RUNOFF-RELATED PESTICIDE INPUT INTO THE LOURENS RIVER, SOUTH AFRICA: BASIC DATA FOR EXPOSURE ASSESSMENT AND RISK MITIGATION AT THE CATCHMENT SCALE

J. M. DABROWSKI[1], S. K. C. PEALL[2], A. J. REINECKE[1], M. LIESS[3]
and R. SCHULZ[1]*

[1] Department of Zoology, University of Stellenbosch, Matieland 7602, South Africa; [2] Forensic Chemistry Laboratory, Department of Health, Cape Town 8000, South Africa; [3] Zoological Institute, Technical University, D-38092 Braunschweig, Germany
(* author for correspondence, e-mail: R.Schulz@tu-bs.de, fax: +49 531 391 8201)

Abstract. The characterization of runoff-related pesticide input and the identification of areas of concern in the field are essential for a comprehensive assessment of risk and the planning of mitigation measures. To this end, the agriculturally-derived aqueous and particle-associated pesticide contamination of the Lourens River and its tributaries was measured in a comprehensive design. Sampling was performed in the beginning of April prior to the first rainfall of the wet season and in the middle of April during high water conditions following the first rainfall of 9.6 mm d^{-1}. Pre-runoff samples indicated contamination with endosulfan at levels up to 0.06 μg L^{-1}, while no other pesticides were detectable. Rainfall-induced runoff resulted in an increase in the levels of the pesticides endosulfan, deltamethrin, azinphos-methyl, chlorpyrifos, and procymidone up to levels of 0.35, 1.4, 0.6, 0.19 and 9 μg L^{-1}, respectively in water samples. Endosulfan, azinphos-methyl, and chlorpyrifos were detected at maximum concentrations of 273, 152, and 245 μg kg^{-1} in suspended sediments. No increased pesticide levels were detected at a control site upstream of the agricultural area. The Lourens River received its contamination via the tributaries discharging the surrounding farming area. Contamination of the six tributaries depended on landuse and slope characteristics and enabled the identification of target sites for risk reduction approaches. Transient pesticide levels exceeded the target water quality limit proposed by the South African Department of Water Affairs and Forestry (DWAF). The Lourens River site downstream of the farming area has been identified as a site where potential toxic conditions could arise.

Keywords: assessment, edge-of-field runoff, hot spots, orchards, partitioning, pesticides, surface waters, sediments, tributaries

1. Introduction

Pesticides are regularly sprayed on orchards, vineyards and on containered nursery plants in the Western Cape, South Africa. These pesticides can enter aquatic eco-systems, posing a threat to non-target species, including mammals, birds, insects as well as humans (Fawell, 1991; Kuivila and Foe, 1995; Domagalski *et al.*, 1997). Assessment of potential side effects of pesticide use includes an estimation of exposure which is usually based on predicted environmental concentrations (PEC)

(Bascietto *et al.*, 1990). However, it has also been pointed out that exposure assessment should rather be substantiated by measuring the real contamination in the field instead of using only modelling approaches (Solomon, 1996).

Non-point source pesticide pollution can enter streams and rivers via three main routes; leaching (Fawell, 1991), spray-drift and run-off (Antonious and Byers, 1997; Fawell, 1991; Merkle and Bovey, 1974). Everts (1997) regards runoff as the most important factor with regard to contamination of surface waters in arid areas such as in the Western Cape of South Africa. Runoff occurs during the rainy season and lasts from April to September in the Western Cape. Runoff-related input usually leads to an increase of total suspended solids and pesticides which may enter the surface water as either water-dissolved or particle-associated chemicals (Wauchope, 1978).

The quantity of pesticides that enter surface waters via runoff are dependent on a number of factors and include the time interval between the application of pesticides and the first heavy rainfall event, the slope and soil types of the catchment, the quantity of applied pesticide, the chemical nature of the pesticide and the size and characteristics of bufferstrips (Cole *et al.*, 1997; Merkle and Bovey, 1974). Studies have shown that the first heavy rainfall after application results in the highest quantity of pesticides in surface waters (Domagalski *et al.*, 1997). Thus, in the context of the Western Cape, a very important period with regards to determining runoff-related contamination is at the beginning of April, when the first heavy rains normally fall after the end of the spraying season in late February.

The aim of this article is (i) to characterize rainfall-induced runoff as a source of pesticides and suspended sediments in the tributaries and main channel of the Lourens River, concentrating specifically on the very first rainfall after the end of the spraying season, (ii) to compare pesticides in suspended sediments and in water, and (iii) to identify areas of concern ('hot spots') through comparison of contamination between sites. Concentrations of pesticides will be compared to toxicity values for aquatic animals, so as to determine whether there might be any potential threat to the faunal communities in the Lourens River.

2. Materials and Methods

2.1. STUDY AREA

The Lourens River originates at an altitude of 1080 m in the Hottentots Holland Mountain range and flows in a south-westerly direction for about 20 km before discharging into False Bay at Strand (34°06′S; 18°48′E). After leaving a naturally vegetated fynbos area, the river runs through intensive farming areas (orchards and vineyards) in its middle reaches before flowing through the town of Somerset West. Orchards are situated against the side of the mountain range on slopes ranging from 2% to as much as 20%, providing suitable conditions for runoff to take place. The

TABLE I

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 R2 and toxicity to standard test organisms *Oncorhynchus mykiss* (96 h LC_{50}) and *Daphnia magna* (48 h EC_{50})

Pesticide name	Water solubility at given temperature[a]		Amount applied[b]	Acute toxicity[c]	
				Rainbow trout	Water flea
	(mg L^{-1})		(kg)	——— (μg L^{-1}) ———	
Azinphos-methyl	28	(20 °C)	771	4.3	1.6
Chlorpyrifos	1.2	(25 °C)	686	9	0.42
Deltamethrin	0.002	(20 °C)	±30	2.3	0.037
Endosulfan	0.32	(22 °C)	158	0.3	250
Procymidone	4.5		±50	7200	4200
Cypermethrin	0.01	(20 °C)	2	8.2	0.2
Fenvalerate	0.3	(25 °C)	5	0.3	1
Prothiofos	1.7	(20 °C)	87	2000 (48 hr)	130
β-cyfluthrin	0.002	(20 °C)	13	0.68	0.00014

[a] USDA ARS database.
[b] Amounts applied are calculated according to the local farmers spraying programme. Deltamethrin and procymidone are not applied to orchards. Growing area is 4 km^2.
[c] Dortland, 1980; EXOXNET, 1996; Johnson and Finley, 1980; Lakota *et al.*, 1989; Lemke, 1981; U.S. EPA, 1986; Van der Hoeven and Gerritsen, 1997; Xiu *et al.*, 1989.

study area has a total catchment area of approximately 44 km^2 and receives an annual mean rainfall of 915 mm. About 87% of the Lourens Rivers 35×10^6 m^3 mean annual discharge occurs during the winter months between April and October (Tharme *et al.*, 1997), as is characteristic of the region's Mediterranean climate. The main soil type is silty loam with an average total organic carbon content of 0.75%; the area does not contain any subsurface drainage systems.

The orchards consist of pears, plums, apples and grape vineyards (total growing area: 4 km^2), on which pesticide application takes place between August and mid February before fruit harvest. Pesticide active ingredients applied on the orchards include the fungicide procymidone and the insecticides endosulfan, chlorpyrifos, azinphos-methyl, deltamethrin, cypermethrin, fenvalerate, prothiofos and β-cyfluthrin. From all these substances, chlorpyrifos and azinphos-methyl were used frequently between October and February on pears and plums, up to about one application every two weeks on each single plot (Table I). Endosulfan is applied mainly onto apple orchards.

2.2. SAMPLING SITES AND RAINFALL

The sampling area comprised an approximately 6-km stretch of the Lourens River and its side streams running between two farms (Figure 1). The orchard plots are separated from the Lourens River itself by a strip of vegetation (Eucalyptus trees, shrubs and grasses) between 30 and 100 m in width, making direct input of edge-of-field runoff into the river highly unlikely. In contrast, most of the six studied tributaries are, at least in some stretches, directly adjacent to orchard plots (distance: about 5 m). Four of the six tributaries (E2, W2, W3 and W4) are man-made ditches, designed specifically to drain excess water from orchard areas. Almost all orchards within close proximity to the tributaries have numerous erosion rills, providing a direct path for surface water to run directly from the orchards into the tributaries. Another study that took place in the spraying season in December gave further indication for the importance of runoff in this catchment (Schulz, 2001). Eight sampling sites were selected for measurement of total suspended solids (TSS), aqueous and particle-associated pesticide levels (Figure 1). Sites were chosen so as to determine the pesticide content in each of the side streams and the cumulative effect that the side streams have on the Lourens River. Three sampling sites were assumed to be uncontaminated (E1, W1 and R1), owing to the lack of any agricultural activity on the banks upstream of these sites (Table II). The remaining sites were expected to be contaminated with sediments and pesticides from orchards and a nursery (Table II and Figure 1). Sites W1 to W4 and E1 to E2 drain sub-catchment areas of approximately 14 km and 5 km^2, respectively.

The last pesticide application in the study area had taken place at the end of February. The first potential runoff event occurred on the 15th April when 9.6 mm of rain fell, followed by another two events with 14.4 mm on the 18th of April and 18.8 mm on the 19th of April (Figure 2). Runoff samples were retrieved during these runoff events (see also Table III). Sampling of suspended sediment took place till 17th May. The total rainfall in May was 75.6 mm.

2.3. SAMPLING PROGRAMME

Water and sediment samples were collected at the end of each tributary, ensuring that the streams were well mixed at the point of collection and that the samples were representative of the agricultural activity bordering the entire length of the stream. Water samples were collected prior to any rain-induced runoff on 2nd April 1999 to provide an indication of the level of pesticides present in the river system after the spraying programme had been completed and before any runoff events had taken place. Water samples were collected in 3-L glass jars. Samples representing the pesticide levels during runoff were accomplished using glass bottles (3-L) stored in the stream or river with the opening approximately 3 cm above the normal water level. During rainfall induced surface runoff, the rising water level filled the bottles passively (Liess and Schulz, unpublished method). A small glass pipe (Pasteur pipette with the tip broken off) was tied in the opening of the bottle,
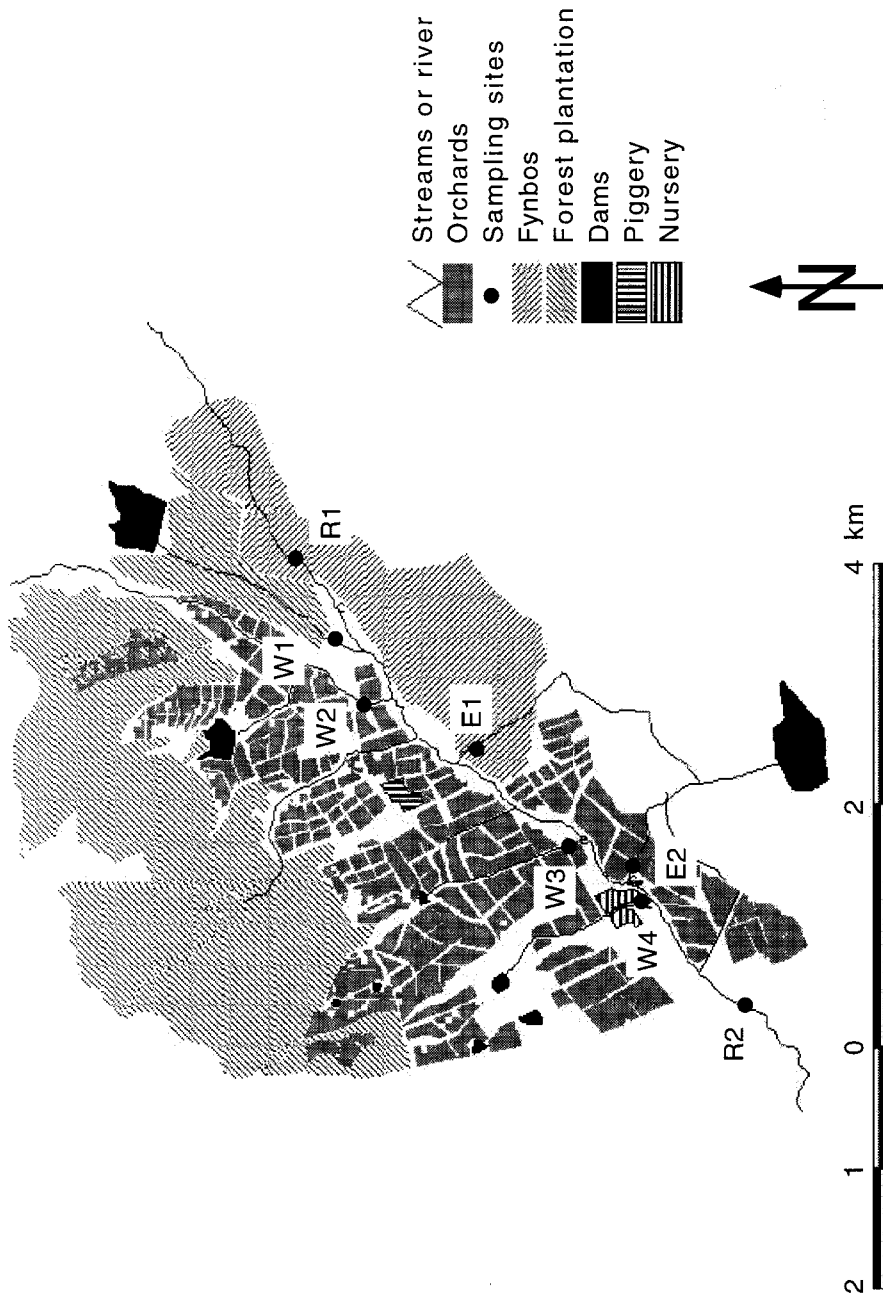
Figure 1. Map showing the landuse and sampling sites in the study area of the Lourens River catchment.

TABLE II

Catchment characteristics: Landuse and slope within a 50-m strip on each side upstream of the respective sampling site. R denotes the Lourens River mainstream itself, while W and E denotes sites in tributaries entering the river from the western or eastern side, respectively (Figure 1)

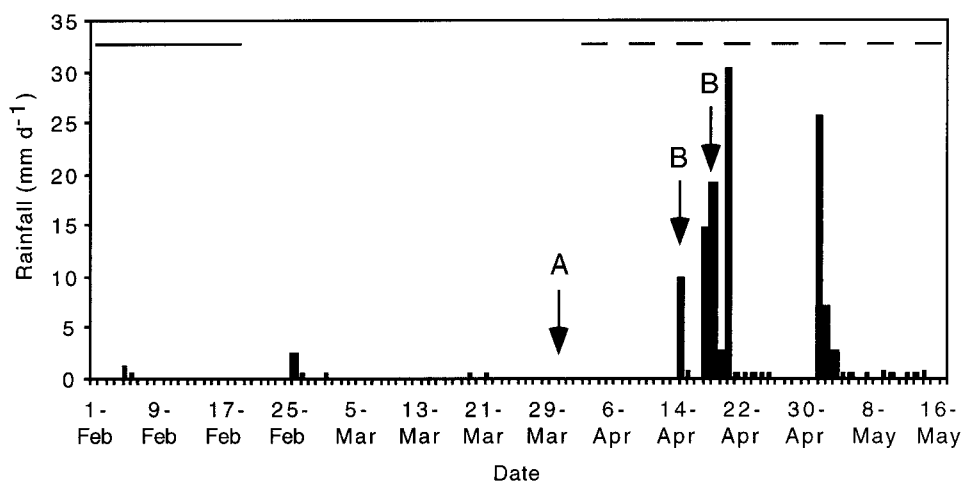| Landuse bordering river/streams (%)	R1	R2	W1	W2	W3	W4	E1	E2
Orchards	–	–	–	76	100	63	–	51
Nursery	–	–	–	–	–	19	–	–
Natural vegetation	70	–	–	10	–	–	75	–
Fallow, pine plots	30	44	100	14	–	–	25	49
Other (i.e. farm houses)	–	56	–	–	–	18	–	–
Total bank length (m)	5000	6743	3976	5092	2548	2100	1894	1617
Slope (%) Average	2	1	5	3	2	2	1	1
Maximum	7	1	10	7	5	3	1	1

Figure 2. Rainfall from February to May 1999. Arrows indicate dates upon which water samples were taken (A = before runoff; B = during runoff). The solid vertical line illustrates the last part of the pesticide application period and the dashed line illustrates the sampling period for suspended sediments.

TABLE III

Pesticide concentrations (μg L^{-1}) in water samples from two sites in the Lourens River (R) and from six of its tributaries (W and E). Samples taken on 2 April represent pre-runoff conditions while samples from 15, 18, and 19 April were taken during runoff

Site	Sampling date	Endosulfan-α	Endosulfan-β	Endosulfan-S	Total Endosulfan	Procymidone	Deltamethrin	Chlorpyrifos	Azinphos-methyl
R1	2 April	0.01	0.01	0.03	0.05	–	–	–	–
	15 April	–	–	–	–	–	–	–	–
R2	2 April	0.02	0.03	0.01	0.06	–	–	–	0.07
	15 April	0.02	0.03	0.10	0.15	0.05	–	–	0.26
	18 April	–	–	–	–	0.63	–	–	–
W1	2 April	0.01	0.01	0.01	0.03	–	–	–	–
	19 April	–	–	–	–	–	–	–	–
W2	2 April	0.01	–	0.01	0.02	–	–	–	–
	15 April	–	–	–	–	–	–	–	0.39
	18 April	–	–	–	–	–	–	–	0.53
W3	2 April	0.01	0.02	0.03	0.06	–	–	–	–
	18 April	0.05	0.05	0.19	0.29	–	1.43	–	0.60
	19 April	0.08	0.07	0.14	0.29	0.08	–	–	0.55
W4	2 April	0.01	0.01	0.02	0.04	–	–	–	–
	15 April	–	–	0.34	0.34	–	–	–	–
	18 April	0.06	0.06	0.20	0.32	–	–	0.19	0.56
	18 April^{a}	–	0.06	0.29	0.35	–	–	0.47	–
E1	2 April	–	–	0.02	0.02	–	–	–	–
	18 April	–	–	–	–	9.06	–	–	–
	19 April	–	–	–	–	6.11	–	–	–
E2	2 April	–	–	0.01	0.01	–	–	–	–
	18 April	–	–	–	–	–	–	–	–
	19 April	–	–	–	–	0.06	–	–	–

^{a} Edge-of-field runoff from a nursery.

using synthetic nylon. This enabled a free flow of water into the bottle while air could flow out via the glass pipe. In order to prevent contamination, all glass jars were thoroughly rinsed with acetone prior to collection of water samples. Retrieval and extraction of water samples took place within 24 hr of the runoff event.

Samples of pesticides associated with suspended sediments were obtained using a suspended sediment sampler (Liess *et al.*, 1996), which consisted of a plastic container (500-mL) with a screw-on lid containing a hole (2 cm in diameter). This plastic container contained an open glass jar that was stored directly under the hole in the lid. The samplers were attached to a metal stake and were stored on the riverbed. This system supplies integrated values for the pesticide contamination of suspended particles, which are often highly contaminated because of the low water solubility of many pesticides.

Turbidity was measured using a turbidity meter (Dr. Lange, Germany). To calibrate the turbidity measurements as described by Gippel (1995), 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 hr. The filter paper was then re-weighed to determine TSS (total suspended solids).

2.4. PESTICIDE EXTRACTION AND ANALYSIS

Water and sediment samples were extracted for pesticides and analysed for all of the pesticides used in the study area (Table I). Analysis was performed by the Forensic Chemistry Laboratory of the Department of National Health, Cape Town.

Water samples (500 to 900 mL) were first filtered (to remove suspended solids) and then solid-phase extracted (SPE) using C18 columns (Chromabond) which 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 sediment samples were placed in 250 mL polypropylene bottles and centrifuged. The supernatant water was discarded and 50 mL methanol was added. The sediment and methanol was shaken until it was well mixed. 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 dissolved in 1 mL hexane. The extracted sediments were transferred into previously weighed beakers and dried at 150 °C. Concentrations for sediments were expressed as μg kg^{-1} dry weight (dw). Water samples were eluted from defrosted SPE columns and then dissolved in 0.5 mL hexane.

Hexane solutions of water samples were analyzed using gas chromatograph/ electron-capture/nitrogen-phosphorous detector (GC/ECD/NPD), ^{63}Ni ECD temperature: 300 °C with nitrogen as make up gas, NPD temperature: 300 °C. The gas chromatograph HP 5890 (Series II; Hewlett-Packard) was equipped with an HP 7673 autosampler (Hewlett-Packard) and a split/splitless injector and capillary column, HP 5 (15 m length, 0.32 mm i.d., 0.25 μm film thickness; HP) and with nitrogen as carrier gas (1.1 mL min^{-1}), temperature programmes: 170 °C (1 min) → 20 °C min^{-1} → 300 °C → (1 min), 5 μL was injected with the splitter closed for 0.75 min. Measurements were confirmed using a gas chromatograph/flame-photometric detector (GC/FPD), FPD temperature: 250 °C. The gas chromatograph HP 5890 (Series II; Hewlett-Packard) was equipped with an HP 7673 autosampler (Hewlett-Packard) and a split/splitless injector and capillary column, DB 210 (30 m length, 0.32 mm i.d., 0.25 μm film thickness; J&W) and with nitrogen as carrier gas (1 mL min^{-1}), temperature programmes: 150 °C (0.5 min) → 30 °C min^{-1} → 210 °C → (1 min) → 30 °C min^{-1} → 240 °C → (1 min), 5 μL was injected with the splitter closed for 1 min.

Identity of the pesticides were established by asking farmers which pesticides they had used and then confirming the identity by matching retention times on 3 different stationary phases in the case of the organophosphates and two stationary phases for the organochlorines. Method validation was conducted on water matrices that were determined to have no detectable levels of the investigated pesticides. The validation consisted of spiking water at 8 spiking levels over the range of concentrations found in the actual samples. Overall mean recoveries were between 79 and 106%. For quality control, a matrix blank was analysed with each extraction set. The investigated pesticides were never detected in matrix blanks. The following detection limits were obtained for water and suspended sediments: 0.01 μg L^{-1} and 0.1 μg kg^{-1} dw.

3. Results

3.1. Pesticide contamination

Pesticides identified in water samples included endosulfan, deltamethrin, chlorpyrifos, azinphos-methyl and procymidone (Table III), all of which were found at increased levels in runoff samples. Endosulfan was present in all pre-runoff samples at moderately high concentrations of up to 0.06 μg L^{-1}. Runoff samples from sites W3, W4 and R2 showed total endosulfan concentrations of 0.29, 0.34 and 0.15 μg L^{-1}, respectively. Most of the total endosulfan can be attributed to endosulfan-sulfate. The only sites with elevated levels of the α- or β-isomer were R2, W3 and W4. Chlorpyrifos was detected in a sample taken during runoff conditions at site W4 at 0.19 μg L^{-1}. A sample of edge-of-field runoff water running directly from an adjacent nursery into W4 contained 0.47 μg L^{-1} chlorpyrifos. Azinphos-methyl

was detected in runoff samples at high concentrations up to 0.6 μg L^{-1} in sites W2, W3 and W4. The azinphos-methyl level at R2 increased during runoff by a factor of five in comparison to the pre-runoff level. A high concentration of 1.43 μg L^{-1} deltamethrin was detected during runoff at W3. Procymidone was detected in high concentrations in runoff samples only, and was predominantly found in the eastern and mainstream sites. An increase in procymidone level by a factor of 12 occurred on site R2 during runoff.

Suspended sediment samples were taken throughout runoff conditions and generally the first samples taken during the first rainfall after the pesticide application period, showed considerably higher concentrations of pesticides than those taken during latter runoff events (Table IV). The highest endosulfan concentrations were detected at sites W1, W3, W4 and R2. Most of the total endosulfan was again attributed to endosulfan sulfate, while both isomers were detected at higher levels at R2, W1 and W4. Chlorpyrifos was detected in high concentrations of up to 152 μg kg^{-1} in suspended sediments in the main river and most of the side-stream sites. Particle-associated azinphos-methyl was detected in fewer sites, at generally lower concentrations than chlorpyrifos, although site R2 showed a notably high concentration of 245 μg kg^{-1}.

The Lourens River site R1 was the only site that did not show an increase in either aqueous-phase or particle-associated pesticide concentrations during runoff conditions. Site E1 showed high concentrations of the fungicide procymidone in water samples taken during runoff conditions, but no insecticides were detected at this site. W1 showed an elevated level of endosulfan in the sediment. The breakdown product endosulfan-sulfate was the only insecticide compound found in the water samples taken from the eastern farm sites. Chlorpyrifos was detected at a relatively high concentration in a suspended sediment sample taken at one of the sites (29.7 μg kg^{-1}). No azinphos-methyl was detected at any of the sites on the eastern farm.

3.2. TOTAL SUSPENDED SOLIDS (TSS)

Turbidity measurements were taken during both runoff events and an average was obtained for each sampling site. During runoff, the TSS levels were considerably increased at all sites relative to the pre-runoff conditions (Figure 3). During normal flow conditions before runoff, all of the sites had TSS levels of less than 100 mg L^{-1}. Apart from site R1 and W1, the TSS levels during runoff were increased to levels higher than 200 mg L^{-1}.

TABLE IV

Pesticide concentrations in suspended sediment samples (μg kg^{-1}) from two sites in the Lourens River (R) and from six of its tributaries (W and E). The first runoff event took place on 15 April during a 9.6-mm d^{-1} rainfall

| Site	Sampling interval	Endosulfan-α	Endosulfan-β	Endosulfan-S	Total Endosulfan	Chlorpyrifos	Azinphos-methyl
R1	1–29 April	–	–	–	–	–	–
	29 April – 17 May	–	–	–	–	–	–
R2	1–19 April	45.5	90.0	110	245	69.0	245
	19 April – 17 May	18.1	20.0	12.7	50.8	9.9	7.0
W1	1–29 April	59.5	–	34.6	94.1	46.7	–
	29 April – 17 May	–	–	9.7	9.7	4.2	–
W2	1–19 April	3.0	7.5	6.1	16.6	18.6	–
	19 April – 17 May	–	–	–	–	6.7	–
W3	1–19 April	10.2	14.3	14.0	38.5	34.5	21.1
	19 April – 17 May	–	5.5	5.8	11.3	32.3	–
W4	1–19 April	20.7	82.1	170	273	152	–
	19 April – 17 May			No sample taken			
E1	1–19 April	–	–	17.3	17.3	–	–
	19 April – 17 May	–	–	–	–	–	–
E2	1–19 April	–	–	–	–	–	–
	19 April – 17 May	–	–	25.8	25.8	29.7	–
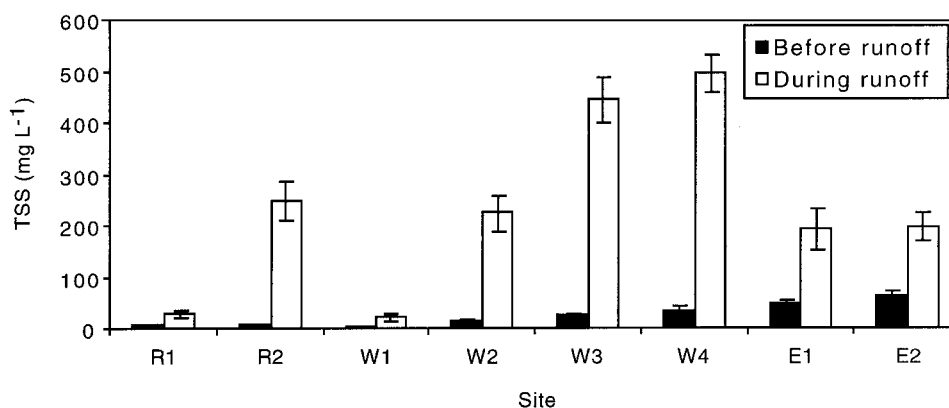
Figure 3. Mean (±SE; n = 6) total suspended solids (TSS) levels before and during runoff conditions at sites in the mainstream of the Lourens River (R) and its tributaries (W and E). TSS was measured during the rainfall events of April 15th and 18th.

4. Discussion

4.1. IMPACT OF RUNOFF

The present results clearly indicate that agricultural runoff is an important source of pesticide and suspended sediment input into the Lourens River and its tributaries. This is evident from the fact that pollution increased considerably during runoff in comparison to pre-runoff conditions. Furthermore, runoff did not result in any increased contamination at the mainstream (R1) control site upstream of the farming area. The fungicide procymidone was however detected at site E1 during runoff conditions, presumably resulting from applications in the adjacent pine plots. Site W1 also showed elevated levels of endosulfan in the sediment during runoff conditions which could indicate a point-source. This tributary also receives some of its water from a small farm dam further upstream and should contamination occur in this dam it is possible that it could land up in the tributary.

Transient increases of agriculturally-derived pesticide levels during runoff have been reported in a number of other studies (e.g. Baughman *et al.*, 1989; Kreuger, 1995; Liess *et al.*, 1999; Schulz and Liess, 1999). The suspended sediment samples revealed that at almost all of the sites where pesticides were detected, concentrations were higher during the first period of sampling than during the second. These results support those of Domagalski *et al.* (1997), highlighting the fact that the first runoff event after a long, dry period of pesticide application results in the highest pesticide input.

Higher azinphos-methyl concentrations than in the present study were found in an estuarine environment receiving agricultural runoff (Scott *et al.*, 1999) or in runoff from a sugarcane area (Smith *et al.*, 1983). However, Wan *et al.* (1994) monitored azinphos-methyl in farm ditch water and sediments and attributed the

lack of any contamination to its rapid degradation in the environment. In contrast, the present results clearly show that azinphos-methyl can be detected even 6 weeks after the last application at increased levels in water and suspended sediments. The azinphos-methyl levels measured in water samples are only slightly below concentrations acutely toxic to *Daphnia magna* (Table I) and exceeded the 96-h LC_{50} of 0.37 μg L^{-1} for the midge *Chironomus tentans* (Ankley and Collyard, 1995).

Endosulfan levels found in the present study were comparable to values reported from other aquatic ecosystems receiving agricultural runoff (Kreuger and Brink, 1988; Miles and Harris, 1971; Scott *et al.*, 1999). All sites showed endosulfan levels exceeding the target water quality limit of 0.01 μg L^{-1}, as proposed by the South African Department of Water Affairs and Forestry (DWAF, 1996). Of particular concern is the fact that levels exceeded even the Acute Effect Value of 0.2 μg L^{-1} (DWAF, 1996) during runoff. Both isomers of endosulfan, as well as the breakdown product (endosulfan sulfate) are highly toxic towards aquatic organisms, particularly fish (Table I; Goebel *et al.*, 1982; Leonard *et al.*, 2001).

Chlorpyrifos was found following runoff in streams discharging water from orchard growing areas in the Central Valley, California at levels between 0.04 and 0.52 μg L^{-1} (Kuivila and Foe, 1995; Werner *et al.*, 2000), which are comparable to levels detected at site W4 in the present study. Chlorpyrifos is highly toxic to fish and aquatic invertebrates (Green *et al.*, 1996), and the concentrations detected exceeded the NOEC value calculated by Van den Brink *et al.* (1996) for macroinvertebrates in outdoor experimental ditches. As chlorpyrifos was also detected in the particle-associated form at levels of up to 152 μg kg^{-1}, it thus also poses a potential hazard to sediment dwelling organisms. Studies on the toxicity of sediment-associated chlorpyrifos revealed acute effects at levels of approx. 70 μg kg^{-1} for the marine copepod *Amphiascus tenuiremis* (Green *et al.*, 1996) and of approx. 300 μg kg^{-1} for the freshwater midge *Chironomus tentans* (Ankley *et al.*, 1994).

Deltamethrin was detected only at site W3. However, the concentration detected was 40 times higher than the acute toxicity level for *D. magna* (Table I). Procymidone has a low acute toxicity to aquatic organisms (Table I), however, an anti-androgen activity was reported for mammals (Ostby *et al.*, 1999). Deltamethrin was not sprayed on any orchards and is also extremely insoluble in water (Table I). It is thus surprising that it was detected at such a high concentration in a water sample from W3. This could indicate a point-source, which might originate from the gardens of households on the farm where deltamethrin is frequently used (pers. comm.).

Cypermethrin, fenvalerate, prothiofos and β-cyfluthrin were also used in the study area, but were never detected in any samples taken over the duration of the study. This is most probably due to the limited number of spray applications (from one to two applications each), resulting in very small quantities of these pesticides being available to runoff (Table I). These applications took place in late September

and early October of 1998, giving a 6-month time period for degradation of the insecticides to take place. Cypermethrin was also only applied on two occasions, but these applications took place in January of 1999. Despite the shorter time interval between application and runoff events studied, the amount of pesticide applied was very small to warrant any possible contamination of the tributaries by this pesticide (Table I).

The TSS increased considerably during runoff conditions (Figure 3). Potential effects of elevated TSS levels on the fauna are not clear, since many authors found no changes in community structure following short-term increases of TSS (Barton, 1977; Smith and Kaster, 1983). However, repeated increase of TSS, e.g. due to the flush out of pools in which they may have accumulated or due to recurring runoff events, may result in long-term changes of communities (Taylor and Roff, 1986). The increased TSS values during runoff clearly exceed the Target Water Quality Criteria established by the South African Department of Water Affairs and Forestry of <10% increase in comparison to the background TSS level at the specific site (DWAF, 1996).

In summary, all detected pesticides were found at ecotoxicologically relevant levels, making the implementation of risk reduction strategies necessary. However, the overall ecological significance of the pesticide pollution reported in this study is difficult to assess at this stage. Impacts on the benthic invertebrate community of the Lourens River, which is dominated by several mayfly species, 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. 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.

There is much evidence to suggest that measured pesticide concentrations were as a result of surface runoff and not via alternate routes such as rapid leaching through the soil substrate. Chlorpyrifos and endosulfan were very prevalent in sediment samples. Both of these pesticides have a high affinity to adsorb to soil particles and are thus relatively immobile in soils (Rauke, 1992; EXTOXNET, 1996). Thus, the most feasible way that these pesticides could land up in the tributaries is via surface runoff (EXTOXNET, 1996). The large increase in turbidity (suspended sediment) is another factor that suggests that runoff had taken place (Schulz, 2001). These large increases in suspended solids must have been as a result of soil and sediment being physically washed into the tributaries, transporting adsorbed pesticides in the process, and is unlikely to have occurred via sub-surface drainage. Furthermore, the edge-of-field sample taken at W4 (Table III) indicates that at least for this tributary, contamination is as a result of surface runoff. Another study that took place in the spraying season in December gave further indication for the importance of runoff in this catchment (Schulz, 2001).

4.2. PESTICIDE PARTITIONING BETWEEN WATER AND SUSPENDED PARTICLES

The partitioning of the pesticides studied here is well in accordance with their reported water solubilities (Table I). The organophosphorous insecticide azinphos-methyl has a high water solubility in comparison with the other pesticides under study (Table I) and as such was more prominent in water samples as opposed to the suspended sediment samples, although R2 also showed a very high concentration of 245 μg kg^{-1} in the sediments.

Endosulfan is semivolatile and photolytically stable in water. The two isomers have a half-life of 150 days, and are persistent in both soil and aquatic environments (EXTOXNET, 1996) and as a result tend to accumulate in the environment (Antonious and Byers, 1997). Owing to the persistent nature of this pesticide, it is therefore not surprising that endosulfan was detected in water samples taken during pre-runoff conditions (Table III). Endosulfan has a low water solubility (0.32 mg L^{-1}), with the result that it readily adsorbs to sediment particles and as such, was widely detected in sediment samples throughout the study area.

Chlorpyrifos has a very low water solubility (Table I), adsorbs strongly to soils, and has been found to be highly persistent in sediments (Green *et al.*, 1996; EX-TOXNET, 1996). This study supports these findings. Although the water samples of only one site showed contamination, chlorpyrifos was detected in many sediment samples from many of the sites (Table IV). The fungicide procymidone was detected at very high concentrations in runoff water samples only. This is in accordance with its relatively high water solubility (Table I).

Although the partitioning behaviour of the detected pesticides is in general accordance with their physicochemical properties, all substances were found at relatively high concentrations in both matrices, water and suspended particles. We did not calculate partitioning coefficients based on our results, since the water samples refer to discrete samples during runoff and the suspended sediment values refer to integrated samples taken over a period of 14 days or longer.

4.3. IDENTIFICATION OF 'HOTSPOTS'

Sites R1, W1 and E1 showed no increased contamination by any of the studied insecticides in water samples taken during runoff conditions. This was expected as there are no orchards directly bordering the river upstream from R1 or the tributary of E1. The fact that the fungicide procymidone was detected at site E1 during runoff conditions indicates that contamination via runoff is a potential problem should orchards be established adjacent to the tributary. Low concentrations of endosulfan were detected at all of these control sites before the large runoff events had taken place which could possibly be attributed to spraydrift events occuring earlier in the year during the spraying period (Schulz *et al.*, 2001).

Pereira *et al.* (1996) showed that tributaries are important sources of pesticide contamination, resulting in high concentrations in the mainstream of the San Joaquin River, California. This study clearly shows that sites W2, W3 and W4 are

important sources of pesticide contamination during runoff conditions and cause high contamination at site R2 in the mainstream of the Lourens River. It is probable that most runoff actually takes place from the agricultural areas into the side-streams as opposed to directly into the mainstream itself. This is illustrated with samples taken from site W4, where 0.47 μg L^{-1} chlorpyrifos was detected in a sample taken of runoff flowing directly from the nursery before it entered the side-stream (Table III) and resulted in a concentration of 0.19 μg L^{-1} in the side-stream itself.

Sites W2, W3 and W4 showed the highest concentrations of pesticides and suspended sediment of all the sites investigated in the study area. These three sites were contaminated with both isomers as well as the sulfate of endosulfan, indicating recent contamination as a result of the runoff activity. Azinphos-methyl was also detected at high concentrations in water samples from all three of these sites. Site R2 is directly affected via the input of the pesticides, as can be seen when comparing pesticide levels in R2 and the control site R1.

Factors influencing runoff of pesticides include the slope of the land and the extent of the land use (Cole *et al.*, 1997; Merkle and Bovey, 1974). Possible reasons for the high contamination detected in sites W2 and W3 are that these tributaries have a long bank length and are extensively bordered by orchards throughout their length (76 and 100%), and have high maximum slope values (5 and 7%, respectively) and average slope values (2 and 3%, respectively) (Table II). W4 has a comparably low slope average (1%) and 63% of its bank length is bordered by orchards. At this site, the influence of the nursery (19% of stream bank length) might be of importance, as is illustrated by the high chlorpyrifos concentration (0.47 μg L^{-1}) that was detected in runoff water flowing directly from the nursery into the side-stream. It is possible that the nursery is responsible for a high proportion of the contamination in this side-stream. Together, the nursery and bordering orchards comprise 82% of the total stream bank length.

The sites on the eastern farm do not appear to play a major role in contributing to contamination of the mainstream. Endosulfan sulfate was the only harmful contaminant detected in water samples during the course of the sampling period (at very low concentrations – 0.025 μg L^{-1}), and as this is a persistent breakdown product, it is likely that it landed up in the side-streams during a previous runoff or spraydrift event. Azinphos-methyl was not detected in any of the water or sediment samples taken in the eastern farm streams. Although chlorpyrifos was detected in sediment samples (29.7 μg kg^{-1}), this concentration was much lower than those detected in the sites of the western farm. The low contamination can be explained by the landuse bordering the stream. The average slope and maximum slope are very low (1% respectively, Table II), and the stream is bordered by only 51% orchards.

It follows from our results that risk reduction strategies are of specific importance at sites W2, W3 and W4 to prevent pesticides and TSS from entering the Lourens River. As a possible strategy, the implementation of constructed wetlands

into these tributaries was suggested. Such wetlands are currently constructed into these tributaries.

Acknowledgements

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