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PREDICTED AND MEASURED LEVELS OF AZINPHOSMETHYL IN THE LOURENS RIVER, SOUTH AFRICA: COMPARISON OF RUNOFF AND SPRAY DRIFT

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Abstract—Runoff and spray drift are important sources of nonpoint pesticide pollution in surface waters, but few studies have directly compared these routes of input in an exposure assessment scenario. To this end, a runoff formula suggested by the Organization for Economic and Cooperative Development (Paris, France) and basic drift values (95th percentiles) were integrated into a geographical information system (GIS) to predict runoff and spray drift–related loading of azinphosmethyl (AZP) in the Lourens River (LR), South Africa. The GIS-integrated calculations were first validated in the tributaries of the river, where measured loads were well predicted for both runoff ($r^2 = 0.95$; $p < 0.0001$; $n = 9$) and spray drift ($r^2 = 0.96$; $p = 0.0006$; $n = 8$). Through extrapolation to the catchment scale containing 400 ha of orchards, the GIS-integrated calculations predicted similar loads of AZP as measured in the Lourens River mainstream for six runoff (between a factor of 1.03 and 1.86 lower) and six spray drift (between a factor of 1.1 and 2.4 higher) events. Mean measured loads per event were significantly ($p = 0.004$) higher for runoff (27.8 ± 19.1 g) than for spray drift (0.69 ± 0.32 g). Based on long-term meteorological data and average application regimes, runoff leads to a higher annual load (47.6 g) than spray drift (5.5 g) in the Lourens River. Runoff is clearly a more important source of nonpoint pollution in the studied catchment, and mitigation strategies should focus first on addressing this aspect on a catchment scale and second on addressing problem areas on a subcatchment scale.

Keywords—Exposure assessment Geographical information system Insecticides Runoff Spray drift

INTRODUCTION

Nonpoint-source pesticide pollution from agricultural areas is widely regarded as one of the greatest threats to contamination of natural surface waters, necessitating the need to predict areas of risk [1]. Spray drift and runoff are considered to be important routes of entry for pesticides [2], and as such, in terms of a risk assessment scenario, it is vital to compare these two processes with regard to their threat to water quality.

Land use, meteorological, and application characteristics directly influence both spray drift [3,4] and runoff [5] and are thus important factors to consider when assessing the risk of these routes of nonpoint pollution to surface waters. Furthermore, runoff is highly dependent on the physicochemical properties of the pesticides themselves, as they determine the amount of pesticide available to surface runoff [6,7].

Nonpoint-source pollution models incorporate all of these variables in an attempt to predict contamination levels and could thus be valuable in comparing runoff and spray drift as important sources of pollution in a river catchment. Such was the focus of this study, which was carried out in the Lourens River catchment, Western Cape, South Africa. Based on intensive studies of nonpoint-source pesticide pollution in this catchment [8–11], a modeling approach was implemented using a simple runoff formula by Reus et al. [12] and basic spray drift values by Ganzelmeier et al. [3].

Standardized drift studies for orchards as summarized by Ganzelmeier et al. [3] are similar to those recommended by the Spray Drift Task Force [4] and are proposed for use in exposure assessments. Prediction of runoff requires a great number of input variables, and complex models such as groundwater loading effects of agricultural management systems, pesticide root zone model, and agricultural nonpoint-source models have been developed for this purpose [13]. However, the formula by Reus et al. [12] is designed as a simple tool for prediction of pesticide loss in runoff and has been proposed as a risk indicator for runoff by the Organization for Economic and Cooperative Development [14]. This formula was used, as almost all input variables are easily available from digital maps and soil databases. The organophosphate pesticide azinphosmethyl [*O*,*O*-dimethyl-*s*-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl)]phosphorodithioate], in comparison with other insecticides, has a relatively low K_{OC} of 1,000 L/kg and a high water solubility of 29 mg/L at 25°C [15]. It has been shown to persist in pond water with a half-life of about 2.4 d [16]. The azinphosmethyl (AZP) is frequently applied to apple, pear, and plum orchards in the catchment and has been regularly detected following runoff and spray drift activity in the mainstream and tributaries [8,11]. The estimated total application in fruit orchards of the Western Cape is 52,000 kg active ingredient (a.i.) per year. It is also one of the most heavily applied pesticides in the United States, and in 1997, almost 950,000 kg a.i. were applied throughout the entire country [17].

The main aim of the present study is to compare spray drift and runoff as routes of nonpoint-source AZP pollution of the Lourens River based on predicted and measured values. Existing predictive approaches were implemented using a geographical information system (GIS) and validated using measured loads from subcatchments of the Lourens River. The ultimate comparison of runoff and spray drift was done at the

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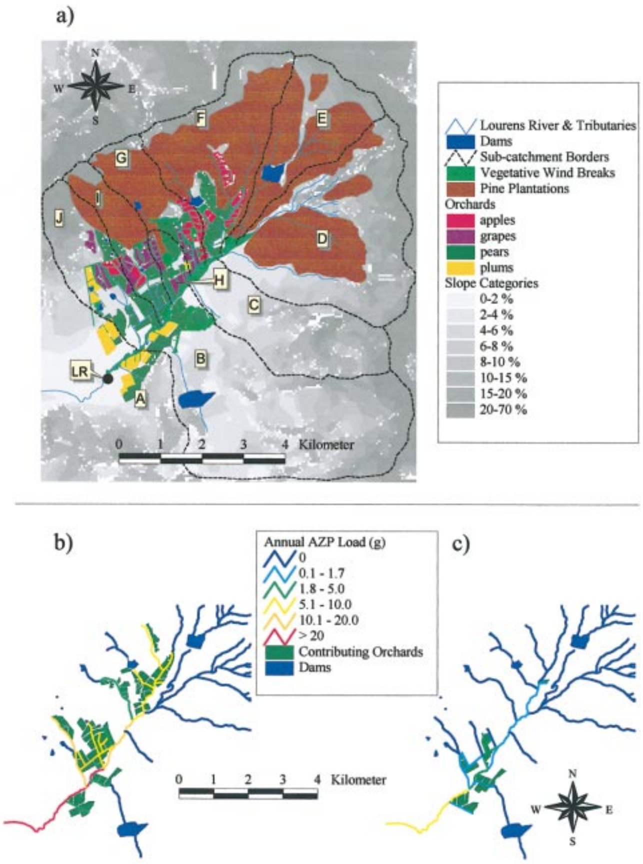

Fig. 1. Scale diagrams of (**a**) the land use of the Lourens River (LR) catchment, South Africa (subcatchments A–J); (**b**) orchards affected by runoff and corresponding predicted annual loads of azinphosmethyl (AZP) in the tributaries and mainstream of the Lourens River; and (**c**) orchards affected by spray drift and corresponding predicted annual loads of AZP in the tributaries and mainstream of the Lourens River.

catchment level by comparing the results of the validated GIS models with measurements of pesticide loads from the field during spray drift and runoff events. Finally, the importance of spray drift and runoff at the catchment level was compared on an annual basis using long-term meteorological data and average application characteristics.

MATERIALS AND METHODS

Study area

The Lourens River emerges from a natural sclerophyllous vegetation area (fynbos), after which it runs through forestry and farming areas in its middle reaches before flowing through the town of Somerset West (34°06′S, 18°48′E) [10]. The total catchment area is approximately 44 km², consisting of 10 subcatchments (A–J), each of which is drained by a tributary that discharges into the Lourens River mainstream, with site LR (Lourens River) representing the catchment outlet (Fig. 1a). The annual mean rainfall is 915 mm, most of which occurs during the winter months between April and October, as is characteristic of the region's Mediterranean climate. Agricultural crops consist exclusively of pear, plum, and apple orchards (total growing area, 4 km²), on which pesticide application takes place between August and mid-February before fruit harvest. Azinphosmethyl is the most commonly applied insecticide and is used frequently on all orchard types between October and February at up to about one application every two weeks on each single plot. During each application, AZP is applied at 0.15 kg a.i./ha on subcatchments A and B and at 0.525 kg a.i./ha in subcatchments E to J [8,10].

General concept

It has been well established that, due to the dense buffer strip (30–100 m wide) lining the mainstream, the Lourens River receives pesticides only via the tributaries [8,10]. Thus, the models would first have to be applied in the tributaries in order to predict contamination in the mainstream. Accordingly, the initial validation of the runoff and spray drift models was done using the tributaries situated in subcatchments A to J. As a second step, the direct comparison of spray drift and runoff based on predicted and measured AZP levels was performed at the catchment level so as to reflect the total contamination at site LR. The predicted AZP loads at this site were represented by the sum of the predicted loads for all affected subcatchment tributaries during a runoff or spray drift event. Finally, annual loads were evaluated by extrapolating average runoff and spray drift predictions to a yearly basis using spraying programs and long-term meteorological data. Predictions were based on levels in the water phase of runoff, as AZP has a relatively low K_{OC} and thus preferably occurs in the water phase [8].

The predicted values at LR were based on the original models used in the tributaries and were not adjusted by a correction factor. It was found, however, that although the measured values at LR were very similar to the predictions made by the models, measured runoff values were systematically slightly underpredicted by the runoff model and systematically slightly overpredicted by the spray drift model. As a result, for the purposes of the predicted annual loads, it made sense to apply the correction factors in order to get a more potentially accurate annual prediction. So the fit was applied to the annual loads and not to the predicted loads at LR.

Runoff prediction and measurement

The runoff formula by Reus et al. [12] was designed to calculate pesticide loads in runoff water. In the present article, the formula was applied to predict AZP loads in the water phase for the tributaries discharging the 10 subcatchments A to J. The runoff formula is as follows:

$$L\%_{\text{runoff}} = \frac{Q}{P} \cdot f \ \exp\left(-t \cdot \frac{\ln 2}{DT50_{soil}}\right) \cdot \frac{100}{1 + K_d}$$

where $L\%_{\text{runoff}}$ = percentage of application dose being available in runoff water as a dissolved substance; Q = runoff amount (mm) calculated according to hydrological models [18,19]; P = precipitation amount (mm); $DT50_{\text{soil}}$ = half-life of active ingredient in soil (10 d for AZP) [15]; $f = f_1 \cdot f_2 \cdot f_3$, the correction factor reflecting the influence of slope (f_1 = $0.02153 \cdot \text{slope} + 0.001423 \cdot \text{slope}^2$), plant interception ($PI$), the percentage of applied pesticide intercepted by trees in the orchards ($f_2 = 1 - PI/100$), and buffer width ($f_3 = 0.83^{\text{WBZ}}$, and WBZ is the width of buffer zone [meters]; if the buffer zone is not densely covered with plants, the width is set to zero); t = time between application and rainfall in days; K_d = ($K_{OC} \cdot$OC), a factor reflecting the tendency of the pesticide to bind to organic carbon in the soil, where K_{OC} is the sorption coefficient of the active ingredient to organic carbon (1,000 L/kg for AZP) and OC% is the organic carbon content of the soil (0.75%; F. Ellis, University of Stellenbosch, South Africa, personal communication).

All land use and catchment variables of the study area representing the input variables for the runoff formula were analyzed using GIS ArcView 3.1 (ESRI™, Redlands, CA, USA). Predictions were based on the assumption that tributaries would only receive runoff-related pesticide input from orchards lying directly adjacent to the tributary. Using GIS, each subcatchment was divided into slope categories (Fig. 1a) and the total area of each slope category covered by relevant orchards was determined. The $L\%_{runoff}$ for each slope category was calculated and, based on the amount of applied pesticide (g/m^2), the loss of AZP (g) per total area of each slope category was calculated. The total loss of AZP (g) per subcatchment was then calculated by summing the loss of AZP in each slope category within the subcatchment. Buffer-strip characteristics (WBZ values) and the number of erosion rills (an eroded drainage channel leading directly from the edge of an orchard plot to the bank of a tributary) per tributary were obtained via field observations. The average rainfall for all the 15 measured runoff events (16 mm per event) between December 1998 and May 2001 was used in the formula to predict the input of AZP for an average runoff event in each subcatchment.

In order to validate the runoff formula, the predicted average loads were compared with average loads measured in each tributary during 3 to 12 runoff-related peak discharge events from December 1998 to May 2001 [8,10]. Measured average loads in the nine tributaries B to J were derived from dissolved AZP concentrations and discharge levels measured during runoff events that were assumed to last 1 h based on detailed monitoring of earlier events [10]. The tributary of subcatchment A was excluded from the regression, as only one runoff event was measured.

Spray-drift prediction and measurement

Prediction and validation of spray drift-related AZP loads in the drift-receiving tributaries discharging subcatchments of the Lourens River was done using basic drift values (95th percentiles) by Ganzelmeier et al. [3] for a total of eight measured spray drift events. Measured loads were derived from replicate ($n = 6$ per event) discrete tributary water samples, representing short-term peak concentrations of AZP present directly after spray deposition, relative to the water volume [11]. The spray drift events were monitored during conditions in which the wind (speed 1.7–2.6 m/s) was blowing from the orchards in a perpendicular direction to the tributaries, according to the methods described in Schulz et al. [11]. Distances between the sprayed orchards and the tributaries varied between 10 and 15 m.

Comparison of spray drift and runoff

The direct comparison of runoff and spray drift was done using six runoff and six spray drift events during which AZP was monitored at site LR (Fig. 1a) between December 1998 and May 2001. Predicted loads (which were based on the validated runoff and spray drift models) as well as measured loads were used for this comparison.

The predicted load for each of the six runoff events measured at LR was calculated by totaling the total loss of pesticide in each of the 10 subcatchments A to J. For each prediction, the rainfall that was measured on the particular day and the corresponding Q value were inserted into the formula. The percentage plant interception was adjusted according to the growth stage at that particular time of year [20]. Composite water samples were collected at site LR during runoff-related peak discharge events according to previously published methods [8,10]. For all runoff events, a load was calculated according to the measured discharge and the assumption that an event lasted 1 h, based on information from detailed runoff-event monitoring [10]. Sediment samples were also collected during runoff events according to methods described by Liess et al. [21].

Spray-drift-related contamination at LR was predicted for each of the six spray drift events between January 1999 and February 2001. The land use of the catchment in relation to potential spray drift contamination via the tributaries was first analyzed using GIS. It was assumed that vegetative windbreaks, such as a dense line of trees, would prevent spray drift from entering the tributaries [22]. The distance between plots and tributaries and the length of orchards bordering tributaries was determined using GIS. The predicted load of AZP in each tributary was calculated separately for each spray deposition event according to the basic drift values [3] and then extrapolated to the total length of orchards adjacent to the tributary. In order to accommodate the influence of wind direction on the exposure of tributaries during each spray drift event, only those sections downwind of sprayed orchard plots were considered in the prediction. The total load of AZP at site LR was determined by adding the loads for the subcatchment tributaries.

Spray-drift sampling was accomplished by collecting discrete water samples every 2 h for a total of 8 h during all of the six spraying days. Previous experiments showed this sampling design to be appropriate [11]. These samples were analyzed and an average concentration was calculated, representing the concentration in the main stream during the 8-h spraying period. Estimated loads were calculated by multiplying the integrated 8-h average pesticide concentration by the mean discharge for the same time interval.

Pesticide analysis

All runoff and spray drift samples were analyzed for AZP by the Forensic Chemistry Laboratory of the Department of National Health, Cape Town. Water samples (500–900 ml) were solid-phase extracted within 10 h after sampling using Chromabond® C18 columns (Macherey-Nagel, Düren, Germany). The columns were air dried for 30 min and kept at −18°C until analysis. Measurements were done using gas-chromatographs (HP 5890; Hewlett-Packard, Avondale, PA, USA) fitted with a standard Hewlett Packard electron-capture, nitrogen-phosphorus detector and confirmed using a flame-photometric detector according to methods outlined in Schulz et al. [9]. Sediment samples were extracted and analyzed according to methods described by Schulz et al. [9]. The detection limit for water and sediment samples were 0.01 μg/L and 0.1 μg/kg dry weight, respectively, and spiked overall recovery efficiencies were between 79 and 106%.

Evaluation of yearly loads

Based on the evaluation of spraying programs and meteorological data, the annual AZP loading by nonpoint-source pollution events at site LR was determined.

The main insecticide application period lasts from early November to the beginning of February, during which time 12 applications are made per plot. Based on 10-year rainfall data, the frequency of rainfall events between 10 and 15 mm/d and above 15 mm/d is 3.4 and 1.7, respectively. A 15-mm event with a frequency of one was used for the first rainfall

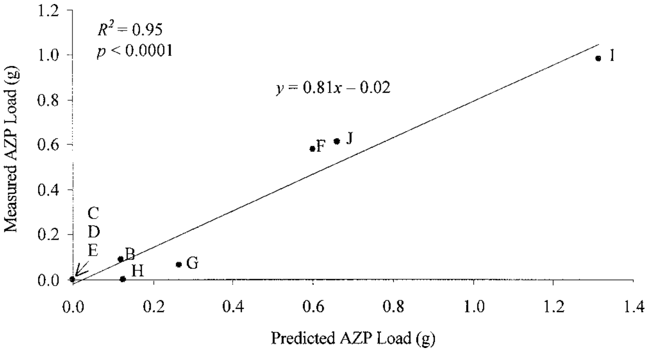

Fig. 2. Linear regression of measured versus predicted loads of azinphosmethyl (AZP) in nine tributaries (B–J) of the Lourens River, South Africa, during runoff. The measured values each represent means of 15 runoff events. No contamination was measured or predicted for subcatchments C–E.

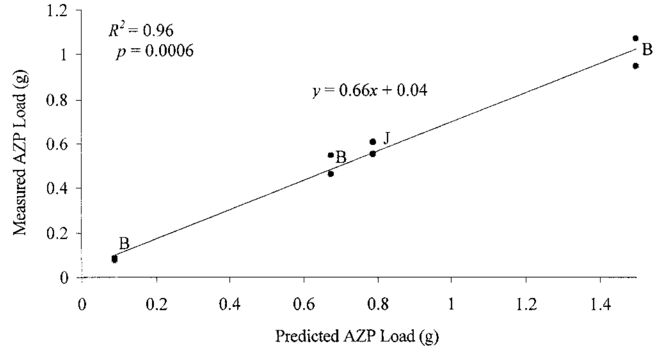

Fig. 3. Linear regression of measured versus predicted loads of azinphosmethyl (AZP) in two tributaries (B and J) of the Lourens River, South Africa, during eight spray drift trials. The measured values each represent means of six samples per spray drift event.

of the wet season following a nonapplication period [9]. Annual loads were calculated by multiplying predicted loads for peak application and postapplication scenarios with the respective frequencies.

An annual load for spray drift was calculated by multiplying the predicted load for the predominant wind direction by the total number of spraying applications (12). The factors obtained for the differences between predicted and measured loads at site LR (1.89 and 1.34 for runoff and spray drift, respectively) were used for correction of the annual loads.

Data analysis

Regression analyses were used to determine whether AZP loads measured in the tributaries during runoff and spray drift events could be predicted by the relevant GIS-based calculations. A Mann–Whitney rank sum test was used to determine significant differences between runoff and spray drift in terms of mean measured AZP loads and concentrations at LR.

RESULTS

Runoff prediction and measurement

According to the definitions of the formula, tributaries A, B, and I had a WBZ of zero and J a WBZ of two. Tributaries F, G, and H ranged between 5 and 6 m. Tributaries I and J had 30 and 18 erosion rills, respectively, the highest among all the tributaries, while the remaining tributaries had between 2 (H) and 12 (F) erosion rills per tributary.

Regression analysis showed a significant positive correlation ($r^2 = 0.95$; $p < 0.0001$; $n = 9$) between predicted and measured average runoff loads in the tributaries of the Lourens River (Fig. 2). Predicted loads were between a factor of 0.81 and 1.34 different from measured loads, apart from site G, at which only three samples during moderate runoff events were analyzed, resulting in an average measured value that was considerably lower than the predicted value. Tributaries F, I, and J showed high average contamination up to 1 g/event, while tributaries A, B, G, and H showed comparatively lower contamination, up to 0.1 g/event. No contamination was measured or predicted for subcatchments C through E.

Spray-drift prediction and measurement

The basic drift deposition values given by Ganzelmeier et al. [3] ($r^2 = 0.96$; $p = 0.0006$; $n = 8$) predicted in-stream loads that were between a factor of 1.2 and 1.58 higher than loads measured in the tributaries (Fig. 3). In-stream concentrations were between 1.5 and 3.6 μg/L and were mainly dependent on the distance of orchards from the tributary and the application rate of AZP.

Comparison of runoff and spray drift

Six runoff events were measured at LR, three during intensive spraying (November and December) and three long after the completion of spraying (April and May) (Table 1). Rainfall varied from 6 to 35 mm and lead to high variations in peak discharges (7.5–28 m^3/s). Based on the GIS-integrated runoff formula, predicted loads were similar to measured loads at LR (between a factor of 1.03 and 1.86 lower). Concentra-

Table 1. Comparison of runoff and spray drift based on measured and predicted loads in the Lourens River (LR), South Africa. The measured concentrations (± standard error [SE]) are also provided

Date	December 14, 1998	April 15, 1999	November 19, 1999	December 20, 1999	May 4, 2001	May 19, 2001	Mean (±SE)
Runoff							
Measured concentration (μg/L)	1.50	0.15	0.52	0.30	0.03	0.02	0.42 (±0.23)
Measured load (g/event)	121.0	5.4	28.2	8.2	3.1	1.0	27.8 (±19.1)
Predicted load (g/event)	78.0	2.9	15.3	4.8	1.2	0.6	17.1 (±12.4)
	January 27, 1999	January 28, 1999	January 21, 2001	February 7, 2001	February 10, 2000	February 12, 2001	
Spray drift							
Measured concentration (μg/L)	0.04	0.031	0.045	0.069	0.294	0.053	0.09 (±0.04)
Measured load (g/event)	0.32	0.25	0.35	0.54	2.25	0.41	0.69 (±0.32)
Predicted load (g/event)	0.60	0.60	0.83	0.83	2.42	0.83	1.02 (±0.28)

tions and loads measured during the November and December events were, in all cases, higher than those measured during the April and May events. Sediment concentrations of AZP ranged from 8 μg/kg (May 19, 2001) to 1,247 μg/kg (December 14, 1998).

Sampling during spray drift events at LR took place on six occasions with average wind speeds of 1.6 to 3.1 m/s. Discharge did not vary between sampling dates and was 0.27 m^3/s. Based on the GIS-integrated calculations for spray drift, predicted AZP loading at LR correlated well to measured 8-h integrated loads (between a factor of 1.1 and 2.4 higher) (Table 1).

Mean measured loads were significantly ($p = 0.004$, Mann–Whitney rank sum test) higher for runoff (27.81 ± 19.06 g) per event than for spray drift (0.69 ± 0.32 g) per event. Only the highest measured load during spray drift (2.25 g) was higher than the lowest value obtained during runoff (0.97 g).

In terms of mean concentrations, runoff (0.42 ± 0.23 μg/L) led to higher values than spray drift (0.09 ± 0.04 μg/L); however, the differences were not significant. This is most probably due to runoff events during the postapplication period, when detected concentrations were in the range of average spray drift events.

Evaluation of annual loads

Based on calculated annual loads, runoff is responsible for considerably higher levels of AZP nonpoint-source pollution than spray drift (Fig. 1b and c). The loads at site LR during runoff and spray drift were 46.7 g/year (89.6% of total AZP load) and 5.5 g/year (10.4% of total AZP load), respectively. Tributaries F, J, and I are responsible for most of the runoff contamination, and tributary I is responsible for most of the spray drift pollution.

DISCUSSION

Runoff prediction and measurement

Measured loads in the tributaries were generally well predicted by the GIS-integrated runoff formula, indicating its suitability for use in South African orchard areas. The original use of the formula is intended to predict the loss of insecticide during a specific event at a specific site and not along the entire length of a tributary. Many assumptions had to therefore be made, which may have resulted in the systematic overprediction of measured in-stream loads. The assumption that could have had the greatest influence on the accuracy of the predictions was that surface runoff from the entire area of an orchard adjacent to a tributary eventually enters the tributary. This may not always be the case, specifically if the orchard is very wide and flat, which might mean that runoff has to travel a distance of up to 200 m to reach the tributary in order to satisfy the assumptions of the model. The maximum distance over which runoff travels for a given slope is not incorporated into the formula and is a difficult parameter to quantify. According to the regression equation (Fig. 2), measured loads were approximately 81% of the value of the predicted loads. This value could be incorporated into the formula as an empirical correction factor to calibrate the model and improve the accuracy of the predictions.

Other runoff models, such as agricultural nonpoint-source models, groundwater loading effects of agricultural management systems, and the pesticide root zone model, have been validated in the field with varying degrees of success [13,23], but normally require a large number of input variables that may not be generally available [24]. The main advantage of the approach used in this study is that it is very simple in its application, has minimal data requirements, and combines field-based measurements with a modeling approach, which is very useful for the assessment of water quality [25]. High AZP input in subcatchments F, I, and J was most probably a result of a high number of erosion rills, in some cases associated with narrow buffer strips and steep slopes, all of which increase surface runoff [26,27].

Spray-drift prediction and measurement

The basic drift values [3] could accurately predict loads measured in the tributaries and thus seem to be suitable for use in South African orchard areas. In a previous study in the same catchment, predictions based on the drift values of Ganzelmeier and the Spray Drift Task Force [4] correlated to measured concentrations in a similar way [11], indicating that the values proposed by the Spray Drift Task Force may also be applicable to South African conditions. Short-term peak concentrations detected in the tributaries were generally very high, which is in accordance with previous studies [28]. Predictions were generally higher than measured loads. While the drift values utilized in this study have been rigorously validated in European countries [3], very few studies have used these values in South African orchards [11] and further validation of the drift values is required in order to determine how applicable they are to South African conditions.

Comparison of runoff and spray drift

This is perhaps the first study that has used and integrated GIS, modeling, and pesticide monitoring to directly compare spray drift and runoff. The result is an efficient, time-saving method to predetermine an area's vulnerability in terms of runoff- and spray drift–induced pesticide contamination of surface waters and thus provides an integrated approach to pesticide management of agricultural catchments.

Runoff-related AZP loading in the Lourens River is clearly a far more important nonpoint source than spray drift–related input (Table 1). This has rarely been shown so far in a direct comparison in the same catchment. Furthermore, this result is unexpected because specific pesticide application in orchards results in a large amount of spray drift due to small droplet size, the crop morphology, and the resulting trajectory of release [2].

One potential reason is related to land use factors and the fact that the spatial and temporal scale of runoff contamination is far greater than spray drift. The GIS analysis clearly shows that each tributary in the catchment is influenced simultaneously during a runoff event, resulting in high potential input of pesticides (Fig. 1b). While buffer strips can reduce pesticide loss [29], the presence of erosion rills may jeopardize their positive effect and can thus result in rapid pesticide input [26]. Furthermore, rainfall is nondirectional and does not restrict the number of orchards prone to runoff. Spray drift on the other hand is dependent on downwind orientation to the point of application [30] and can be prevented by windbreaks [31]. Thus, the land use and the meteorological conditions restrict the number and length of tributaries that can possibly be affected by spray drift.

Results from this and other studies [32,33] show that runoff-induced pesticide loading can occur long after the previous application, indicating that runoff integrates chemical input over a large time span. In comparison, spray drift is instantaneous and contamination can only occur during application, in combination with specific meteorological requirements, which further restricts the potential for contamination.

Azinphosmethyl concentrations detected during peak pesticide application periods (November and December) were higher than any other concentrations detected during spray drift events and are potentially toxic to macroinvertebrates [16,34]. Furthermore, water-quality criteria defined by the U.S. Environmental Protection Agency for AZP (0.01 μg/L) were greatly exceeded [35].

Although there was not a significant difference in the concentrations of pesticides during runoff and spray drift events at LR, the fact that all tributaries in the catchment are simultaneously subjected to pesticide contamination during runoff may be of ecotoxicological significance. The fact that runoff is associated with higher loads but not significantly higher concentrations is most likely as a result of the increased discharges associated with runoff, which dilutes pesticide concentrations. Further research should compare the duration of exposure of typical runoff and spray drift events, which could give more insight into the ecotoxicological implications of the two exposure scenarios. The comparison of different flow velocities characteristic of runoff and spray drift conditions in combination with pesticide contamination is also worthy of further investigation, as toxicity of pollutants has been shown to be dependent on flow velocities [.36]

Sediment-associated loads of AZP were of minor importance during most of the measured runoff events (less than 0.18 g), which is most probably as a result of the relatively low K_{OC} value and high water solubility of AZP [15]. However, in extreme cases, contamination of sediments by AZP has been known to occur [37], and on December 14, 1998, loads as high as 52.3 g of AZP were measured [10], indicating the added risk of sediment-associated input of pesticides during runoff conditions.

It is important to note that the different routes of entry could be heavily influenced by the physicochemical characteristics of the substance under consideration. For example, it has been shown that the chemistry of atrazine plays a far more important role than land use in determining its loss in surface runoff [6,7]. In the case of less water-soluble pesticides, such as organochlorines and pyrethroids, sediment loadings and the resulting chronic effects may become more important [38].

Both modeling approaches predict accurate loads of AZP at the catchment level, highlighting the importance of the contribution of tributaries to the nonpoint-source pollution of the Lourens River. Similar conclusions have been implicated by other workers [39]. In contrast with the predictions made in the tributaries, the runoff predictions at the catchment level were underpredicted. Given the size of the catchment, it is most probable that a number of smaller intermittent streams (which only flow during heavy rainfall conditions) were not considered in the catchment-based predictions.

The predictions of spray drift loads at LR were consistent with the predictions in the tributaries and were also overpredicted by the model.

Evaluation of annual loads

Annually, runoff is responsible for greater nonpoint AZP pollution than spray drift (Fig. 1b and c). This has major implications on the implementation and focus of mitigation strategies designed to improve surface-water quality. Pesticide loss via runoff is assumed to be more important than via leaching [40], necessitating the need to reduce this route of contamination. Based on the results of this study, it is now possible to plan mitigation strategies, first in relation to the most important route of pollution of surface waters and second in relation to problem areas (subcatchments) responsible for large proportions of the contamination. It must be noted, however, that the findings of this study may be specific to the land use of the area and the fact that there are a high number of windbreaks in the catchment. The physicochemical properties of pesticides also play an important role, and other more insoluble pesticides with higher adsorption coefficients may lead to spray drift being a more important route of aqueous dissolved pesticide exposure and runoff contributing mainly to particle-associated contamination.

Several options are available for agricultural best management practice or the implementation of buffer strips in order to mitigate the risk of nonpoint-source pollution [41]. Furthermore, constructed wetlands are effective in mitigating agricultural runoff and have been shown to significantly reduce aqueous and suspended particle–associated pesticide input from tributaries into the Lourens River mainstream [42].

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