risk assessment, that further studies are required for risk investigation. However, endosulfan was not used during the study period in the catchment of Brown so that no statement could be made about the potential risk of this compound.

In the sampling period 2001/2002 in Horqueta the concentration of chlorpyrifos in runoff water on three sampling dates exceeded the water quality criteria for aquatic life (Table 4). Given this exposure to insecticide, a potential risk could be inferred for this stream. The concentrations in suspended particles suggested transient insecticide pollution in Horqueta. Effects on aquatic macroinvertebrates were suspected by Jergentz et al. (2004a), who described the relationship between runoff-related endosulfan contamination and decrease of Odonata and Ephemeroptera species as well as an increased drift of aquatic macroinvertebrates in this stream.

5. Conclusion

There is reason for concern about the insecticide pollution of Brown in the Argentine pampa when the current standard risk assessment scheme (in the EU) is applied. Mitigation measures need to be implemented to reduce input of insecticides into this stream via runoff. The farming practice has to be reviewed according to potential risk to nearby water resources. Further studies on these effects, such as explained by Jergentz et al. (2004a,b), should be carried out on the catchment level to investigate risk of insecticide contamination in this region under intensive agricultural use.

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