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RAINFALL-INDUCED SEDIMENT AND PESTICIDE INPUT FROM ORCHARDS INTO THE LOURENS RIVER, WESTERN CAPE, SOUTH AFRICA: IMPORTANCE OF A SINGLE EVENT

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Abstract—Rainfall-induced runoff transported sediments and pesticides into the Lourens River and its tributaries during a 28.8-mm rainstorm in mid-December 1998. Average 1-h peak levels of current-use insecticides applied to adjacent orchard plots were $1.5 \mu\text{g l}^{-1}$ azinphos-methyl, $0.2 \mu\text{g l}^{-1}$ chlorpyrifos and $2.9 \mu\text{g l}^{-1}$ total endosulfan (α , β , S) in the river itself. Respective average 1-h pesticide levels associated with suspended particles were 1247, 924 and $12082 \mu\text{g kg}^{-1}$, along with $980 \mu\text{g kg}^{-1}$ of prothiofos. Total suspended solids increased during runoff from 32 to 520 mg l^{-1} . The contaminated edge-of-field runoff entered the river via the tributaries directly bordering the orchard-growing areas. Increased concentrations of azinphos-methyl and prothiofos associated with suspended sediments were demonstrated to persist for about 3.5 months without any further input in one of the tributaries. This illustrates that the short-term exposure has the potential to result in long-term contamination of surface waters. In terms of chemical load during the 1-h peak discharge period, the single rainfall event caused a loss of 173 g h^{-1} azinphos-methyl, 55 g h^{-1} chlorpyrifos, 740 g h^{-1} total endosulfan (α , β , S) and 41 g h^{-1} prothiofos. Levels of contamination were extremely high; they exceed the national water quality standards and those established by the US EPA. A comparison with standard toxicity data and 24-h LC_{50} s for the local amphipod species *Paramelita nigroculus*, obtained during this study, indicates that the concentrations found in the river may result in acute toxic effects on aquatic invertebrates and fishes. A probability analysis of 10-y rainfall data revealed that the frequency of a similar storm event occurring within the main spraying season is 1.7 y^{-1} .
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Key words—edge-of-field runoff, insecticides, nonpoint-source pollution, orchards, toxicity

INTRODUCTION

Runoff and spraydrift are the major mechanisms for transporting pesticides from orchards and fields into rivers. Pesticide application in orchards of the Western Cape coincides with periods of high rainfall. It follows that a better understanding of the input and effects of pesticides is needed. Factors that influence the runoff of pesticides include timing of application relative to rainfall, total amount of rainfall and physicochemical properties of the particular pesticides being used (Wauchope, 1978). In this study, the importance of a single heavy rainfall event occurring within the spraying season was investigated with regard to pesticide and sediment input.

Only a few studies deal with pesticide levels in aquatic systems of farm dams, lakes or river ecosystems in South Africa (Davies and Peall,

1997). None of these studies have attempted to establish a direct link between current-use chemicals in agriculture and contamination of the aquatic environment. Moreover, they have not addressed the problem of spraydrift or runoff as potential routes of entry into freshwater ecosystems. A factor that has contributed to the lack of research is the shortage of laboratories with the equipment and expertise to carry out complex analyses. The transient character of pesticide peak levels in streams (Schulz *et al.*, 1998) adds a further problem to monitor pollution, since the sampling programme must be well adapted to include the short periods with peak contamination.

During recent decades a shift to lower water quality in Western Cape rivers has been observed. This shift has also occurred in the middle and lower reaches of the Lourens River, and is attributed to intensified agriculture, erosion problems and loss of indigenous vegetation (Tharme *et al.*, 1997). No information is available regarding the extent to which toxic substances are responsible for the degradation of the Lourens River.

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The aim of this study was to determine the contamination of a typical Western Cape stream and its tributaries with pesticides and sediments from the surrounding orchard areas. Runoff-related input following a heavy rainfall event within the dry season was studied with the emphasis on long-term contamination. Toxicity tests with a local amphipod species were undertaken in order to assess potential toxicological effects.

MATERIALS AND METHODS

Study area

The Lourens River originates at an altitude of 1080 m in a naturally vegetated fynbos area and flows in a southwesterly direction for approximately 20 km before discharging into False Bay at Strand (S34°06'; E18°48'). The catchment is characterized by an intensive farming area with orchards and vineyards in its middle reaches. The Lourens River has a total catchment area of approximately 92 km² and receives an annual mean rainfall of 915 mm. Approximately, 87% of its 35 × 10⁶ m³ mean annual discharge occurs during winter between April and October (Tharme *et al.*, 1997), as is characteristic of the region's Mediterranean climate. The main soil type is silty loam.

The orchards mainly consist of pears, plums and apples (total growing area: 4 km²), with pesticide application taking place between early August and early March before fruit harvest. Pesticide active ingredients applied to the orchards and analysed in this study include the fungicide procymidone and insecticides endosulfan, chlorpyrifos, azinphos-methyl, permethrin, fenvalerate, deltamethrin, prothiofos and β -Cyfluthrin. Of all these substances, chlorpyrifos and azinphos-methyl were applied between

October and February quite frequently to pears and plums approximately one application every fortnight on each single plot (Table 1). Endosulfan is applied mainly to apples. The fungicides captab, benomyl, mancozeb and penconazol as well as the insecticides flufenoxuron, vamidothion, cyhexatin and fenthion are occasionally used and were not included in the analytical procedure.

Sampling sites and rainfall event characteristics

The sampling area comprised a stretch of approximately 6 km of the Lourens River and its tributaries running between the farms on both sides. The orchard plots are separated from the Lourens River by a strip of vegetation (eucalyptus trees, shrubs and grasses) between 20 and 100 m in width, making direct input of edge-of-field runoff into the river highly improbable. In contrast, most of the tributaries are, at least in some stretches, directly adjacent to orchard plots (distance: about 5 m). Seven sampling sites were chosen (Table 2). Two of the seven sampling sites were assumed to be uncontaminated (LR1 and T1), owing to the lack of any agricultural activity on the banks upstream of these river and stream sections. The remaining five sites were expected to be potentially contaminated with sediments and pesticides from orchards and a nursery (Table 2). The slope in the orchard growing area surrounding T1, T3 and T5 is <2%, while the upper stretches of T2 and T4 have slopes up to 5%. Apart from the tributaries monitored in this study there are four other tributaries that were not sampled. Most of them are dry during summer and discharge into the Lourens River only during rainfall events.

A heavy rainfall event commenced at 3 p.m. on December 14, 1998 and continued until 8 a.m. on December 15, 1998. Total rainfall during this event was 28.8 mm d⁻¹, of which approximately 80% occurred in an initial period between 3 and 9 p.m. on December 14, 1998. The last rainfall before this date had been 2.2 mm d⁻¹ on December 7, 1998 and the last heavy rainfall (≥ 10 mm d⁻¹) occurred

Table 1. Characteristics of important current-use pesticides: water solubility, amount of pesticides applied to orchards between August and February in the Lourens River catchment upstream site LR2 (growing area: 400 ha) and toxicity to standard test organisms *Oncorhynchus mykiss* (LC₅₀) and *Daphnia magna* (EC₅₀)

Pesticide name	Water solubility at given temp. (mg l ⁻¹) ^a	Amount applied (kg) ^b	Acute toxicity (μ g l ⁻¹) ^c	
			Rainbow trout	Water flea
Azinphos-methyl	28 (20°C)	771	4.3 (96 h)	1.6 (48 h)
Chlorpyrifos	1.2 (25°C)	686	9 (96 h)	0.42 (48 h)
Endosulfan	0.32 (22°C)	158	0.3 (96 h)	250 (48 h)
Prothiofos	1.7 (20°C)	87	2000 (48 h)	130 (48 h)

^aUSDA ARS database and Jinno Laboratories database.

^bAccording to local farmers' spraying programme.

^cAQUIRE database (US EPA).

Table 2. Nomenclature, location and description of sampling sites, as well as characterization of potential agricultural nonpoint-source pollution (AZP = azinphos-methyl)^a

Site	Location, Stream order	Catchment characteristics	Last pesticide application on adjacent plots
LR1	Lourens River, upstream control site, above T1	Natural fynbos vegetation	No application
LR2	Lourens River, downstream below farming area, below T5	Orchards along the tributaries	3–7 h ago at tributary T5
T1	First tributary on the left	Fynbos, fallow	No application
T2	First tributary on the right	Orchards	5–7 d ago; various pesticides
T3	Second tributary on the left	Orchards	7–10 d ago; various pesticides
T4	Second tributary on the right	Orchards, nursery	3–7 d ago; various pesticides
T5	Third tributary on the left	Orchards	3–7 h ago; AZP: 180 g a.i. h ⁻¹ a ⁻¹

^aAll tributaries discharge into the Lourens River between site LR1 and LR2. Sampling took place on December 14, 1998 between 3 and 9 p.m. during the initial period of a runoff event following a total of 28.8 mm rainfall.

on November 5, 1998. Average total rainfall in December was 23.2 mm. At three of the five tributaries, the last pesticide application had been 3–5 days before December 14, 1998-rainfall event, while the last spraying at T5 was completed about 3–7 h before rainfall began (Table 2).

Sampling procedure

Standard sampling procedure during the rainfall event included measurement of discharge and total suspended solids (TSS) as well as collecting of water and suspended sediments for pesticide analysis at all sites. Additionally, site LR1 was sampled at 8 a.m. on December 14, 1998 to reflect the pre-runoff situation and at 8 a.m. on December 16, 1998 to reflect the post-runoff situation. Discharge was calculated based on standard formulas using velocity measurements along cross-sectional profiles. TSS was measured using a turbidity metre (Dr. Lange) with two different sensors enabling measurements between 5 and 2000 mg l⁻¹. To calibrate the turbidity measurements, certain samples were filtered through pre-weighed Whatman GF/F (0.45 µm pore-size) glass microfibre filters and dried at 60°C for 48 h. The filter paper was then re-weighed to determine TSS.

Samples of water were collected in 3-l glass jars as 1-h composite samples (150 ml every 10 min between 5 and 6 p.m.) at sites LR1 and LR2 and as discrete samples at all tributary sites, as well as in erosion rills between plots and tributaries (Schulz *et al.*, 1998). Water samples (500–900 ml) were solid-phase extracted (SPE) within 10 h after sampling using C18 columns (Chromabond) that had been previously prepared with 6 ml methanol and then 6 ml water. The columns were air-dried for 30 min and kept at -18°C until analysis. Suspended sediments were obtained from large volume samples (about 15 l) collected parallel to some of the water samples. After a settling time of 24 h, supernatant water was aspirated and sediments were frozen (-18°C) in glass bottles until analysis. Suspended sediments were obtained from continuously operating suspended particle samplers (Liess *et al.*, 1996) installed in the stream bottom. Suspended particle samplers were emptied approximately every 2 weeks between 14 December 1998 and 31 March 1999 and were analysed for pesticides. On the 14 December 1998 the suspended particle samplers were installed before the rainfall event.

Pesticide analysis

Analysis was performed at the Forensic Chemistry Laboratory of the Department of National Health, Cape Town. Suspended sediment samples were placed in 250-ml polypropylene bottles and centrifuged. The supernatant water was discarded and 50-ml methanol was added. The sediment was shaken until it was mixed well with methanol. The polypropylene bottles were then placed in an ultrasonic bath for 30 min and centrifuged. The supernatant methanol was filtered through glass-fibre filter paper, into 500-ml measuring cylinders. Another 50-ml methanol was added to the sediment and the samples were again mixed well, placed

in the ultrasonic bath and centrifuged. The methanol extracts for each sample were pooled and made up to 350 ml with pure water. A 50-ml aliquot of the extract was passed through a C18 column.

The pesticides were eluted with 2-ml hexane and then 2-ml dichloromethane. These extracts were dried in a stream of nitrogen and then taken up in 1-ml hexane. The extracted sediments were transferred into previously weighed beakers and dried at 150°C. The sample extracts were injected into gas chromatographs (HP 5890's) fitted with standard HP electron-capture, nitrogen-phosphorus and flame-photometric detectors. The capillary columns installed in the GCs were DB-1, DB-5, DB-210 and DB-1301. Concentrations for sediments are expressed as µg kg⁻¹ dry weight (dw). Water samples were eluted from SPE columns and then taken up in 0.5 ml hexane and measured in a GC as described above. The following detection limits were obtained for water and suspended sediments: 0.01 µg l⁻¹ and 0.1 µg kg⁻¹ dw. Spiked recovery efficiencies were between 79 and 106%.

Ecotoxicological testing

The acute toxicities (24-h LC₅₀s) of azinphos-methyl, chlorpyrifos and endosulfan to the amphipod species *Parameletia nigroculus* (Barnard) were determined in laboratory tests. *P. nigroculus* is an endemic species in the Western Cape; it occurs in the upper stretches of the Lourens River and is abundant in upstream areas of many Western Cape rivers. The amphipods were obtained from Skeleton Gorge Stream, which drains the eastern slopes of Table Mountain (S33°58'; E18°25'). They are easy to maintain in the laboratory and have been employed previously for toxicity testing; e.g. with acidity and heavy metals (Musibono and Day, 1999). Five serial dilutions of the emulsifiable concentrates (GusathionTM, DursbanTM and ThiofloTM) together with an untreated control were tested in four replicate glass dishes, each containing 200 ml of test solution (river water from site LR1) and 10 animals. The number of dead animals was determined after 24 h, the criterion for death being an absence of response to mechanical stimulation. The LC₅₀s and the corresponding confidence intervals were determined (using nominal concentrations) by probit analysis according to the maximum-likelihood procedure (statistics package SPSS[®]).

RESULTS

Discharge, TSS and sediment load

A few hours after the commencement of rainfall the stream flow increased, reaching a maximum between 5 and 6 p.m. on December 14, 1998. Average discharge increased at all sites with average 1-h peak values of 9.78 m³ s⁻¹ at LR1 and 22.4 m³ s⁻¹ at site LR2 (Table 3). Thus, peak discharge during the

Table 3. Flow characteristics and TSS of the Lourens River and its tributaries during dry and wet season and peak values during a rainfall-induced runoff event on December 14, 1998. Values for LR1 and LR2 are integrated for a 1-h period from 5 to 6 p.m.

Site	Discharge (m ³ s ⁻¹)			TSS (mg l ⁻¹)		
	Average in January	Average in July	Peak on December 14, 1998	Average in January	Average in July	Peak on December 14, 1998
LR1	0.07	1.91	9.78	8	11	58
LR2	0.28	3.48	22.4	16	32	520
T1	0.02	0.11	1.59	28	38	329
T2	0.03	0.15	1.33	32	39	730
T3	0.03	0.32	1.86	21	28	180
T4	0.04	0.54	2.84	43	68	820
T5	0.03	0.37	1.02	39	54	717

rainfall event was approximately 80–130 times higher than the average dry season discharge. TSS levels were approximately 5–32 fold higher during the rainfall event than the average dry season values (Table 3).

Suspended sediment load was calculated as 41.9 tons h^{-1} leaving the agricultural area at site LR2, of which about 42% (17.6 tons h^{-1}) can be attributed to the tributaries T1–T5 draining the orchard area.

Pesticide concentrations and loads

Average 1-h concentrations detected in water samples at LR2 during the storm event were 1.5 $\mu\text{g l}^{-1}$ for azinphos-methyl, 0.2 $\mu\text{g l}^{-1}$ for chlorpyrifos and 2.9 $\mu\text{g l}^{-1}$ for total (α , β , S) endosulfan (Fig. 1). At upstream control sites without any agricultural activity in the surrounding environment (LR1 and T1), no pesticides were detected during runoff. All tributaries showed peak contamination with azinphos-methyl and endosulfan, while chlorpyrifos was found only in T4. Figure 1 also highlights the importance of edge-of-field runoff for the input of pesticides: increased levels of chlorpyrifos were found in the edge-of-field runoff at T4 and a very high concentration of azinphos-methyl (15.3 $\mu\text{g l}^{-1}$) was discharging from the previously sprayed pears plot into tributary T5. Water samples taken at LR2 before the runoff event contained 0.026 $\mu\text{g l}^{-1}$ of total endosulfan, whereas those taken two days after the runoff contained 0.059 $\mu\text{g l}^{-1}$ endosulfan, 0.011 $\mu\text{g l}^{-1}$ chlorpyrifos and 0.036 $\mu\text{g l}^{-1}$ azinphos-methyl.

Suspended particles sampled at LR2 were contaminated with azinphos-methyl (1247 $\mu\text{g kg}^{-1}$), chlorpyrifos (924 $\mu\text{g kg}^{-1}$), total endosulfan (12082 $\mu\text{g kg}^{-1}$) and prothiofos (980 $\mu\text{g kg}^{-1}$). Again, LR1 showed no measurable pesticide concentrations (Table 4). Suspended particles were contaminated at both tributaries T4 and T5 with a high peak concentration of 2683 $\mu\text{g kg}^{-1}$ azinphos-methyl at T5. Samples taken in a large puddle under the pear trees at T5, from which the runoff water flowed into the tributary, showed an azinphos-methyl concentration of 17831 $\mu\text{g kg}^{-1}$ in the suspended particles (Table 4), while the water contained 105 $\mu\text{g l}^{-1}$.

Figure 2 illustrates the concentration of azinphos-methyl and prothiofos in suspended particles at T3 over a 3.5-month period following the rainfall-induced runoff event in mid-December. Azinphos-methyl concentrations declined from an initial 43.3 $\mu\text{g kg}^{-1}$ within 3 months to non-detectable levels, whereas prothiofos was present even after 3.5 months at levels of 0.8 $\mu\text{g kg}^{-1}$ in comparison to an initial concentration of 6 $\mu\text{g kg}^{-1}$. Maximum daily rainfall during the 3.5-month period was 3 mm (December 21, 1998), indicating that no further runoff had occurred till the end of March 1999.

Pesticide load for site LR2 was calculated by multiplying the integrated 1-h average pesticide

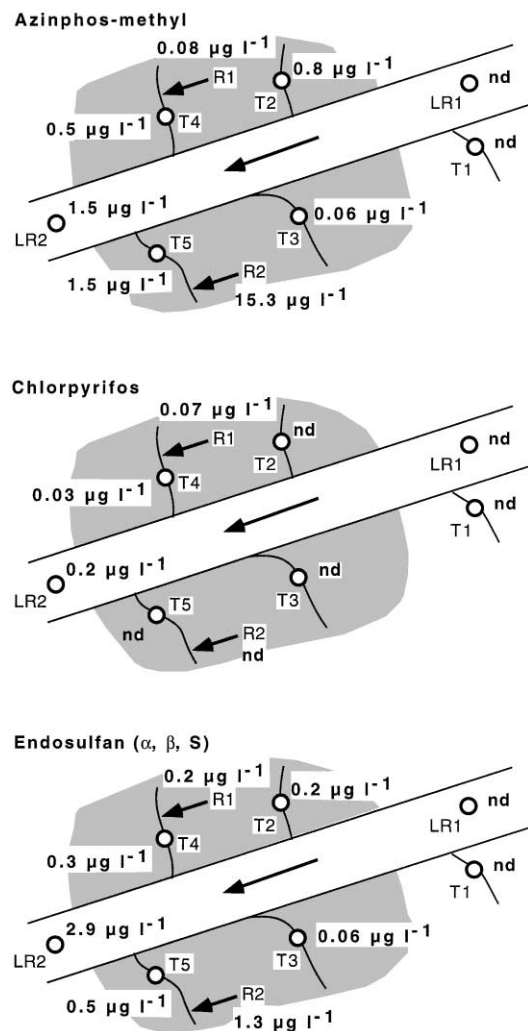


Fig. 1. Concentrations of azinphos-methyl, chlorpyrifos and endosulfan (total of α , β and S) in water samples taken during runoff following a rainfall event on December 14, 1998. Circles indicate sampling stations in the Lourens River (LR1 and LR 2, 1-h composite sampling) and in the tributaries (T1–T5, discrete sampling). The arrows R1 and R2 indicate sites where contaminated edge-of-field-runoff originating from a nursery area (R1) or a pear-tree plot (R2) was sampled and analysed (nd = not detectable). The central arrow denotes the direction of flow in the Lourens River.

concentration by the mean discharge for the same time interval. Azinphos-methyl load at site LR2 was higher in the water phase (120.9 g h^{-1}) than in the suspended sediment-associated form (52.2 g h^{-1}), contrary to that of chlorpyrifos with levels of 16.1 and 38.7 g h^{-1} , total endosulfan with 233.8 and 506.2 g h^{-1} and prothiofos with 0 and 41.1 g h^{-1} , respectively.

Ecotoxicological testing

Control mortalities in the laboratory toxicity tests were 0.025%. The 24-h LC_{50} (95% CI) values obtained for the local amphipod species *P. nigroculus*

Table 4. Concentrations of azinphos-methyl, chlorpyrifos, endosulfan (total of α , β and S) and prothiofos in suspended particle samples taken during runoff following a rainfall event on the December 14, 1998 ($\mu\text{g kg}^{-1}$)^a

	Azinphos-methyl	Chlorpyrifos	Endosulfan (α , β , S)	Prothiofos
LR1	nd	nd	nd	nd
LR2	1247	924	12082	980
T4	216	83	179	15
Runoff into T5	2683	11	395	44
T5, on the plot	17831	48	175	378

^a Sampling took place in the Lourens River (LR1 and LR2) as 1-h composite sampling, as well as in the tributary T4, in the edge-of-field runoff entering T5, and in a puddle under the pear trees at T5 as discrete sampling (nd = not detectable).

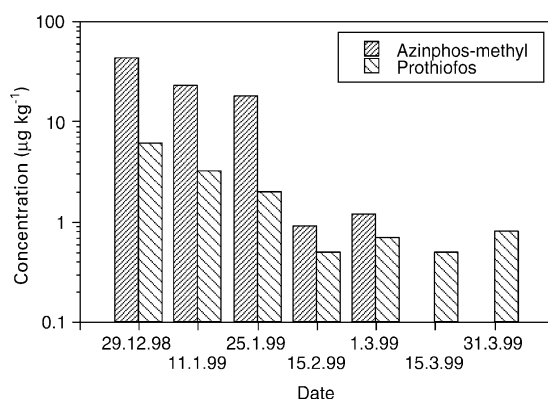


Fig. 2. Concentrations of azinphos-methyl and prothiofos in suspended sediment samples taken with a continuously operating suspended-particle sampler at site T3. Dates refer to the end of each sampling interval (duration approximately 2 weeks) beginning at the preceding date. The first sampling interval started before the rainfall event on December 14, 1998. Total rainfall was 8.4 mm in the second half of December, 5.4 mm in January, 3.4 mm in February and 0.6 mm in March.

were 1.4 (0.6–2.8) $\mu\text{g l}^{-1}$ azinphos-methyl, 0.9 (0.3–1.6) $\mu\text{g l}^{-1}$ chlorpyrifos and 19.2 (12.9–31.4) $\mu\text{g l}^{-1}$ endosulfan.

DISCUSSION

Levels of sediments and pesticides

Concentrations of both total suspended sediments and current-use pesticides showed remarkable peak values during the rainfall-induced runoff event described in this study. TSS increased to 520 mg l^{-1} in the river at LR2, which is equivalent to an increase by a factor of 16 in comparison to the normal values for this clearwater stream. The observation that TSS levels in the Lourens River vary considerably depending on the rainfall and flow conditions has been addressed in earlier studies (Tharme *et al.*, 1997). Potential effects of increased TSS levels on the fauna are not yet clear, since in other studies many authors have found that the community structure changed only after a long-term increase of TSS (Chessman *et al.*, 1987). Barton (1977) found that short-term increases of TSS to 352

or 567 mg l^{-1} due to highway construction or runoff did not cause any noticeable change in the community structure in comparison with control sites. However, repeated increases of TSS, e.g. due to the flushing out of pools in which they may have accumulated or due to recurring runoff events, may result in long-term changes of communities. The increase of TSS values during runoff in this study clearly exceeds the target water quality range of <10% increase in comparison to the background TSS level at the specific site established by the South African Department of Water Affairs and Forestry (DWAF, 1996).

Levels of azinphos-methyl found in the present study were between 0.06 and 1.5 $\mu\text{g l}^{-1}$ in water and between 216 and 1247 $\mu\text{g kg}^{-1}$ in the suspended sediments. High concentrations of up to 7 $\mu\text{g l}^{-1}$ were found by Scott *et al.* (1999) in an estuarine environment receiving agricultural runoff. Runoff from a sugarcane area contained between 2.3 and 417.5 $\mu\text{g l}^{-1}$ (water + sediment) azinphos-methyl (Smith *et al.*, 1983) and application to cranberry bogs in British Columbia resulted in peak levels as high as 1.9 $\mu\text{g l}^{-1}$ and 289 $\mu\text{g kg}^{-1}$ in ditch water 100 m downstream (Wan *et al.*, 1995). In another study, Wan *et al.* (1994) monitored azinphos-methyl in farm ditch water and sediments. The lack of any contamination implied that a rapid degradation of this chemical in the environment had taken place. In contrast, the present results clearly show that azinphos-methyl was detectable in the suspended particles for periods of at least 3 months following a single rainfall-induced input.

Endosulfan levels found in the present study in the river or its tributaries (0.05–2.9 $\mu\text{g l}^{-1}$ and 179–12,082 $\mu\text{g kg}^{-1}$) were high in comparison with values reported from other aquatic ecosystems receiving agricultural runoff (Scott *et al.*, 1999). Wauchope (1978) reported concentrations of up to 18 $\mu\text{g l}^{-1}$ in a stream receiving agricultural edge-of-field runoff, illustrating the potential of this route of entry for endosulfan input. Approximately, 96% of the total endosulfan detected in the present study was identified as the α and β isomers, and can therefore be attributed to recently applied chemical instead of residual concentrations.

Chlorpyrifos was detected following runoff in streams discharging from orchard-growing areas in

the Central Valley, CA, at levels up to $0.52 \mu\text{g l}^{-1}$ (Werner *et al.*, 2000). The present findings of $0.2 \mu\text{g l}^{-1}$ are in a similar range. However, the concentrations of chlorpyrifos in the suspended particles were considerably higher ($924 \mu\text{g kg}^{-1}$), indicating low water solubility of this chemical (Table 1).

Results on environmental concentrations of prothiofos are scarce. In a study of pesticide levels in 28 farm dams in the Elgin area, Western Cape, prothiofos was found once at a level of $0.28 \mu\text{g l}^{-1}$ (Davies and Peall, 1997).

Hardly, any permissible maximum levels for pesticides in South African surface waters have been established. However, the concentration of $2.9 \mu\text{g l}^{-1}$ endosulfan measured at LR2 and the concentrations measured at T2 to T5 clearly exceed the Target Water Quality Range of $<0.01 \mu\text{g l}^{-1}$ established by the Department of Water Affairs and Forestry (DWAf, 1996). According to DWAf (1996), all measurements in the field should be below the chronic effect value of $0.02 \mu\text{g l}^{-1}$. Values measured during runoff in this study even exceeded the acute effect value of $0.2 \mu\text{g l}^{-1}$ at sites LR2, T2, T4 and T5. Additionally, the water quality criteria defined by the US EPA were exceeded at LR2 and some of the tributaries for endosulfan ($0.01 \mu\text{g l}^{-1}$), for chlorpyrifos ($0.08 \mu\text{g l}^{-1}$) and for azinphos-methyl ($0.01 \mu\text{g l}^{-1}$). When one takes these circumstances into account, it is clear that it is absolutely essential to undertake measures to reduce the input of chemicals via runoff.

It can be deduced from the results that the chemicals detected during runoff in the Lourens River and its tributaries stem from the pesticides used in agriculture. No pesticides were detected during runoff in water or suspended sediments at the control site LR1 or in water at the control site T1. Before and after runoff pesticide levels at site LR2 were low in comparison with the peak concentrations. This illustrates the transient character of the pollution in the water phase. Similar findings have been reported in other studies (Schulz and Liess, 1999). However, as discussed above, the values found for suspended sediment at site T3 indicate the potential long-term pollution occurring following a single runoff event. The concentration levels that were measured at LR2 were higher than the levels detected in the five investigated tributaries. Other small tributaries discharging water into the Lourens River only during rainfall events and therefore not monitored in this study may make a considerable contribution to the high pesticide levels at LR2.

Importance of a single runoff event

A review of the 10-yr rainfall data between 1982 and 1991 for the area under study revealed that a similar rainfall event ($>15 \text{ mm d}^{-1}$) occurred during December in 6 of the 10 years. This means that more frequently than every second year a rainfall-induced

runoff event similar to the one described in this study may occur. Given that November until January is the main spray period within the dry season, then the frequency for occurrence of a 15 mm d^{-1} rainfall is 1.7. It can therefore be deduced that a similar event occurs statistically at least once during every spray period within each growing season.

If the orchard plots along the tributaries and the pesticide applications between middle of November and middle of December are taken into account, the calculated pesticide loads in the river at LR2 would equal the following rates of loss of applied substance: 0.3% azinphos-methyl, 0.2% chlorpyrifos, 5.4% total endosulfan (α , β , S) and 0.3% prothiofos. Following Wauchope (1978), the total runoff-related loss of pesticide per season is usually less than 0.5% of applied substance. Regarding this generic value, the single runoff event investigated in this study resulted in a relatively high rate of pesticide loss, specifically for endosulfan. This may be due to higher field half-life of endosulfan or to a different mobility of this chemical in comparison to the organophosphorous pesticides. The pesticide contaminations following lower rainfall events at the beginning of the wet season and following spraydrift during pesticide application are not considered here, but are subject of separate publications.

Ecotoxicological evaluation

The pesticide concentrations measured during runoff exceed the levels acutely toxic for freshwater animals as described in Table 1. Consequently, the endosulfan levels are expected to be toxic to fish and the azinphos-methyl and chlorpyrifos concentrations may have harmful effects on macroinvertebrates. The 24-h LC_{50} of azinphos-methyl obtained for the local amphipod species *P. nigrocylus* in this study is also lower than the concentration present at LR2 during runoff. Tanner and Knuth (1995) reported significant decreases of copepod nauplii and cladoceran populations following the contamination of littoral enclosures with 1 or $4 \mu\text{g l}^{-1}$ azinphos-methyl. A 96-h LC_{50} of $0.29 \mu\text{g l}^{-1}$ azinphos-methyl was detected for *Mysidopsis bahia* (Morton *et al.*, 1997). Chlorpyrifos levels similar to those present during runoff at LR2 have been shown to produce 100% mortality in the zooplankton species *Ceriodaphnia dubia* after 24-h exposure (Werner *et al.*, 2000). Muirhead-Thomson (1973) reported that 1 h of exposure to levels of endosulfan as low as $5 \mu\text{g l}^{-1}$ can cause 44% mortality after 24-h observation in baetid mayflies, which are the predominant mayfly genera in the Lourens River (Tharme *et al.*, 1997).

It can be expected that a considerable proportion of the pesticide contamination detected at site LR2 will reach the estuary of the Lourens River about 9 km downstream. The endosulfan levels measured at LR2 in suspended sediments ($12082 \mu\text{g kg}^{-1}$), for example, are far above the concentration

values which reduce survival and reproduction in meiobenthic polychaetes and copepods ($50\text{--}200\ \mu\text{g kg}^{-1}$) (Chandler and Scott, 1991), while those measured in the water ($2.9\ \mu\text{g l}^{-1}$) exceeded the reported 96-h LC_{50} ($0.43\ \mu\text{g l}^{-1}$) for the estuarine amphipod *Gammarus palustris* (Leight and van Dolah, 1999). The 96-h LC_{50} of azinphos-methyl for the estuarine shrimp *Palaemonetes pugio* is $1.05\ \mu\text{g l}^{-1}$ (Scott *et al.*, 1999), a value lower than the concentration of $1.5\ \mu\text{g l}^{-1}$ measured at site LR2 during runoff. It has also been reported that the pesticide azinphos-methyl was responsible for a large number of fish killed in estuarine areas adjacent to sugarcane and vegetable crops (Scott *et al.*, 1999).

The overall ecological significance of the pesticide pollution reported in this study is difficult to assess. Impacts on the benthic invertebrate community of the Lourens River may be detrimental during certain months of the year. Furthermore, a decline in food organisms can seriously impact survival of fish in both larval and adult stages. As has been shown, pesticides may persist for relatively long times in sediments following a single input event. These chemicals may cause secondary increases in aqueous exposure due to resuspension processes. Ecological effects of pollution in Western Cape rivers have to be considered carefully since many of the aquatic invertebrate and fish species occurring in the rivers are endemic to a relatively small area, and their extinction cannot be compensated by recolonisation from other regions.

CONCLUSIONS

- Runoff events lead to increases in total suspended sediment levels exceeding the target water quality range.
- Aqueous-phase and particle-associated pesticide levels transiently detectable during runoff are above legislative threshold values. They even reach levels acutely toxic to the aquatic fauna, making measures to reduce the input of chemicals via runoff necessary.
- Single rainfall events that cause considerable input of pesticides into the study river occur statistically at least once per season.

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