Spray deposition of two insecticides into surface waters in a South African orchard area

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Abbreviations: AZI, azinphos-methyl; BBA, Federal Biological Research Centre for Agriculture and Forestry, Germany; END, endosulfan; PLSD, protected least significant difference; SDTF, spray drift task force; U.S. EPA United States Environmental Protection Agency.

ABSTRACT

Drift from pesticide spray application can result in contamination of non-target environments such as surface waters. Azinphos-methyl (AZI) and endosulfan (END) deposition in containers of water was studied in fruit orchards in the Western Cape, South Africa. Additionally, attention was given to the contamination in farm streams at distances from the sprayed plot of 10 m for AZI trials and 15 m for END trials, as well as to the resulting contamination of the subsequent main channel (Lourens River) approx. 2.5 km downstream of the tributary stream inlets. Spray deposit decreased in an exponential manner with increasing distance downwind and ranged from 4.7 mg m^{-2} within the target area to 0.2 mg m^{-2} at 15 m downwind (AZI). Measured in-stream concentrations of both pesticides compared well with theoretical values calculated from deposition data for the respective distances. Furthermore, they were in the range of values predicted by an exposure assessment based on 95th-percentile values for basic drift deposition (German BBA and U.S. EPA). Pesticide deposition in the tributaries was followed by a measurable increase of contamination in the Lourens River. Mortality of midges (*Chironomus* spec.) exposed for 24 h to samples obtained from the AZI trials decreased with decreasing concentrations (estimated LC_{50} from field samples = 10 µg L^{-1} AZI; lethal distance: LD_{50} = 13 m). Mortality in the tributary samples averaged 11% (0.5-1.7 µg L^{-1} AZI), while no mortality was discernible in the Lourens River samples (0.041 µg L^{-1}). The sublethal endpoint failure to form tubes from the glass beads provided was significantly increased at all sites in comparison to the control (ANOVA, Fisher´s PLSD, $p < 0.01$).

INTRODUCTION

A considerable amount of research has been conducted on the development and optimization of air-assisted orchard sprayers during recent decades (Hislop, 1991). However, drift from orchard sprayers remains an important environmental problem. Drift of pesticides is not only wasteful, but also represents a loss in efficiency and incurs increased costs to the user and the non-target environment (Davis et al., 1994). There have been several studies of drift from orchard sprayers (Gilbert and Bell, 1988), and the effects of physical variables are sufficiently well understood to allow a modelling approach (Walklate, 1992). There is now a need to link measurements of drift with studies on real contamination of water bodies and to ascertain the biological impact. The following study was undertaken for this purpose.

Spraydrift is regarded as one of the major routes of nonpoint-source pesticide input into surface waters (Groenendijk et al., 1994). Since spraydrift may result in high concentrations of water-diluted chemicals in surface waters, it usually serves as an exposure scenario for the aquatic risk assessment of pesticides (Gilbert and Bell, 1988). Specifically, orchard mist blowers result in a large amount of drift due to small droplet size and trajectory of release (Groenendijk et al., 1994). According to Payne et al. (1988), the combination of stable boundary layer, light wind, low relative humidity and high air temperature results in large deposits on downwind water bodies from spray applications employing small drops. Droplet size distribution has been shown to be an important factor influencing the extent of spraydrift; the prevailing view has been that small droplets increase biological efficacy, whereas large droplets reduce downwind drift (Matthews, 1994). Recent results based on a stochastic model for pesticide application through hydraulic nozzles demonstrated that application of small droplets does not necessarily increase field efficacy (Ebert et al., 1999). Furthermore, very small droplets (< 50 μm) are most exposed under field conditions to any convective upward air movement and are most liable to travel considerable distances from their source (Matthews, 1994). These atmospheric transport processes may result in contamination of nontarget ecosystems by pesticides applied in agricultural areas situated far away (Le Noir et al., 1999).

In addition to the physical properties of the spray itself, crop characteristics such as height, the amount of open area between trees, diffuse noninterceptance and leaf area index influence the production and extent of pesticide that may be subject to drift (U.S. EPA, 1999). Spray deposits downwind from orchard sprays reflect the atomizing system, orchard geometry, seasonal and meteorological conditions, as well as the non-target surface characteristics (Hall et al., 1996).

There are several generic scenarios for spray drift and spray deposition on surface waters. A large number of standardized drift studies conducted in Germany have been summarized by Ganzelmeier et al. (1995). The results for orchards were differentiated according to early and late growth stage; these were used to derive basic drift values widely used in EU countries for regulatory risk assessment and 95th-percentile values for deposited drift material for distances between 5 and 50 m. Predicted environmental concentrations of a chemical for regulatory exposure assessment purposes are then calculated by relating drift deposit rates per square meter to a water volume of 300 l (30 cm water depth) assuming immediate perfect mixing. Similar depths are used in the Netherlands (25 cm) and Canada (15 cm). The Environmental Fate and Effects Division (EFED) of the United States Office of Pesticide Programs uses a standard value of 5% of the application rate on 10 hectares which deposits on a one-hectare pond (2 m water depth) immediately adjacent to the orchard as an aquatic exposure scenario for airblasts (AEDG, 1992). Recently, the Spray Drift Task force´s (SDTF) data set was analysed and used to develop generic deposition curves with 95% confidence limits for distances between 0 and 549 m (U.S. EPA, 1999), which are proposed for use in risk assessment. Deposition data were grouped into high drift potential orchards and low drift potential orchards.

Fruit orchards form an important agricultural crop in the Western Cape, South Africa, comprising some 440 km^2 of growing area, which equals 82% of the orchards in South Africa. In contrast to other extensive fruit growing areas, e.g. the Central Valley in California, which is protected from sea breeze by the coastal range of mountains, the orchards in the Western Cape are exposed to constantly high southwesterly winds during the pesticide application period (Table 1). This may cause spraydrift to be an important route of pesticide entry into non-target ecosystems. However, spray deposition has not previously been investigated in this area.

Table 1

The aim of the present study is to investigate the potential of spraydrift-related pesticide input from fruit orchards into a Western Cape river and to assess its biological effects. The Lourens River, flowing from a natural mountainous area through agricultural farm land into the Indian Ocean, is of ecological importance in terms of river conservation on a national scale (Tharme et al., 1997). The river itself is at low risk of direct spray input due to its orientation parallel to the main wind direction (see also Fig. 1) and due to a broad strip of emergent forest vegetation bordering both banks of the main channel. However, the tributaries flowing into the river are directly bordered by orchard plots. Consequently, a special emphasis was placed in this study on the spray input into the tributaries as a potential source of pollution for the main river.

MATERIALS AND METHODS

Description of study area

The Lourens River originates at an altitude of 1080 m in a naturally vegetated fynbos area and flows in a southwesterly direction for approx. 20 kilometers before discharging into False Bay at Strand (S34°06′; E18°48′). The catchment is characterized by an intensive farming area with orchards and vineyards in its middle reaches. The Lourens River has a total catchment area of approx. 92 km^2 and receives an annual mean rainfall of 915 mm. Approximately 87% of its $35x10^6$ 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.

In the 400-ha orchard area, mainly pears, plums and apples are grown. The pesticide application period in the study area´s orchards proceeds from early August to the end of March. Organophosphorous insecticides, such as AZI and chlorpyrifos, are applied between October and

February quite frequently to pears and plums. Endosulfan is applied mainly in apple orchards (Table 2).

Table 2

The summer months December to February, when the present study took place, are characterized by high temperatures and low rainfall (Table 1). The constantly high wind speeds, indicated by the high average minimum values, may cause spraydrift to be an important route of potential pesticide contamination of surface waters. Wind speeds below 1 m s^{-1} occur in January only for approx. 20% of the days, in contrast to approx. 35% in April or July.

The orchard plots are separated from the Lourens River itself by a strip of vegetation (eucalyptus trees, shrubs and grasses) between 20 and 100 m in width. In contrast, most of the tributaries are, at least in some stretches, directly bordering on orchard plots (distance: approx. 10-15 m). The Lourens River flows in a southwesterly direction, opposite to the main wind direction coming from the sea southwest of the farming area (Fig. 1). The orientation of the main river parallel to the main wind direction and the vegetated strips along the river make direct spray input into the river highly unlikely. Small side streams forming tributaries of the Lourens River flow more or less at a right angle to the river and to the main wind direction, with no vegetated strips, and are therefore at considerable risk of spraydrift-related pesticide input. Approximately 30 % of the tributary surface area is covered by macrophytes, with cattail *Typha capensis* Rohrb. and rush *Juncus kraussii* Hochst predominating.

Fig. 1

Application characteristics

On January 27 and 28, 1999, a total of four trials with application of AZI to bearing pear orchards (average tree height: 6 m) were investigated. Normal spraying events with Jacto Arbus air-assisted mist blowers (nozzle type: J5-3; nozzle height: 0.7 to 1.6 m) that delivered AZI at

0.15 kg a.i. ha^{-1} in 1000 L of water at a pressure of approximately 1200 kPa were monitored. The manufacturer stated a mean droplet diameter of 125 to 150 μm at the given spray volume and pressure. The registered formulation of AZI was Guthion® (350 g kg^{-1} a.i.), a wettable powder with a recommended application rate of 0.5 kg ha^{-1}. On 2 February, 1999, a total of three trials with application of 1.425 kg a.i. ha^{-1} END to bearing apple orchards (average tree height: 4.5 m) were investigated. Thioflo®, an emulsifiable concentrate (475 g L^{-1} a.i.), was used to supply the END, recommended at 3 kg ha^{-1} of product. Canopy and spacing characteristics in both orchard plots were of moderate density, with no space between trees.

Wind speed was measured during each trial at a height of 1.5 m above the ground in the tree row and 5 m downwind of the sprayed tree row using a portable anemometer (Ferropilot, Rellingen). Wind speeds were averaged for 1-minute intervals from five measurements. During the AZI trials the average wind speed was 1.7±0.1 m s^{-1}, relative humidity 81.8±0.8% and air temperature 18.9±0.4 °C. The respective values for the END trials were 4.5±0.2 m s^{-1}, 77.6±0.8% and 20.9±0.3 °C.

Sampling setup

Spray deposition during applications was studied at orchard plots adjacent to two different tributaries of the Lourens River situated downwind of the plots (Fig. 1). Distances of the tributaries from the edge of the treated area were 10 m and 15 m for the AZI and END trials, respectively. Height of the vegetation layer in the area between orchard plots and tributary including stream banks was ≤ 25 cm. Average width and depth of the tributaries was 0.89 m × 0.30 m in the case of the AZI trials and 1.13 m × 0.39 m in the case of the END trials. The current velocities were approx. 0.1 m s^{-1} in both tributaries.

Drift deposit was sampled at distances of 0, 5, 10 (tributary site) and 15 m downwind from the edge of the treated area during the AZI spraying (Fig. 1) and only at 15 m (tributary site) during the END spray application. Two replicate collectors were employed at each distance per trial, giving a total of 8 replicates at each distance for AZI. A total of 6 replicates were performed only at the 15-m distance for the END spray application trials.

The drift deposit collectors consisted of acetone- and distilled water-rinsed flat straight-sided glass bowls containing 300 ml of distilled water and providing a surface area of 75 cm^2 at a water depth of 4 cm. The sampling bowls were set horizontally on the ground. Vegetation in the vicinity of deposit samplers was removed to eliminate the possibility of spray interception. The bowls exposed at 10 m during the AZI trials, like those exposed at 15 m during the END trials, were supported 5 cm above the stream water surface by wooden supports. These bowls represented the drift deposition on the stream surface. Their collection surface was lower, due to the fact that the stream water surface was approx. 1 m below the average ground level. Following the spray event, the contents of the bowls were thoroughly stirred with a clean glass rod, poured into acetone- and distilled water-rinsed glass jars and kept at 4°C in the dark until solid phase extraction was carried out.

Orchard tree rows were orientated perpendicular to the tributary, so that a more or less well-defined cloud of spraydrift moved from the orchard in the direction of the tributary. Each time the spraying machine turned around at the end of a row, it was observed in the field that between 10 and 15 m of stream length were exposed to spraydrift. Spraying was stopped when the spraying machine reached the end of one row and commenced again at the beginning of the next row (Fig. 1). In addition to the drift deposit collection, two different types of water samples were taken in 3-liter glass jars from the tributaries in stretches without macrophyte coverage: First, 1-h composite samples (by combining 150 ml samples taken every 10 minutes) were collected at a site approximately 50 m downstream of the spray-receiving stretch of the tributary while the spraying took place on the adjacent orchard plots. Second, discrete water samples were taken approx. 30 sec after the chemical had reached the water surface (visual determination) from the downstream section of the tributary stretch, which was covered with spray deposition (Fig. 1). All samples were taken by dipping closed sampling jars into the water column and opening the jars approx. 10 cm below the water surface to avoid contamination with surface film. The samples thus represent subsurface concentrations. Both types of samples were replicated 6 times during the AZI trials and 3 times during the END trials. The composite samples represent the average stream contamination for a time period of 1 h, whereas the discrete samples are intended to

contain the potential peak pesticide concentrations, once the chemical has reached the water body. However, both types of samples may contain a certain amount of additional contamination due to airborne pesticide transport from orchard areas further away from the stream. To determine the potential contamination of the Lourens River, which receives the discharge of the investigated tributaries, 5-h composite samples (100 ml every 10 minutes) were taken at a site downstream of the farming area. This site was approx. 2.5 km downstream of the inlets of the two tributaries used for spraydrift monitoring. The river at this site has an average discharge in January of 0.28 m^3 s^{-1}. Sampling in the Lourens River was carried out on three days with spray application in the catchment and on three days without any spray application. On spraying days, pesticide application took place in parallel on approx. 3 plots adjacent to tributaries of the Lourens River.

Distilled water (300 ml), tributary and river water samples (700 to 900 ml) were solid-phase extracted (SPE) within 10 h after sampling using C18 columns (Chromabond) which had been previously conditioned with 6 ml methanol and then 6 ml water. Samples were not filtered prior to solid phase extraction since all samples represent clear water samples with total suspended solid contents of less than 10 mg L^{-1}. The columns were air-dried for 30 minutes and kept at –18°C until analysis.

Pesticide analysis

Analysis was performed at the Forensic Chemistry Laboratory of the Department of National Health, Cape Town. Water samples were eluted from SPE columns with 2 ml hexane and then 2 ml dichloromethane. These extracts were dried in a stream of nitrogen and then taken up in 1 ml hexane. The 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.

Method validation was conducted on water matrices that were determined to have no detectable levels of AZI or END. 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. AZP and END were never detected in matrix blanks. The detection limits were 0.01 µg L^{-1}.

Toxicity tests

One additional bowl, containing water taken from the tributary before spraying, was placed next to the sampling bowls at the above-mentioned distances during each of the four AZI trials. Additionally, samples of the water taken from the tributary during spraying and from the Lourens River on spray application days were used for toxicity tests. Tributary water taken before spraying and more than 48 h after the last spraying anywhere in the catchment had taken place served as a control. The quantified characteristics of the waters are given in Table 3. The metal content of those waters (aluminium, copper, zinc, mercury and lead) was lower than detection limits (0.005-0.25 mg L^{-1}). Test water was taken to the laboratory and temperature-equilibrated in a water bath. Tests were commenced within 4 h after sampling. During the tests the jars were not aerated, and temperature, pH and dissolved oxygen were monitored. Static 24-h acute toxicity tests were performed in 1-L glass jars following the general procedures of acute aquatic toxicology (Sprague, 1969; Sprague, 1970). Four replicates each containing 500 ml of test substance were performed for each sample. Short-term exposures were employed because they most closely

represent the „pulse“ exposure typical of contamination from operational sprays.

Table 3

Midges (*Chironomus* spec.) were employed as a test organism. Animals were obtained from a clean water pond at Somerset West Water Treatment Plant. The organisms (4th-instar larvae) were collected 2 days before the beginning of the toxicity tests and were held in aerated tributary or river water until use. The animals were not fed during either the holding or the exposure periods. A small amount (100 mg) of finely grained glass beads (100-250 µm) was provided as tube-building material. The measured effect parameters were mortality (no response to mechanical stimulation) and failure of tube formation from the glass beads (less than 25% of the body covered with a tube). In order to obtain 24-h LC_{50}/EC_{50}, Lourens River water spiked with Guthion® (AZI) at 330, 100, 33, 10, 3.3, 1, 0.3 and 0.1 µg L^{-1} (a.i.) was used in a test procedure as described above. Test solutions were prepared by serial dilution of a 1 g L^{-1} stock of AZI.

RESULTS AND DISCUSSION

Spray deposition

The deposition of AZI at varying distances from the orchard tree row was calculated by extrapolating from the collection bowl size to an area of 1 m^2. The amount of pesticide deposited on the ground was found to decrease with increasing distance from the tree row (Fig. 2). At 5 m, 10 m and 15 m depositions were 30.8%, 10.9% and 3.7%, respectively, of the deposition at 0 m. In relation to the application rate, the deposition at 0, 5, 10 and 15 m was 31.6, 9.7, 3.5 and 1.2%, respectively.

Fig. 2

This exponentially decreasing spray deposit curve is similar to those reported by the German BBA (Ganzelmeier et al., 1995) and the United States SDTF (U.S. EPA, 1999). Comparison of our data with the SDTF´s data set is possible only for the SDTF high-drift orchard values. It is not clear whether these high-drift orchard values are applicable to late growth stage of the fruit orchards that were used in the present study. Since the U. S. EPA (1999) compared their SDTF high-drift orchard values also with late growth stage values according to Ganzelmeier et al. (1995), the same procedure was regarded as appropriate here. Use of the SDTF´s low-drift orchard values would lead to drift rates considerably lower than those measured in the present study or suggested by Ganzelmeier et al. (1995).

Spray deposition measured for AZI was compared with median basic drift values used in exposure assessment for orchard spraying in Germany and those suggested for use in the United States (Fig. 3). Measured deposition rates at distances of 10 and 15 m were approximately 25% and 59% lower than these basic drift values, which are in fact very similar in the BBA and U.S. EPA approach for distances up to 20 m. One possible reason might be that the average wind speed during AZI application was only 1.7±0.1 m s^{-1}, so it cannot be considered a worst-case scenario. Average wind speeds in the BBA trials with late growth stage orchards (downwind of plot) and in the SDTF trials with high-drift orchards (inside orchard) were 3.1±0.4 and 2.8±0.5 m s^{-1}. Our wind speed values were all obtained at approx. mid-crop height downwind of the orchard plots and should therefore be comparable with inside-orchard readings. At distances of 0-5 m, measured deposition of AZI was not appreciably different from BBA and SDTF estimates (Fig. 3).

Fig. 3

Another set of spray deposition trials was conducted with END in bearing apple orchards. At a distance of 15 m from the treated plot, an average END deposition of 5.1±0.21 mg m^{-2} was detected, which equals 9.1% of the applied rate. This deposition is approx. a factor of 1.4 higher than the 95th-percentile drift deposition values of Ganzelmeier et al. (1995) (Fig. 5). The high

average wind speed of 4.5±0.2 m s^{-1} during our trials may contribute to this difference. Gilbert and Bell (1988) provide a graphical relationship between spray drift and wind speed for air-assisted orchard sprayers. Under the conditions of their trials, an increase of wind speed from 2.0 to 3.6 m s^{-1} would increase drift from 7% to 11% of the applied spray. Another parameter contributing to the relatively high deposition may be that our END trials were performed in apple orchards late in the season, shortly before harvest time. Hall et al. (1996) demonstrated that pesticide retention on apple foliage decreased significantly with season, which is mainly attributed to decreasing leaf hair density.

For both insecticides investigated, physical parameters such as droplet size may contribute to differences in the extent of spraydrift following air-assisted application (Matthews, 1994; Ebert et al., 1999). Furthermore, differences in physicochemical properties of the two studied insecticides may be of importance for the extent of spraydrift, when field values are compared with standard values according to BBA or SDTF that do not allow for predictions including differing physicochemical pesticide properties as a model variable. The Henry´s law constant for END is higher than those for AZI (Table 2), suggesting that END is more subject to volatilization. Our results suggest that a risk assessment for the conditions in the Western Cape of South Africa based on BBA/EPA values would probably not yield a reasonable worst case, but may rather underestimate the exposure.

Resulting in-stream concentrations

Measured tributary water peak concentrations from discrete sampling were compared with the calculated concentrations based on deposit in the water bowls (Fig. 4 and 5). To calculate the concentrations, deposition rates (mg m^{-2}) measured at 10 m in the AZI trials and at 15 m in the END trials were related to the water volume covered by 1 m^2 tributary surface area (for the AZI tributary 300 L and for the END tributary 390 L).

The measured peak concentration in the tributary was 1.68±0.22 µg L^{-1} (column B2 in Fig. 4), which is very similar to the calculated value based on measured spray deposition rates(1.73±0.14 µg L^{-1}; column B1 in Fig. 4). The estimated in-stream concentration according to the basic drift

deposition values given by Ganzelmeier et al. (1995) using a depth of 0.3 m was 2.2 μg L^{-1} (column A in Fig. 4), which is slightly higher than the measured peak concentrations. The measured 1-h average concentration of AZI in the tributary was 0.51±0.09 μg L^{-1} (column C in Fig. 4).

Fig. 4

The maximum END concentration in the tributary directly after settling of spraydrift was calculated, on the basis of an average stream depth of 0.39 m, to be 13.0±0.54 μg L^{-1} (column B1 in Fig. 5), which is approx. 3 μg L^{-1} higher than the measured peak concentration in the tributary (10.1±1.2 μg L^{-1}; column B2 in Fig. 5). The estimated in-stream concentrations according to the basic drift values given by Ganzelmeier et al. (1995) and SDTF (U.S. EPA, 1999) are 9.1 μg L^{-1} (column A in Fig. 5) and 12.1 μg L^{-1}, respectivley, which are slightly different from the measured peak concentrations. The measured 1-h average concentration of END in the tributary was 0.9±0.16 μg L^{-1} (column C in Fig. 5).

Fig. 5

The fact that for both pesticides the measured and calculated in-stream concentrations were very similar is evidence of the efficiency of the collection methods and their suitability for spray deposit measurements. It has been shown that results from water-filled bowls are also well in accordance with those from glass fibre filter collectors (Ernst et al., 1991).

Pesticide spray deposit produced detectable contamination in the drift-receiving tributaries. The subsurface peak concentrations of AZI (0.3 m stream depth; 1.68 μg L^{-1}) and END (0.39 m stream depth; 10.1 μg L^{-1}) measured in tributary water (B2 in Fig. 4 and 4) were slightly lower than estimates based on Ganzelmeier et al. (1995) for AZI (2.2 μg L^{-1}; A in Fig. 4), and slightly higher than estimates for END (9.1 μg L^{-1}; A in Fig. 5). Apart from physical spray parameters, the differences in wind conditions, as discussed above, may be one reason for this. An assessment

of exposure based on EFED (AEDG, 1992) would, in contrast, predict much lower contamination if the usual depth of 2 m is used (0.4 μg L^{-1} and 3.6 μg L^{-1}). On the other hand, an EFED assessment using 0.3 m water depth would overestimate the AZI trials (2.5 μg L^{-1}) and strongly overestimate the END contamination (23.7 μg L^{-1}). A prediction based on SDTF´s data set and 0.3 m water depth gives 2.4 μg L^{-1} for AZI, and 12.1 μg L^{-1} for END.

The derivation of worst-case scenarios is usually based on the assumption of immediate perfect mixing of the deposited chemical into the water column, which is probably not the case under field conditions. The water depth used for these calculations is of particular importance. The subsurface peak tributary concentrations measured during this study compare quite well with calculations based on a 0.3-m-deep water body assuming perfect mixing, while a depth of 2 m would lead to a considerable underestimation of the concentrations. Both current and macrophyte vegetation might contribute to a relatively fast dissipation of the chemical into the water column. A different situation may prevail when a body of standing water receives spray drift.

Pesticide concentrations in the Lourens River

Both pesticides occurred in the Lourens River at increased 5-h average levels during days with pesticide spray application to fruit orchards in the river catchment compared to those without any spraying. On days when field plots were sprayed, the AZI concentration was increased by more than a factor of 4, from non-detectable levels (<0.01 μg L^{-1}) to 0.041 μg L^{-1}, while the increase for END amounted to a factor of 11, from 0.006 to 0.067 μg L^{-1} (Table 4). The fact that END was detectable even during days without spray application in the catchment may be related to the tendency of END to accumulate in the environment, as it is not readily detoxified by soil microorganisms (Goebel et al., 1982).

Table 4

Generally, the pesticide concentrations measured in the Lourens River were lower than those detected in the tributaries, which may be mainly attributed to dilution in the larger volumes of

water. It has been demonstrated for runoff-related insecticide input that concentrations in smaller tributaries may be considerably higher than in the subsequent main channels (Miles and Harris, 1971; Schulz and Liess, 1999). A similar situation may be applicable to spraydrift-related pesticide input. It can, however, be concluded that the pesticide input via tributaries is of importance with regard to subsequent contamination of the Lourens River, specifically when the total rates of pesticide application in the orchard areas (Table 2) and the frequency thereof are taken into account. In addition to spraydrift, other routes of pesticide entry such as edge-of-field runoff are of importance (Schulz, 2000).

Ecotoxicity testing

Mortality of midges exposed for 24 h during the AZI field trials decreased with decreasing pesticide concentration in the samples (Table 5). Mortalities of 56.3% and 45% occurred at AZI concentrations of 17.2 µg L^{-1} and 5.1 µg L^{-1}, respectivley.

Failure of tube formation has been suggested as an endpoint for toxicity in *Chironomus yoshimatsui* Martin et Sublette exposed to different organophosphate insecticides (Tabaru, 1985). In the present study, this endpoint represents a sensitive sublethal parameter that differed significantly from the control at all sites tested (ANOVA, Fisher´s PLSD, $p < 0.01$). More than 85% of the animals exposed to the drift samples were unable to build tubes within the exposure period (Table 5).

Table 5

For both endpoints, the effects decreased with increasing distances from the sprayed orchard, which is in accordance with the measured concentration levels, as well as with the results of other studies employing aquatic or terrestrial test species (Davis et al., 1994; Helson et al., 1993).

It follows from the results with field samples that a mortality of 50% occurred at an estimated concentration of aproximately 10 µg L^{-1}, which equals a distance of aproximately 13 m downwind from the edge of the sprayed area. This estimated field LC_{50} compares fairly well with the 24-h

LC_{50} (95% C.I.) obtained from spiked water tests with AZI in the laboratory: 7.3 (5.7-9.9) μg L^{-1}. This laboratory-measured 24-h LC_{50} implies that the unidentified *Chironomus* species we used is less sensitive than *Chironomus tentans* Fabricius, which has a 96-h LC_{50} of 0.37 μg L^{-1} (Ankley and Collyard, 1995). The estimated EC_{50} for tube formation in the field samples is approximately 2.4 μg L^{-1}. It also compares fairly well with the 24-h EC_{50} (95% C.I.) of 2.0 (1.7-2.4) μg L^{-1} obtained from spiked water tests.

The fact that the toxicity data obtained from field samples indicate LC_{50} and EC_{50} concentrations similar to those found from laboratory data gives evidence for the comparability of the two test designs. A potential reason might be that water samples from surface waters contaminated by drift are quite comparable in their physicochemical conditions (e.g. turbidity and bioavailability) to those used in the laboratory.

Mortality in the tributary samples averaged 11%, while no mortality was discernible in the Lourens River samples. Failure of tube formation in the tributary water samples ranged between 22 and 40%, and was thus significantly increased compared to the control group with a level of 1.2%. Failure of tube formation was also significantly increased in the Lourens River samples in 12% of the test organisms.

The results of this study indicate that the transient (≤ 1 h) pesticide concentrations measured in tributary water were in the range of concentrations that require longer exposure periods in order to be acutely toxic for a number of other test species (Table 2). For example the 48-h EC_{50} of 1.6 μg L^{-1} AZI for *D. magna* (Dortland, 1980) as well as the 96-h LC_{50} of 0.3 μg L^{-1} END for rainbow trout *O. mykiss* (Lemke, 1981) and the 24-h LC_{50} of 7.75 μg L^{-1} END for threespined stickleback *Gasterosteus aculeatus* L. (Ernst et al., 1991) were exceeded. The detected END levels in tributary water and in the Lourens River on spraying days exceed the target water quality range (TWQR) of <0.01 μg L^{-1} established by the South African Department of Water Affairs and Forestry (DWAF, 1996).

Based on the measured short-term peak concentrations, toxic effects in the tributaries or the Lourens River as a result of spray deposit in its tributaries are unlikely. However, much concern has been voiced about potential chronic effects following short-term exposure of aquatic

organisms (Hosmer et al., 1998; Liess and Schulz, 1996; Schulz and Liess, 2000). Ecological effects of pollution in Western Cape rivers have to be considered carefully since many of the aquatic invertebrate and fish species present in the rivers are endemic to a relatively small area (Davies and Day, 1998), and their extinction cannot be compensated by recolonisation from other regions.

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Table 1. Meteorological conditions in relation to the usual pesticide application period in orchards along the Lourens River.

	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
Temperature (°C)	11.1	12.3	12.8	15.7	16.9	20.6	21.5	22.2	20.3	16.8	14.4	13.5
Rainfall (mm)	138.1	85.8	64.3	48.4	21.3	23.2	12.5	22.8	32.2	88.6	103.7	156.8
Avg. wind speed (m s^{-1})	2.42	1.96	2.27	1.89	2.02	1.95	2.04	2.28	1.81	1.75	1.49	2.30
Avg. maximum (m s^{-1})	7.59	6.21	6.83	4.09	4.02	3.85	4.01	4.24	3.34	5.51	4.93	5.91
Avg. minimum (m s^{-1})	0.94	1.01	1.18	1.15	0.98	1.17	1.29	0.90	1.08	0.79	0.72	0.81
Pesticide application		X	X	X	X	X	X	X				

Table 2. Characteristics of the studied pesticides: water solubility, Henry´s law constant, amount of pesticides applied to orchards between August and February in the Lourens River catchment area, and toxicity to standard test organisms rainbow trout (*Oncorhynchus mykiss* Walbaum; 96-h LC_{50}) and water flea (*Daphnia magna* Straus; 48-h EC_{50}).

Pesticide name	Water solubility at given temp.†	Henry´s law constant‡	Amount applied§	Acute toxicity¶	
				Rainbow trout	Water flea
	$mg\ L^{-1}$	$atm\ m^3\ mol^{-1}$	kg	——————$\mu g\ L^{-1}$——————	
Azinphos-methyl	28 (20°C)	$9.5\ 10^{-11}$	771	4.3	1.6
Endosulfan	0.32 (22°C)	$1.05\ 10^{-5}$	158	0.3	250

† USDA ARS database.

‡ Altenburger et al. (1993).

§ According to local farmers' spraying programme.

¶ Dortland (1980); Johnson and Finley (1980); Lemke (1981).

Table 3. Quality characteristics of water used in bioassays to measure toxicity due to contamination by drift of azinphos-methyl (mean ± SE; n = 4).

Parameter	Tributary water	Lourens River water
pH	6.9±0.05	7.0±0.04
Hardness (mg L^{-1})	75±2.0	54±0.9
Conductivity (µS cm^{-1})	1738±8	1107±8
Turbidity (FTU)	10.7±0.6	6.8±0.1
Nitrate (mg L^{-1})	1.3±0.2	4.2±0.9
Nitrite (mg L^{-1})	<0.05	<0.05
Ammonia (mg L^{-1})	<0.005	<0.005
Ortho-phosphate (mg L^{-1})	0.2±0.06	0.1±0.04

5

Table 4. Mean±SE (n = 3) of integrated 5-h pesticide concentrations in Lourens River water downstream of the farming area on days with spray application and those without any spraying in the catchment area.

	Spraying days†	Non-spraying days
	——————————μg L^{-1}——————————	
Azinphos-methyl	0.041±0.01	nd‡
α + β endosulfan	0.067±0.02	0.006±0.0001

† Range of wind speeds downwind of orchard plots (n = 8 sites): 1.2±0.2 to 3.8±0.5 m s^{-1}.

‡ nd = not detectable (<0.01 μg L^{-1}).

Table 5. Test conditions and test results for 24-h exposure (mean±SE; n = 4) of *Chironomus* spec. to either water contaminated with azinphos-methyl by drift or samples from the drift-receiving tributary and the subsequent main river.

Distance to tree row (m) or type of sample	Pesticide concentration	Range of test conditions			Mortality	Failure of tube formation
		DO	pH	T		
	µg L^{-1}	mg L^{-1}		°C	%	%
0	111.1±19.7	8.3-9.7	6.8-7.1	19-21	93.8±3.7	100*
5	48.4±17.6	8.2-9.6	6.8-7.1	19-21	65.0±20	100*
10	17.2±4.7	8.3-9.8	6.8-7.1	19-21	56.3±2.4	96.3±3.4*
15	5.1±1.2	8.3-9.7	6.8-7.1	19-21	45.0±42.0	87.5±3.2*
Tributary peak sample	1.7±0.2	8.4-9.6	6.8-7.1	19-21	13.8±2.4	40.0±3.5*
Tributary, 1-h average	0.5±0.09	8.1-9.7	6.8-7.1	19-21	8.7±2.4	22.5±3.3*
Tributary, control	nd†	8.2-9.7	6.8-7.1	19-21	0	1.2±1.2
Lourens River	0.041	8.1-9.8	6.9-7.2	19-21	0	12.5±1.4*

† nd = not detectable (<0.01 µg L^{-1}).

* significant difference from tributary control value, ANOVA Fisher´s PLSD, $p < 0.01$.

Figure captions

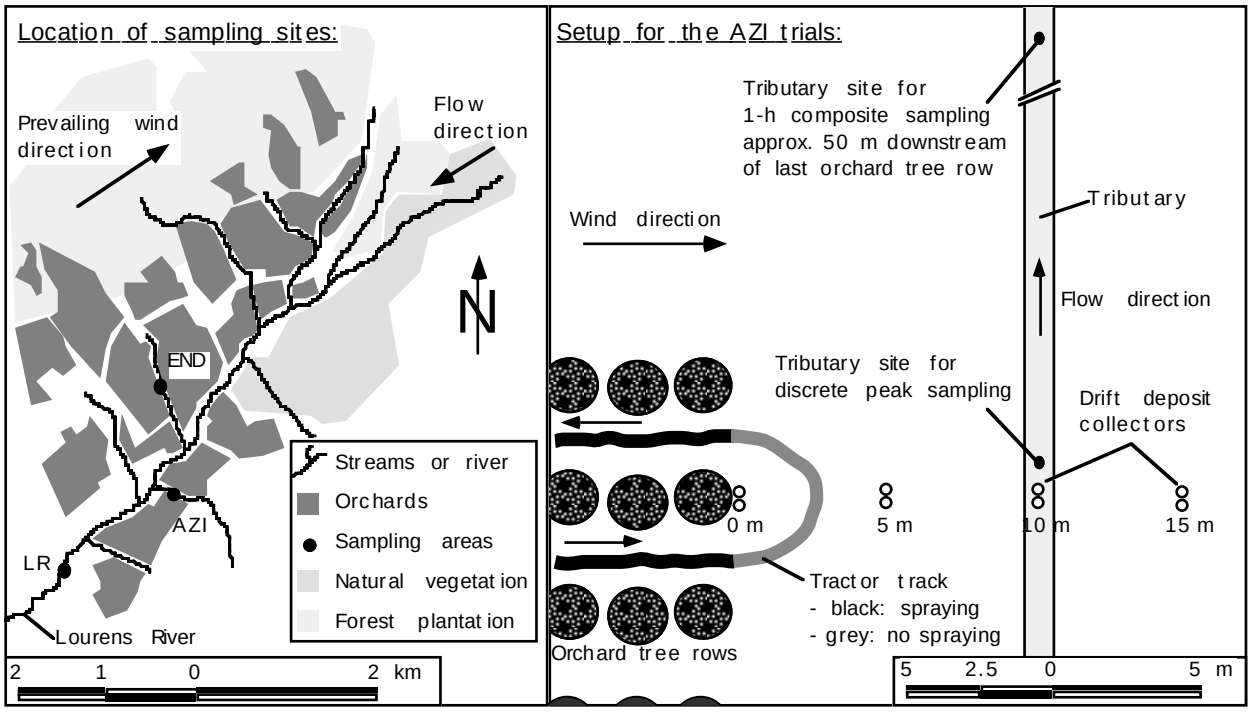

Fig. 1. Location of sampling sites (left): LR: sampling site in the Lourens River; END: site for the endosulfan trials; AZI: site for the azinphos-methyl trials. Plot schematic (right) depicting the orientation of spray deposit collectors and sampling sites for tributary water samples during the azinphos-methyl trials with a 10-m distance between tree row and tributary.

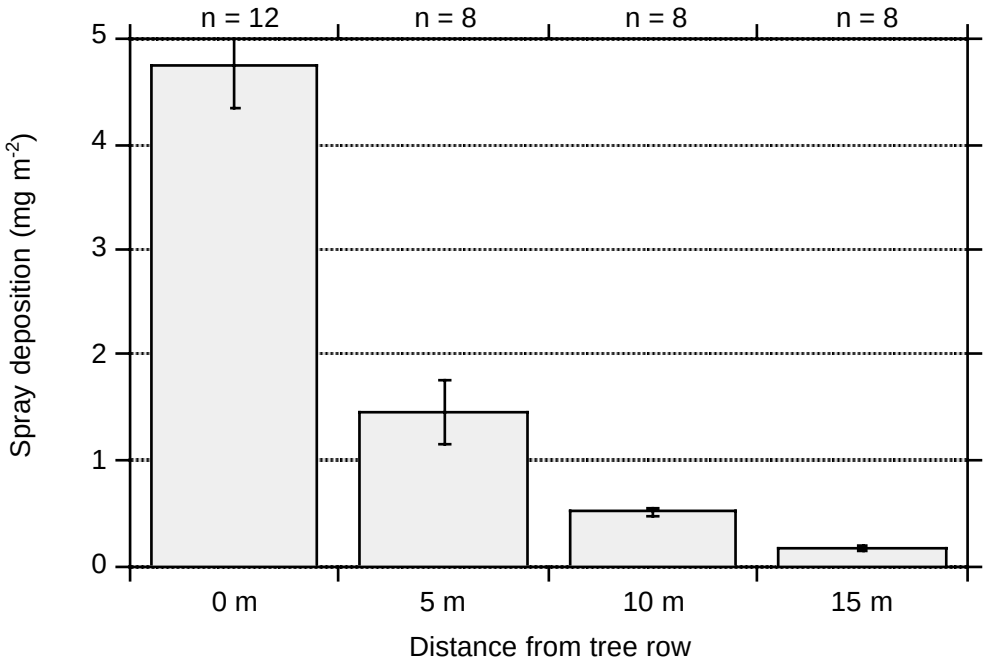

Fig. 2. Spray deposition (±SE) of azinphos-methyl at different distances downwind of the orchard tree row (bearing pears). Squared regression coefficient for an exponential regression is R^2 = 0.99.

5

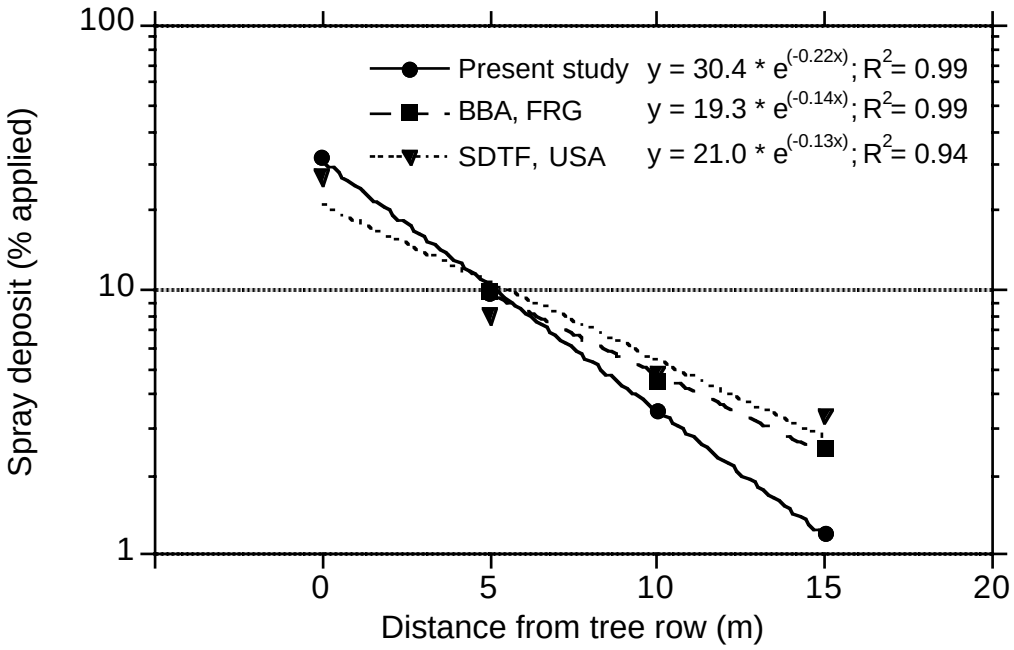

Fig. 3. Spray deposition rates of azinphos-methyl measured in the present study and 95th-percentile values for basic drift deposition according either to the German exposure assessment procedure (Federal Biological Research Centre for Agriculture and Forestry; BBA) (Ganzelmeier et al., 1995) using late growth stage or to the U.S. Spray Drift Task Force (SDTF) data set (USEPA, 1999) using high drift potential orchards.

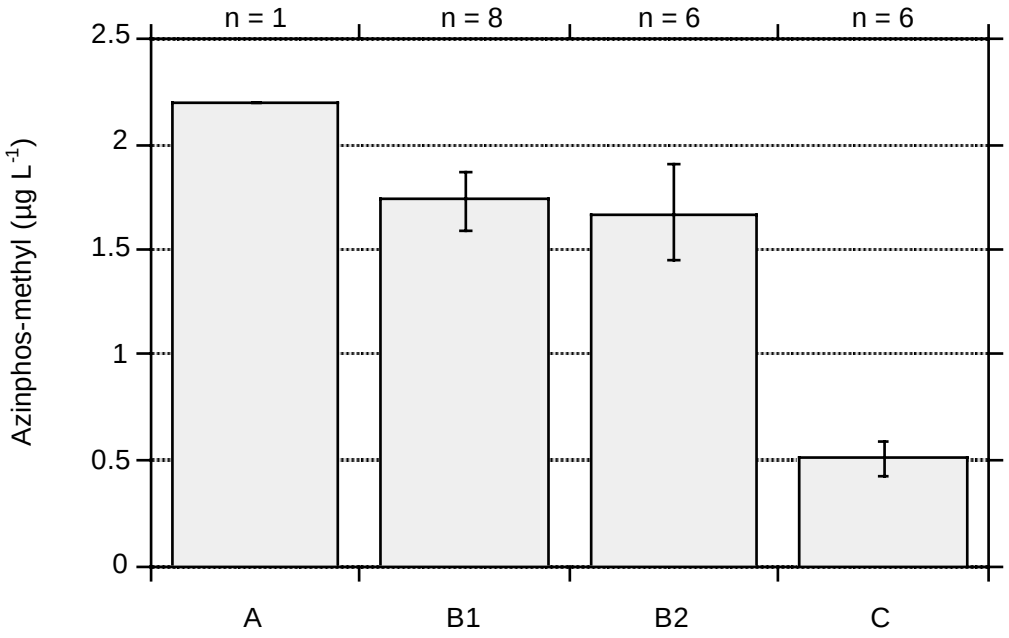

Fig. 4. Concentrations (±SE) of azinphos-methyl in tributary water 10 m downwind of the sprayed plot. Column A: calculated peak concentrations based on 95th-percentile values for basic drift deposition (Ganzelmeier et al., 1995); B1: calculated peak value based on measured deposition rate; B2: measured peak value; C: measured 1-h average value.

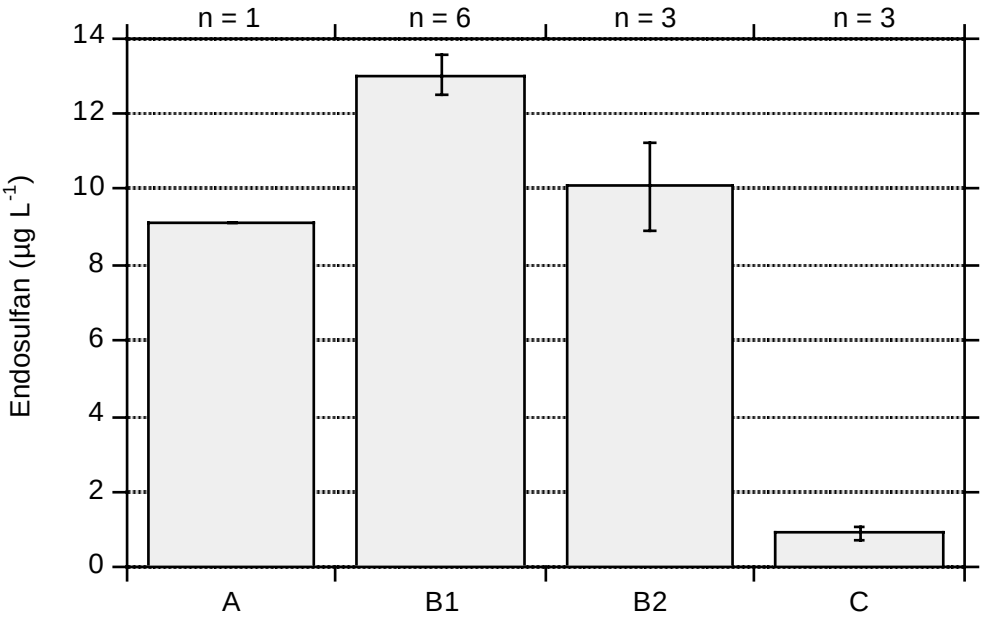

Fig. 5. Concentrations (±SE) of endosulfan in tributary water 15 m downwind of the sprayed plot. Column A: calculated peak concentrations based on 95th-percentile values for basic drift deposition (Ganzelmeier et al., 1995); B1: calculated peak value based on measured deposition rate; B2: measured peak value; C: measured 1-h average value.