Current-use insecticides, phosphates and suspended solids in the Lourens River, Western Cape, during the first rainfall event of the wet season

Ralf Schulz[1]*, Sue KC Peall[2], James M Dabrowski[1] and Adriaan J Reinecke[1]
[1] Department of Zoology, University of Stellenbosch, Matieland 7602, South Africa
[2] Forensic Chemistry Laboratory, Department of Health, Cape Town 8000, South Africa

Abstract

Pesticide contamination resulting from agricultural runoff depends on the time period between application and rainfall. In Western Cape orchard areas, the last pesticide application of the growing season in summer takes place at the end of February. Pesticides, total phosphates and total suspended solids (TSS) were measured in the Lourens River at the beginning of April 1999 prior to the first rainfall of the rainy season and in the middle of April during high discharge following the first rainfall of 9.6 mm/d. Pre-runoff samples indicated only contamination with total endosulfan (α, β, sulphate) at levels up to 0.06 μg/l. Runoff during the first rainfall event resulted in an increase in the levels of endosulfan, chlorpyrifos and azinphos-methyl, to 0.16, <0.01 and 0.38 μg/l, respectively, in water samples and 245, 344, and 244 μg/kg in suspended sediments. In terms of chemical load the single rainfall event caused a loss of 15.1 g/h endosulfan, 1.8 g/h chlorpyrifos and 20.5 g/h azinphos-methyl. The second rainfall event caused no measurable increase in pesticide levels, although the amount of rain was even higher (14.4 mm/d). Levels of both total phosphate and TSS were also increased during the first runoff event. Transient contamination levels exceeded the target water quality range proposed by the South African Department of Water Affairs and Forestry (DWAF). The Lourens River site downstream of the farming area is identified as a site where potentially toxic conditions might arise.

Introduction

Runoff is regarded as an important route of entry of non-point source pollutants in surface waters in agricultural areas (Cooper, 1993). Runoff occurs during the rainy season, which lasts from April to December in the Western Cape. Runoff-related input usually leads to an increase of water level, nutrients and total suspended solids (TSS); pesticides may enter the surface water as either water-dissolved or particle-associated chemicals (Wauchope, 1978).

Pesticide quantities that enter surface waters via runoff are dependent on a number of factors, including the time interval between the application of pesticides and the first heavy rainfall event, the slope and soil types of the catchment, the pesticide application, and the size and characteristics of buffer strips (Wauchope, 1978). Thus, in the context of the Western Cape, a very important period with regard to determining runoff-related contamination is in April, when the first heavy rains normally fall after the end of the spraying season in late February.

Only a few studies deal with pesticide levels in aquatic systems in South Africa: farm dams (Davies and Peall, 1997; Hassett et al., 1987), lakes (Greichus et al., 1977) or river ecosystems (Grobler, 1994; Roux et al., 1994). None of these studies has attempted to establish a direct link between chemicals currently used in agriculture and contamination of the aquatic environment. Moreover, they have not addressed the problem of runoff as a potential route 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 (Dallas and Day, 1993). The transient nature of pesticide peak levels in streams (Kreuger, 1995; Schulz et al., 1998) adds a further problem to the monitoring of pollution, since the sampling programme must be well-adapted to cover the short periods with peak contamination. During recent decades a deterioration in 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 about the extent to which toxic substances are responsible for the degradation of the Lourens River.

The aim of this study was to determine the extent to which pesticides, phosphates and suspended solids from the surrounding orchard areas contaminated a typical Western Cape stream. Runoff-related input following the first rainfall events of the wet season was investigated. Pesticide concentrations were compared to standard toxicity values, to determine whether there might be any potential threat to the aquatic communities in the Lourens River.

Materials and methods

Study area

The Lourens River rises at an altitude of 1080 m in a naturally vegetated fynbos area and flows in a southwesterly direction for 20 km before discharging into False Bay at The Strand (S34°06′; E18°48′). The catchment region is characterised by intensive farming, with orchards and vineyards in its middle reaches. The Lourens River has a total catchment area of 92 km² and receives an annual mean rainfall of 915 mm. Roughly 87% of its 35×10^6 m³ mean annual discharge occurs during the autumn, winter and early

TABLE 1
Characteristics of pesticides: water solubility, amount of pesticides applied to orchards between August and February in the Lourens River catchment (orchard growing area: 400 ha) and acute toxicity to the standard test organisms *Oncorhynchus mykiss* (96h LC$_{50}$) and *Daphnia magna* (48 h EC$_{50}$)

Pesticide name	Water solubility at given temp. (mg/l)[a]	Amount applied (kg)[b]	Acute toxicity[c]	
			Rainbow trout (µg/l)	Water flea (µg/l)
Azinphos-methyl	28 (20°C)	771	4.3	1.6
Chlorpyrifos	1.2 (25°C)	686	9	0.42
Endosulfan	0.32 (22°C)	158	0.3	250

[a] USDA ARS database.
[b] according to local farmers' spraying programme.
[c] (Dortland, 1980; Johnson and Finley, 1980; Lemke, 1981; USEPA, 1986; Van der Hoeven and Gerritsen, 1997).

TABLE 2
Pesticide concentrations (µg/l) in water samples from six sites in the Lourens River, Somerset West, South Africa

Site	Sampling date[1]	Endo-sulfan-α	Endo-sulfan-β	Endo-sulfan-S	Total endo-sulfan	Chlor-pyrifos	Azinphos-methyl
R1	2 April	0.01	0.01	0.03	0.05	-	-
	15 April	-	-	-	-	-	-
R2	2 April	0.01	0.01	0.02	0.04	-	-
	15 April	-	-	-	-	-	0.38
R3	2 April	-	-	-	-	-	-
	15 April	-	-	-	-	-	-
	19 April	-	-	-	-	-	-
R4	2 April	-	-	0.03	0.03	-	-
	15 April	-	-	-	-	-	-
	18 April	-	-	-	-	-	-
R5	2 April	-	-	0.06	0.06	-	-
	15 April	-	-	0.03	0.03	-	-
R6	2 April	0.02	0.03	0.01	0.06	-	0.07
	15 April	0.02	0.03	0.11	0.16	-	0.26
	18 April	-	-	-	-	-	-

[1] 2 April: pre-runoff conditions; 15, 18, and 19 April: during runoff.

the insecticides endosulfan, chlorpyrifos and azinphos-methyl (Table 1). Chlorpyrifos and azinphos-methyl were applied frequently between October and February to pears and plums, up to approximately one application every two weeks in each single plot. Endosulfan is applied mainly to apple orchards.

Sampling sites and rainfall event characteristics

The sampling area stretched over almost 6 km of the Lourens River. The orchard plots are separated from the Lourens River itself by a strip of vegetation (eucalyptus trees, shrubs and grass) between 15 m and 40 m in width, making direct input of edge-of-field runoff into the river highly improbable (Table 2). In contrast, most of the tributaries are at least in some stretches directly adjacent to orchard plots (distance: approx. 5 m) and may therefore present potential routes of entry. Six sampling sites in the Lourens River were selected for measurement of TSS, total phosphate, aqueous and particle-associated pesticide levels. Site R1 was assumed to be uncontaminated, owing to the lack of any agricultural activity on the banks upstream of this site. The remaining Sites R2 to R6 were expected to be contaminated with sediments, nutrients and pesticides from the orchards.

The last pesticide application in the study area had taken place at the end of February. The first runoff-inducing rainfall event with 9.6 mm/d was on 15 April and was followed by other events on 18, 19 and 21 April (Fig. 1).

Sampling programme

Water samples were collected prior to any rain-induced runoff on 2 April 1999 to provide an indication of the level of contami-

spring 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 and the slopes in the catchment vary between <2% in the area near the river and <8% in the upstream stretches of the river and some of the tributaries.

Pesticides are applied to orchards between August and February before the harvesting of fruit, consisting mainly of pears, plums and apples (total growing area: 4 km²). The active ingredients of pesticides applied in the orchards and analysed in this study include

nation 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 contamination levels during runoff were collected in glass bottles (3 l) set into the stream or river with the opening of the bottle approximately 3 cm above the normal water level. During rainfall-induced surface runoff, the rising water level filled the bottles passively. A small glass pipe (Pasteur pipette with the tip broken off) was tied in the opening of the bottle, using synthetic nylon. This

Figure 1
Rainfall during April and May 1999 at a meteorological station near Helderberg in the Lourens River valley. Arrows indicate dates on which water samples were taken (A = before runoff; B = during runoff). Pesticide application ended at the end of February. Total rainfall values for January, February and March were 5.2, 3.4 and 0.6 mm/d, respectively. Suspended particles were sampled between 1 April and 17 May.
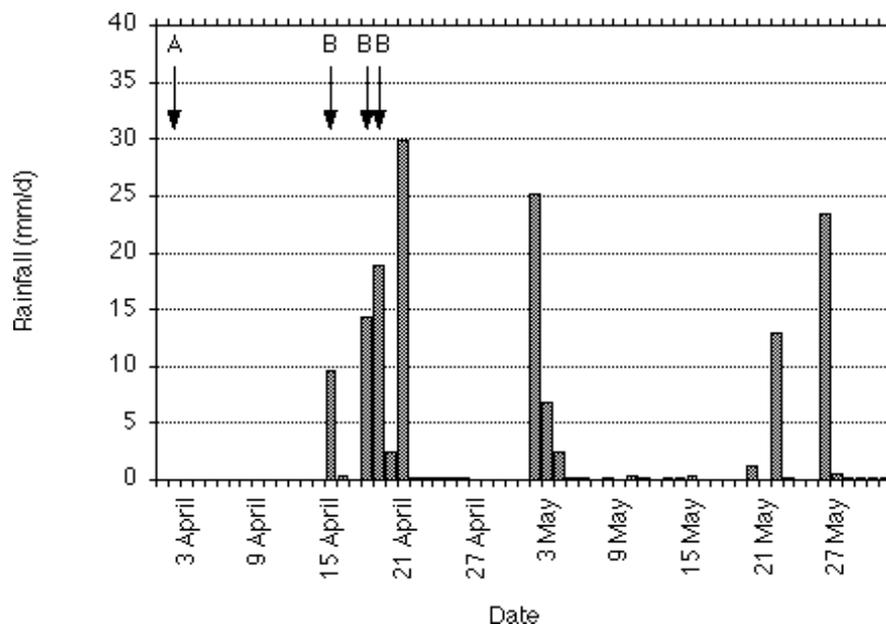
enabled a free flow of water into the bottle while air could flow out via the glass pipe. Water samples (500 to 900 ml) were solid-phase extracted (SPE) using C18 columns (Chromabond) which had previously been prepared with 6 ml methanol and then 6 ml water. The columns were air-dried for 30 min and kept at –18°C until analysed.

Samples for determining pesticides associated with suspended sediments were obtained using a suspended sediment sampler (Liess et al., 1996), which consisted of a plastic jar (500 ml) with a screw-on lid containing a hole (2 cm in diameter). An open glass jar was placed into this plastic jar directly beneath the hole in the lid. Each sampler was attached to a metal stake, which was driven into the river bed. This system supplies samples representing 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, Duesseldorf). 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 h. The filter paper was re-weighed to determine TSS (total suspended solids). Total phosphate levels were measured photometrically after disintegration using the total-phosphate kit of Dr. Lange, Duesseldorf. Discharge was calculated by means of standard formulas using velocity measurements along cross-sectional profiles. Measurements were done before runoff occurred on 2 April and during runoff on 15 April in order to calculate contaminant loads.

Pesticide extraction and 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 bottles containing sediment and methanol were shaken until the contents were well mixed, placed in an ultrasonic bath for 30 min and then centrifuged. The supernatant methanol was filtered through glass fibre filter paper into 500 ml measuring cylinders. Another 50 ml of methanol was added to the sediment and the samples were again mixed well, placed in the ultrasonic bath and centrifuged. The two methanol extracts from 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 dry mass (dm). 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 was 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 had been assayed and were known 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 and 0.1 µg/kg dm.

TABLE 3
Pesticide concentrations in suspended sediment samples (μg/kg dm) from six sites in the Lourens River and its tributaries

Site	Sampling interval[1]	Endo-sulfan-α	Endo-sulfan-β	Endo-sulfan-S	Total endo-sulfan	Chlor-pyrifos	Azinphos-methyl
R1	1-29 April	-	-	-	-	-	-
	29 April - 17 May	-	-	-	-	-	-
R2	1-18 April	-	-	-	-	15.5	-
	29 April - 17 May	-	-	4.3	4.3	2.0	3.4
R3	1-18 April	-	-	-	-	344.2	-
	29 April - 17 May	-	-	3.9	3.9	-	4.5
R4	1-18 April	-	-	-	-	243.2	-
	19 April - 17 May	4.2	2.8	4.3	11.4	-	-
R5	1-18 April	-	-	-	-	189.7	-
	29 April - 17 May	-	13.1	29.6	42.8	29.0	6.7
R6	1-18 April	45.5	90.0	109.8	245.3	69.0	244.6
	18 April - 17 May	18.1	20.0	12.7	50.8	9.9	7.0

[1] The first runoff event took place on 15 April during a 9.6 mm/d rainfall.

Results

Pesticide concentrations and loads

Pesticides that were identified in the water samples included endosulfan, chlorpyrifos and azinphos-methyl (Table 2). Endosulfan was present in many pre-runoff samples at concentrations of up to 0.06 μg/l. The runoff sample from Site R6 contained a total endosulfan concentration of 0.16 μg/l. Most of the total endosulfan can be attributed to the metabolite endosulfan sulphate; the only site with relatively high levels of the α- or β-isomer was R6. Azinphos-methyl was detected during pre-runoff only at Site R6 at a concentration of 0.07 μg/l. Levels of azinphos-methyl were increased during runoff at Sites R2 and R6, to 0.38- and 0.26-μg/l, respectively. Water samples taken during rainfall events after the 15th of April at Sites R3, R4 and R6 never contained any pesticides.

Suspended sediment samples were taken throughout runoff conditions and the first samples, taken during the first rainfall after the pesticide application period, generally showed considerably higher concentrations of pesticides than those taken during subsequent runoff events (Table 3). The highest endosulfan concentration, 245 μg/kg, was detected at Site R6. Most of the total endosulfan was again attributed to endosulfan sulphate. However, the isomers were present at increased levels at R5 and R6. Chlorpyrifos was found in high concentrations of up to 344 μg/kg in suspended sediments at Sites R2 to R6. Particle-associated azinphos-methyl was detected at Sites R2, R3, R5 and R6. Site R6 revealed a high concentration of 245 μg/kg.

The Lourens River Site R1 was the only site that did not show an increase in pesticide concentrations during runoff conditions. At the most downstream Lourens River Site R6 high levels of endosulfan, chlorpyrifos and azinphos-methyl were observed during runoff conditions.

Discharge at Site R6 was 0.3 m³/s before runoff on 2 April and 15 m³/s during runoff on 15 April. The peak discharge during runoff remained at this level for approximately 1 h. Aqueous pesticide load for Site R6 was calculated by multiplying the simultaneously measured peak pesticide concentration by the peak discharge. Particle-associated pesticide load was calculated in the same way including the TSS concentrations. Chlorpyrifos load was higher in the suspended sediment-associated form (1.8 g/h) than in the water phase (0 g/h), while it was the opposite for azinphos-methyl (6.5 and 14 g/h) and total endosulfan (6.5 and 8.6 g/h, respectively).

Total phosphate and total suspended solids (TSS)

Total phosphate levels were between 0.13 and 0.22 mg/l before runoff (Table 4). During runoff, total phosphate remained in the same range at Sites R1 to R3, but increased at Sites R4 to R6. Levels during runoff depicted a successive increase from Sites R2 to R6. During runoff, the TSS levels increased considerably at all sites relative to the pre-runoff conditions (Table 4). During normal flow conditions before runoff, all of the sites had TSS levels of less than 10 mg/l. Apart from Sites R1 and R4, the TSS levels increased during runoff to levels higher than 100 mg/l, with the highest values being measured at Sites R5 and R6.

Discussion

The present results clearly indicate that agricultural runoff is an important route of pesticide, phosphate and suspended sediment input into the Lourens River. This is evident from the fact that pollution increased considerably during runoff in comparison to pre-runoff conditions. Furthermore, no contamination was detected at the river Site R1 upstream of the farming area. Transient

TABLE 4
Mean (±SE) of total phosphate and total suspended solid (TSS) levels in the Lourens River before (2.4.1999, n = 3) and during (15.4.1999, n = 1) runoff conditions

Site	Total phosphate (mg/l)		TSS (mg/l)	
	Pre-runoff	During runoff	Pre-runoff	During runoff
R1	0.19±0.05	0.13	1.0±0.02	5.6
R2	0.13±0.05	0.12	1.0±0.01	274.1
R3	0.22±0.08	0.28	1.3±0.04	105.1
R4	0.18±0.01	0.40	3.6±0.03	62.9
R5	0.13±0.01	0.46	4.7±0.01	471.9
R6	0.17±0.01	0.75	6.2±0.01	486.2

increases of agriculturally derived pesticide levels during runoff have been reported in several other studies from Europe and North America (Baughman et al., 1989; Kreuger, 1995; Schulz and Liess, 1999). However, information on levels of current-use insecticides in South African surface waters is sparse (Davies and Day, 1998). The suspended particle samples revealed that at almost all of the sites where pesticides were detected, the total pesticide concentrations were higher during the first runoff event than during the second. The same trend is obvious from the water samples taken at Site R6, showing a certain contamination during the first runoff event on 15 April, but no detectable contamination during the second runoff event, which occurred only three days later. These results support those of Domagalski et al. (1997), highlighting the fact that the first runoff event after a long, dry period results in the highest pesticide input.

Endosulfan levels found in the present study were comparable to values reported for other aquatic ecosystems receiving agricultural runoff (Miles and Harris, 1971; Kreuger and Brink, 1988; Scott et al., 1999). The levels detected in water samples on 2 April are regarded as background contamination in this agriculturally used catchment. All sites yielded endosulfan levels higher than the target water quality range of 0.01 μg/l, as proposed by the South African Department of Water Affairs and Forestry (DWAF, 1996). Of particular concern is the finding that levels during runoff almost reached the acute effect value of 0.2 μg/l (DWAF, 1996). Both isomers of endosulfan, as well as the breakdown product (endosulfan sulphate), are highly toxic towards aquatic organisms, particularly fish (Table 1; Goebel et al., 1982)). The level of endosulfan found at Site R6 was above the 10 d LC_{50} found for the mayfly species *Jappa kutera* (Leonard et al., 2000). With respect to particle-associated contamination, endosulfan levels were not detectable at the sites R1 to R5 during the first sampling interval, but were very high at Site R6, indicating that this endosulfan input had taken place via one of the tributaries entering the Lourens River between Sites R5 and R6.

Chlorpyrifos was detected following runoff in streams draining orchard growing areas in the Central Valley, California at levels of between 0.04- and 0.52-μg/l (Kuivila and Foe, 1995; Werner et al., 2000). In the present study, this pesticide was only observed in association with suspended particles, at levels of up to 344 μg/kg, which is in accordance with its relatively low water solubility (Table 1). Furthermore, the very long time span between the last application of chlorpyrifos in December and the runoff in April may have contributed to the fact that this pesticide was found only in particle-associated form. As a particle-associated pesticide,

chlorpyrifos 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 for the marine copepod *Amphiascus tenuiremis* (Green et al., 1996) and of approx. 300 μg/kg for the freshwater midge *Chironomus tentans* (Ankley et al., 1994). Green et al. (1996) calculated a sediment quality criterion of 38 μg/kg based on equilibrium partitioning theory.

Higher azinphos-methyl concentrations than in the present study were found in an estuarine environment receiving agricultural runoff (Scott et al., 1999) and in runoff from a sugar-cane area (Smith et al., 1983). The aqueous azinphos-methyl levels measured in the present study are below concentrations acutely toxic to *D. magna* (Table 1), but in the same range as the 96-h LC_{50} of 0.37 μg/l for the midge *Chironomus tentans* (Ankley and Collyard, 1995).

It can be expected that the pesticide load detected at Site R6 will affect the estuary of the Lourens River approx. 9 km downstream. For example, the endosulfan levels measured at R6 in suspended sediments (245 μg/kg) are above the concentrations reducing survival and reproduction in meiobenthic polychaetes and copepods (50 to 200 μg/kg) (Chandler and Scott, 1991). It was reported that azinphos-methyl has been responsible for a large number of fish kills in estuarine areas adjacent to sugar-cane and vegetable crops (Ross et al., 1996).

Levels of total phosphate were already quite high in some of the pre-runoff samples, with maximum values of 0.22 mg/l. However, they were increased during runoff to maximum values of 0.75 mg/l. The subsequent increase of total phosphate in the downstream direction of the Lourens River is evidence for the negative influence of the farming area on the trophic status of the river.

The TSS increased considerably during runoff conditions (Table 4). Potential effects of increased 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 increases in TSS, for instance 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 (Taylor and Roff, 1986). The increase of TSS values during runoff clearly exceeds the target water quality range established by the South African Department of Water Affairs and Forestry, which is an increase of <10% compared to the background TSS level at the specific site (DWAF, 1996). Monthly measurements of water quality parameters in the lower reaches of the Lourens River undertaken by the Department of Water Affairs and Forestry (DWAF, unpublished data) between 1996 and 1999 revealed PO_4-P levels between 0.03 and 0.12 mg/l and TSS levels between 9 and 17 mg/l. The total phosphate levels measured at Sites R4 to R6 and the TSS levels measured at R2 to R6 during runoff are considerably higher than these monthly averages, indicating the importance of runoff events for the introduction of nutrients and sediments.

Acknowledgements

Victor Krause, Helderberg Nature Reserve for co-operating in the field technical operations, and Jenny Day, UCT for co-operation and helpful comments on the manuscript. Wilna Kloppers from DWAF in Bellville gave permission to use their water quality data.

References

ANKLEY GT, CALL DJ, COX JS, KAHL MD, HOKE RA and KOSIAN PA (1994) Organic carbon partitioning as a basis for predicting the toxicity of chlorpyrifos in sediments. *Environ. Toxicol. Chem.* **13** 621-626.

ANKLEY GT and COLLYARD SA (1995) Influence of piperonyl butoxide on the toxicity of organophosphate insecticides to three species of freshwater benthic invertebrates. *Comp. Biochem. Physiol.* **110** 149-155.

BARTON BA (1977) Short-term effects of highway construction on the limnology of a small stream in southern Ontario. *Freshwater Biol.* **7** 99-108.

BAUGHMAN DS, MOORE DW and SCOTT GI (1989) A comparison and evaluation of field and laboratory toxicity tests with fenvalerate on an estuarine crustacean. *Environ. Toxicol. Chem.* **8** 417-429.

CHANDLER GT and SCOTT GI (1991) Effects of sediment-bound endosulfan on survival, reproduction and larval settlement of meiobenthic polychaetes and copepods. *Environ. Toxicol. Chem.* **10** 375-382.

COOPER CM (1993) Biological effects of agriculturally derived surface-water pollutants on aquatic systems - A review. *J. Environ. Qual.* **22** 402-408.

DALLAS HF and DAY JA (1993) The Effect of Water Quality Variables on Riverine Ecosystems: A Review. Report for the Water Research Commission, Pretoria.

DAVIES BR and DAY JA (1998) *Vanishing Waters*. UCT Press, Cape Town. 485 pp.

DAVIES HE and PEALL SKC (1997) A study of pesticide residue levels in farm dams in the Western Cape, South Africa. *Fitzpatrick Institute* 1-12.

DOMAGALSKI JL, DUBROVSKY NM and KRATZER CR (1997) Pesticides in the San Joaquin River, California: Inputs from the dormant sprayed orchards. *J. Environ. Qual.* **26** 454-465.

DORTLAND RJ (1980) Toxicological Evaluation of Parathion and Azinphos-methyl in Freshwater Model Ecosystems. Agricultural Research Report 898, Wageningen. 112 pp.

DWAF (1996) Draft of South African Water Quality Guidelines. Volume **7**: Aquatic Ecosystems. Department of Water Affairs and Forestry, Pretoria.

GIPPEL CJ (1995) Potential of turbidity monitoring for measuring the transport of suspended solids in streams. *Hydrol. Processes* **9** 83-97.

GOEBEL H, GOREBACH S, KNAUF W, RIMPAU RH and HUTTEN-BACH H (1982) Properties, effects, residues, and analytics of the insecticide endosulfan. *Residue Rev.* **83** 1-165.

GREEN AS, CHANDLER GT and PIEGORSCH WW (1996) Life-stage-specific toxicity of sediment-associated chlorpyrifos to a marine, infaunal copepod. *Environ. Toxicol. Chem.* **15** 1182-1188.

GREICHUS YA, GREICHUS A, AMMAN BD, CALL DJ, HAMMAN DCD and POTT RM (1977) Insecticides polychlorinated biphenyls and metals in African lake ecosystems. I. Hartbeespoort Dam, Transvaal and Voëlvlei Dam, Cape Province, Republic of South Africa. *Arch. Environ. Contam. Toxicol.* **6** 371-383.

GROBLER DF (1994) A note on PCBs and chlorinated hydrocarbon pesticide residues in water, fish and sediment from the Olifants River, Eastern Transvaal, South Africa. *Water SA* **20** (3) 187-194.

HASSETT AJ, VILJOEN PT and LIEBENBERG JJE (1987) An assessment of chlorinated pesticides in the major surface water resources of the Orange Free State during the period September 1984 to September 1985. *Water SA* **13** (3) 133-136.

JOHNSON WW and FINLEY MT (1980) Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. United States Department of International Fish and Wildlife Service, Resour. Publ. 137, Washington D.C. 98 pp.

KREUGER J (1995) Monitoring of pesticides in subsurface and surface water within an agricultural catchment in southern Sweden. *British Crop Protection Council Monograph No. 62: Pesticide Movement to Water* 81-86.

KREUGER JK and BRINK N (1988) Losses of pesticides from agriculture. In: IAEA (ed.) *Pesticides: Food and Environmental Implications.* International Atomic Energy Agency, Vienna. 101-112.

KUIVILA KM and FOE CG (1995) Concentration, transport and biological effects of dormant spray pesticides in the San Francisco Estuary, California. *Environ. Toxicol. Chem.* **14** 1141-1150.

LEMKE AE (1981) Interlaboratory comparison acute testing set. EPA-600/3-81-005, Environ. Res. Lab., USEPA, Duluth, MN. 29 pp.

LEONARD AW, HYNE RV, LIM RP, LEIGH KA, LE J and BECKETT R (2000) Fate and toxicity of endosulfan in Namoi River water and bottom sediment. *J. Environ. Qual.* (In press).

LIESS M, SCHULZ R and NEUMANN M (1996) A method for monitoring pesticides bound to suspended particles in small streams. *Chemosphere* **32** 1963-1969.

MILES JRW and HARRIS CR (1971) Insecticide residues in a stream and a controlled drainage system in agricultural areas in southwestern Ontario, 1970. *Pestic. Monit. J.* **5** 289-294.

ROSS P, SCOTT GI, FULTON MH and STROZIER ED (1996) Immuno-assays for rapid, inexpensive monitoring of agricultural chemicals. In: Richardson M (ed.) *Environmental Xenobiotics*. Taylor and Francis, London. 161-178.

ROUX DJ, BADENHORST JE, DU PREEZ HH and STEYN GJ (1994) Note on the occurrence of selected trace metals and organic compounds in water, sediment and biota of the Crocodile River, Eastern Transvaal, South Africa. *Water SA* **20** (4) 333-340.

SCHULZ R, HAUSCHILD M, EBELING M, NANKO-DREES J, WOGRAM J and LIESS M (1998) A qualitative field method for monitoring pesticides in the edge-of-field runoff. *Chemosphere* **36** 3071-3082.

SCHULZ R and LIESS M (1999) A field study of the effects of agriculturally derived insecticide input on stream macroinvertebrate dynamics. *Aquat. Toxicol.* **46** 155-176.

SCOTT GI, FULTON MH, MOORE DW, WIRTH EF, CHANDLER GT, KEY PB, DAUGOMAH JW, STROZIER ED, DEVANE J, CLARK JR, LEWIS MA, FINLEY DB, ELLENBERG W and KARNAKY (Jr.) KJ (1999) Assessment of risk reduction strategies for the management of agricultural nonpoint source pesticide runoff in estuarine ecosystem. *Toxicol. Indust. Health* **15** 200-213.

SMITH ME and KASTER JL (1983) Effect of rural highway runoff on stream benthic macroinvertebrates. *Environ. Pollut.* **32** 157-170.

SMITH S, REAGAN TE, FLYNN JL and WILLIS GH (1983) Azinphos-methyl and fenvalerate runoff loss from a sugarcane-insect IPM system. *J. Environ. Qual.* **12** 534-537.

TAYLOR BR and ROFF JC (1986) Long-term effects of highway construction on the ecology of a southern Ontario (Canada) stream. *Environ. Pollut.* **40** 317-344.

THARME R, RATCLIFFE G and DAY E (1997) An Assessment of the Present Ecological Condition of the Lourens River, Western Cape, with Particular Reference to Proposals for Stormwater Management. Freshwater Research Unit, UCT, Cape Town. 289 pp.

USEPA (1986) Ambient Water Quality Criteria for Chlorpyrifos. EPA 440/5-86-005, Criteria and Standards Division, Office of Water Regulations and Standards, Washington, D.C.

VAN DER HOEVEN N and GERRITSEN AAM (1997) Effects of chlorpyrifos on individuals and populations of *Daphnia pulex* in the laboratory and field. *Environ. Toxicol. Chem.* **16** 2438-2447.

WAUCHOPE RD (1978) The pesticide content of surface water draining from agricultural fields - A review. *J. Environ. Qual.* **7** 459-472.

WERNER I, DEANOVIC LA, CONNOR V, DEVLAMING V, BAILEY HC and HINTON DE (2000) Insecticide-caused toxicity to *Ceriodaphnia dubia* (Cladocera) in the Sacramento-San Joaquin River Delta, California, USA. *Environ. Toxicol. Chem.* **19** 215-227.