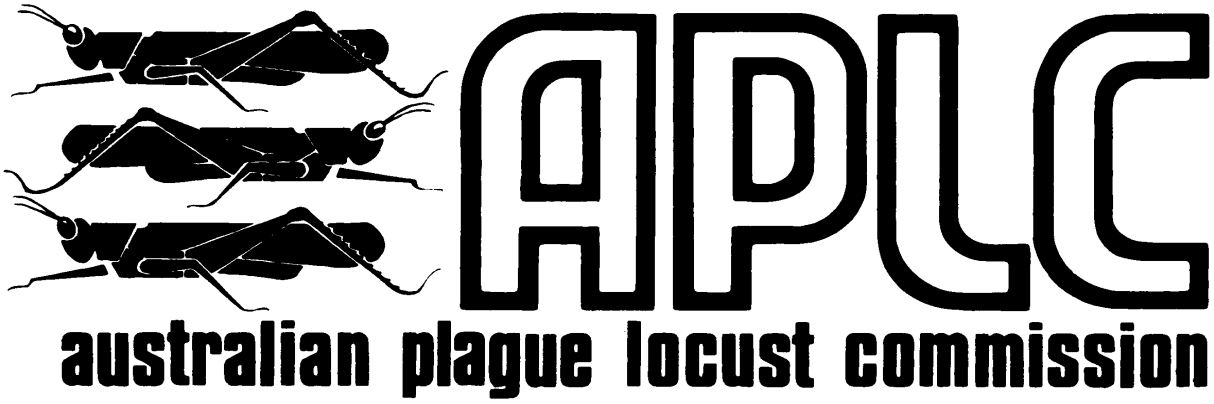

Applications of Equilibrium Passive Samplers to Monitor Pesticides in Water Bodies During a Locust Control Event – Quilpie 2002

Australian Plague Locust Commission

Research Report

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Applications of Equilibrium Passive Samplers to Monitor Pesticides in Water Bodies During a Locust Control Event – Quilpie, Queensland 2002

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Applications of equilibrium passive samplers to monitor pesticides resulting from a locust control event

Summary

Guidelines used to protect aquatic ecosystems are only available for a small number of common pesticides and are generally based on the analytical limits of detection. To avoid contamination of waterways during it's locust control operations, the Australian Plague Locust Commission (APLC) employs conservative down wind buffer zones between a spray target and a water body of ~1500 m. To date the APLC does not collect regular environmental monitoring data in relation to these buffer zones, primarily because the use of active air and water sampling methodologies is labour intensive and requires significant numbers of samples to be taken for the time integration of residue data. Currently, this falls outside the resources available during locust control campaigns. Therefore, if off-target residue data is to be collected as part of a structure environmental monitoring program, sampling methodologies need to be developed that enable adequate spatial and temporal scaling of residue sampling within the current resource constraints experienced by the APLC.

In the current study the application of polyethylene (PE) as an equilibrium passive sampler was investigated using two types of PE. Firstly, low density PE (LDPE) was used and the polyethylene/water partition coefficient (C_{PE}/C_W or K_{PEW}) determined. Although LDPE returned suitable partition coefficients for fenitrothion, the relatively small partition coefficient obtained for fipronil made LDPE unsuitable for field use for this pesticide. High density polyethylene (HDPE) provided good partition coefficients for both fenitrothion and fipronil and so was used in the field component of this project.

Field evaluations of HDPE took place during locust control operations near Quilpie in February 2002. Samplers were deployed in dams and/or borrow pits and fenitrothion and fipronil were aerially applied at various distances upwind to simulate different buffer zone widths, thereby testing sampler sensitivity. Fenitrothion applied at the standard APLC operational dose rate (267 g ai ha^{-1}) was detected using HDPE samplers in water bodies 400 m down wind of the application 24 hours post exposure. Fenitrothion was also detected in samplers placed 100 m down wind of the spray application up to 7 days post exposure. Dams directly over-sprayed contained the highest concentrations of fenitrothion in samplers 24 hours post exposure and these levels remained relatively high up to 7 days after the spray application. All water bodies contained sampler concentrations of fenitrothion that exceeded the Australia and New Zealand Environment and Conservation Council (ANZECC) freshwater trigger values, as outlined in the Australia and New Zealand Guidelines for Fresh and Marine Water Quality 24 hours after application. However, samplers placed in water bodies 400 m down wind of the spray application were unable to detect fenitrothion by 7 days post treatment.

HDPE samplers failed to detect fipronil in any water body at 0, 100 or 400 m downwind of a spray application.

Introduction

The use of pesticides for crop protection in Australia has increased considerably (Boulton and Brock 1999) and the guidelines used to protect aquatic ecosystems are only available for a handful of common compounds, usually based on the analytical limits of detection (Kookana *et al.* 1998). There is increased interest in ultra-low concentrations of pesticides in the aquatic environment as these can be accumulated to potentially toxic levels by organisms. Numerous studies have used aquatic organisms as bioindicators to assess the levels of contaminants in water (Cuppen *et al.* 2000; Herve *et al.* 1991, 1995; Lahr *et al.* 2001; Leonard *et al.* 1999, 2000; Petty *et al.* 2000a; Prest *et al.* 1992, 1995; Schulz and Liess 1999; Wang *et al.* 1999).

The use of biota to monitor pesticide levels in the environment is problematic. The Huckin's-developed semi-permeable membrane device (SPMD) presents a widely used alternative to biomonitoring and is used to mimic the processes by which aquatic organisms concentrate lipophilic organic contaminants (Huckins *et al.* 1993; Lebo *et al.* 1992, 1995). Generally, an SPMD passive sampler consists of membrane material that allows selected contaminants to pass through it. This membrane encapsulates a solvent phase (such as the fat of an organism in the case of biota-based samplers) and this solvent should have a higher affinity for hydrophobic compounds and act like a sink, concentrating and storing contaminants. Rantalainen *et al.* (1998) found similar profiles of contaminants in both passive samplers and fish tissue.

The passive sampling process is often referred to as "passive partitioning" (Wang *et al.* 1999) and the coefficient obtained is comparable to octanol/water partition coefficients (Ellis *et al.* 1995; Prest *et al.* 1992) widely available for a range of chemicals. Sodergren (1987) states that passive samplers can be used to confirm bioaccumulation mechanisms, to predict environmental hazards of bioavailable compounds and to monitor lipophilic pollutants, particularly in environments considered too severe for biological indicators to survive. A wide range of passive sampler designs has been used to successfully sample various contaminants (Booij *et al.* 2002; Huckins *et al.* 1990; Kingston *et al.* 2000; Litten *et al.* 1993; Muschal 1999; Sabaliunas and Sodergren 1996; Sodergren 1990). However, solvent filled passive samplers require relatively lengthy exposure periods (~30 days) to accumulate contaminants (Petty *et al.* 2000a; Sabaliunas and Sodergren 1997) and their use to monitor "pulse" pollution events such as the application of pesticides for locust control is, as yet, untested.

Polyethylene (PE) has been used successfully as a passive sampler to monitor chlorinated pesticides, polychlorinated biphenyl (Lefkovitz *et al.* 1996) and polycyclic aromatic hydrocarbons (Muller *et al.* 2001). To obtain a reliable partitioning coefficient, it's crucial that the water and PE system reach a state of partitioning equilibrium for the compound of interest (Muller 2001). However, the abovementioned studies did not aim to sample a pulse event and the compounds of interest were relatively constant in the environment. Polyethylene, in the form of a large sheet, has a relatively large surface area to volume ratio and may be advantageous in situations where rapid uptake of the xenobiotic being sampled is necessary. Lefkovitz *et al.* (1996) and Muller *et al.* (2001) have demonstrated that samplers made from PE are relatively simple to prepare and, following exposure, the PE extract can be easily analysed. Moreover, PE is cheap and readily available.

Chemical locust control occurs via the application of ultra-low volume (ULV)

formulations of the organophosphorus compound, fenitrothion (O,O-dimethyl O-(3-methyl-4-nitrophenol) phosphorothioate, Sumitomo Chemical Company, Japan) or of the phenyl pyrazole insecticide, fipronil (5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole, BASF, Melbourne Australia), both broad spectrum pesticides (see Table 1 for pesticide properties). To avoid freshwater contamination, conservative upwind buffer zones of ~1500 m are employed between the target site and any area sensitive to the application of chemicals, such as water bodies, organic farming enterprises or the habitat of rare and threatened species (Story *et al.* 2005).

Table 1. Physical properties of fipronil and fenitrothion

Properties		*Fipronil (phenyl-pyrazole)*	*Fenitrothion (organophosphate)*
Molecular formula		$C_{12}H_4Cl_2F_6N_4OS$	$C_9H_{12}NO_5PS$
Molecular weight		437.2	277.2
Melting point		200-201°C	0.3°C ^
Vapour pressure		3.7 x 10^{-4} mPa (25°C)	18 mPa (20°C)
Log K_{ow}		4 (shake flask method)	3.43 (20°C), 3.3 $^+$, 3.16 ^
Henry's Law Constant		3.7 x 10^{-5} Pa m^3 mol^{-1}	9.5 x 10^{-2} Pa m^3 mol^{-1} ~
Density		1.6262 g/ml (20°C)*	SG 1.328 (20°C)
Solubility:	Water	1.9 (pH 5), 2.4 (pH 9) all mg/L, 20°C	14 mg/L (30°C), 30 mg/L (20°C) $^+$
	Hexane	0.028 g/L (20°C)	24 g/L (20°C), 42 g/kg (20-25°C) ^
	Octanol	12.2 g/L *	

*Revised from Tomlin (2000), *(Tingle et al. 2000), ^(WHO 1992); $^+$(Pehkonen and Zhang 2002); ~(Sudo et al. 2002)*

Australian environmental legislation, at both the Federal and State levels, places an increasing emphasis on proponents of potentially threatening actions to demonstrate environmental due diligence (also termed duty of care) during the course of their activities. Such provision has been in existence since changes to Commonwealth and State environmental legislation in the early 1990s. Consequently, the development of PSDs to monitor waterways for pesticides used during locust control has value for both State and Federal locust control agencies to ensure that currently employed spray buffer zones deliver the level of environmental protection required.

The present study aimed to determine the potential of PE as a passive sampler and to assess it's applicability for monitoring events such as the application of ultra-low volume (ULV) pesticide applications for locust control in Australia's arid and semi-arid rangelands. Pesticides used by the Australian Plague Locust Commission (APLC) are relatively short-lived in the environment and consequently, the sampler developed would have to rapidly accumulate pesticides to detectable quantities before significant losses were observed, often under severe environmental conditions.

Materials and Methods

Polyethylene (PE) material, used widely as fruit and vegetable bags, has been employed previously as an inexpensive source of PE in passive sampling devices (Muller *et al.* 2001). A batch of ~5,000 HDPE bags was obtained from Cospak Pty Ltd (Brisbane, Australia). The bottom seal of each bag was removed and cut open on one side, thus opening up into a sheet. All sheets were weighed and the dimensions of at least 5% randomly selected HDPE sheets were measured (length and breadth) with a metal ruler. Thickness was measured using an electric micrometer (Micromaster® TESA capa*μ*system IP54, VHS International NATA, Swiss made, see Table 2 for physical properties of HDPE).

All HDPE sheets were pre-extracted by washing in hexane (to obtain "clean" HDPE sheets). To do this, approximately 10 HDPE sheets were placed into a 500 ml clean glass jar filled with 250 ml of hexane and sealed. After leaving the sheets on a shaker (Adolf Kühner AG, Schweiz) at 110 rpm overnight the hexane was changed and the procedure was repeated three times. Following pre-extraction, sheets were washed with deionised water, placed back into glass jars and submerged in deionised water and then left on the shaker overnight. The following day the water was discarded, the sheets were quickly shaken dry in the fume cupboard and stored in tightly sealed glass jars ready for laboratory or field experiments.

Table 2. Physical properties of high density polyethylene (HDPE) sheets used in laboratory experiments

Property	***HDPE***
Weight per sheet (g)	1.43 (SD ±0.013)
Length (cm)	58.3 (SD ±0.47)
Breadth (cm)	42 (SD ±0.41)
Total surface area per sheet (cm^2)	4897.2 (SD ±62)
Mean sheet thickness (μm)	7.33 (SD ±0.49)

Insecticide stock standards and solvents

All insecticide standards used were certified to at least 98% purity and obtained from ChemService, NARL or Rhone-Poulenc. Redistilled hexane was used to dilute the standards to required concentrations. Stock standards were stored in dark glass vials in the freezer and the prepared standards were always kept in the refrigerator. All hexane was redistilled and regularly tested for impurities by Queensland Health and Scientific Services (QHSS) laboratory staff. Acetone (CH_3COCH_3) with purity of 99.81 % and dichloromethane (CH_2Cl_2) with purity of 99.97% was also used in laboratory procedures. Both solvents were high purity solvents from OmniSolv® (EM-Science, Merck KgaA, Darmstadt, Germany).

Instrument details

The quantification of fipronil (including fipronil derivatives) and fenitrothion was performed using gas chromatography coupled with mass spectroscopic detection (GC-MS), operating in the selected ion monitoring mode (SIM). The Varian 3400 GC was equipped with a Finnigan A200S liquid autosampler operating in splitless mode (injector temperature 295°C) with a 20 m DB-1 fused silica capillary column (0.2 mm ID and 0.33 μm film thickness)

from J & W Scientific. The delay time was 8.5 min and the MS operated under electrical ionisation (source: 180°C, pressure –78 millitorr, filament 250 μA).

All samples were spiked with 2μl of internal standard solution prior to analysis, which included 4000 μg ml^{-1} of each of the following compounds; acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, napthalene-d8, perylene-d12 and phenanthrene-d10. The instrumental detection limit was 0.01 μg L^{-1}.

Analytical limits of detection and limits of quantification

Recovery efficiency from the HDPE/water system following a 7 day equilibration period in the laboratory experiment was 68 and 77 % for fipronil and fenitrothion respectively, higher recovery rates were experienced with shorter exposure times.

To determine the recovery efficiency of insecticides from HDPE alone, without the influence of water, insecticide standards were directly applied to the HDPE sheets. This process involved a direct dripping of a known amount of insecticide standard onto a HDPE sheet that was enclosed in a 1 L round bottom flask. Following an equilibration period, HDPE sheets were extracted and the extract analysed. The recovery of fipronil was just over 60%, which suggest that there is a loss of fipronil that is not accounted for. The recovery of fenitrothion was almost 100%.

Quality control and quality assurance

All samples were prepared and analysed at Queensland Health and Scientific Services pesticide laboratory (39 Kessels Road, Coopers Plains, Queensland, Australia) and followed the standard procedures practiced by this laboratory. All experiments were replicated to result in a total of three samples. However, only two replicates were analysed due to the cost associated with analysis. In circumstances where the results between replicates were highly variable, the third replicate was analysed thus accounting for any discrepancies. Possible contamination was accounted for through the analysis of laboratory and field blanks. These included the deionised water used, the redistilled hexane and the hexane extracts of the clean HDPE sheets. Glassware was rinsed after use and this rinse was analysed to determine how much insecticide was left behind. Both field blanks and trip blanks were used during the field trials.

Laboratory calibration of HDPE samplers

The objective of the laboratory study is to calibrate the HDPE for the insecticides of interest as well as to determine the time taken for fipronil and fenitrothion to reach equilibrium in the HDPE and water system. To do this, water and HDPE were analysed at different time intervals after insecticide exposure enabling calculation of the equilibrium time in the PE/water system. Therefore, the partition coefficient of each pesticide between PE and water at equilibrium can be determined.

Glass jars filled with 0.5 L of deionised water were spiked with fipronil and fenitrothion to a concentration of 19.92 and 19.296 μg L^{-1} respectively. Three HDPE sheets were placed into each jar to simulate one sampler with a total surface area of approximately 1.5 m^2. The water in this process was the source of pesticide and the clean HDPE sheets began to accumulate the pesticides after exposure. This is referred to as the uptake process hereafter.

Eighteen samples were prepared along with 2 blank samples made similarly but with no added pesticide. All samples were left undisturbed in a cool dark position in the laboratory. Two samples were removed following a 24 hour period and one of these was used to extract the pesticide from the HDPE phase and the water phase separately, as described below. This would indicate how the pesticide concentration was distributed in the HDPE/water system following 24 hours of exposure. For the second sample, the water was drained and discarded and the HDPE was placed in a fresh sample of water (0.5 L) and left in a cool dark place for another 24 hours. Following this period, both the HDPE and water phases were analysed separately. During this process the HDPE was the source of pesticides and not the water, therefore a loss of pesticide from the HDPE to the water was observed. This process is hereafter referred to as elimination.

The same process was repeated for two more samples following 7 days of exposure. The HDPE and water phases were extracted and analysed for pesticide concentration, while the other sample was drained of all water and placed into clean water (0.5 L) and left in a cool dark place for a further 7 days. The HDPE and water phases were then extracted and analysed separately.

Extraction of insecticides from HDPE

HDPE sheets were carefully removed from their flasks and shaken in fume hood to remove any bulk adhering water and placed into a labelled clean glass jar filled with 200 ml hexane, shaken and left overnight in cool dark position. The following day, hexane was changed 3 times with a 1 hour agitation period following each change. The hexane extracts were passed through anhydrous sodium sulphate, and concentrated to just above 5 ml on a rotary evaporator (Buchi Rotavapour R-114). Hexane extract was then transferred to a clean 15 ml graduated vial and further concentrated to 1 ml by using a gentle stream of nitrogen gas. The 1 ml samples were transferred into analysing vials tightly sealed and stored ready for clean up by adsorption chromatography or direct analysis by GC-MS.

Liquid-liquid extraction of insecticides from water

Sample water (usually 1 L) was transferred into a 2 L separating funnel and 60 g NaCl was added to the water. After a 2 minute agitation period, 150 ml dichloromethane (DCM) was added followed by another 2 minute shaking period. After the DCM layer settled it was slowly released and passed through anhydrous sodium sulphate containing conical funnel and into a 500 ml round bottomed flask. A further 90 ml DCM was added into the water sample, shaken for 2 minutes and passed through filter funnel as before. The DCM in the round bottomed flask was concentrated by using the rotary evaporator to approximately 5 ml and a solvent exchange with hexane was performed. Following transfer of sample into a 15 ml vial, the sample was concentrated to 1 ml as before by using a gentle stream of nitrogen gas. The 1 ml samples were transferred into analysing vials, tightly sealed and ready for analysis by GC-MS

Clean-up of field samples

HDPE samplers were left in the field for up to 7 days and thus sedimentation and algal growth presented a problem when hexane extracts were analysed. To achieve good analytical detection Florisil adsorption chromatography was necessary. Glass mini columns (0.5 cm ID, 20 cm length) were plugged with glass wool and 2 g of 5% deactivated Florisil was added

followed by 0.2 g of anhydrous sodium sulphate, after which 12 ml of hexane was passed through the column to decontaminate the system. The standards were eluted with 12 ml of 6% diethyl ether in hexane, followed by 24 ml of 10% acetone in hexane and finally 12 ml of 50% acetone in hexane. The fractions were collected in separate 15 ml vials and were concentrated by using a gentle stream of nitrogen gas and transferred into hexane, resulting in a final volume of 1 ml. Elution procedure calibrations determined previously that the 10% acetone in hexane was the mobile phase for both fipronil and fenitrothion and therefore retained for analysis. The recovery efficiency for the adsorption chromatography procedure was 54 and 83 % for fipronil and fenitrothion respectively.

Treatment of data

The compound concentration was expressed in volumetric terms for both the HDPE (referred to as S in the following equations revised from Muller *et al.* 2001) and water concentrations. The compound concentration in the HDPE sampler (S) can be calculated by using Equation 1 as follows:

$$C_S = \frac{m_S \times \rho_S \times 1000}{M} \qquad (1)$$

where,

C_S is the volumetric compound concentration in HDPE sampler (µg/L)

m_S is the mass of compound in HDPE sampler (µg)

ρ_S is the density of HDPE (g/cm^3)

M is the mass of HDPE (g)

1000 is a conversion factor, cm^3 to dm^3 (or L)

The compound concentration in the extracted water is simply converted to the original volume of water extracted (if original water volume was 1 L and this was reduced to 1 ml) by using Equation 2 as follows:

$$C_W = C_{Ex} \times F \qquad (2)$$

where,

C_w is the compound concentration in water (µg/L)

C_{Ex} is the compound concentration of the analysed water extract (µg/ml)

F is the concentration factor (usually 1 x 10^3 ml)

Expressing both the compound concentration in the HDPE sampler and the compound concentration in the water in like terms allows for the dimensionless HDPE sampler/water

partition coefficient ($K_{S/W}$) to be obtained. Assuming equilibrium, $K_{S/W}$ can be estimated as follows:

$$K_{S/W} = \frac{C_S}{C_W} \quad (3)$$

where,

$K_{S/W}$ is the partition coefficient of the compound between the HDPE sampler and water at equilibrium (unitless)

C_S is the volumetric compound concentration in the HDPE sampler (µg/L)

C_w is the compound concentration in water (µg/L)

Field evaluation of HDPE samplers

Prior to field evaluation, HDPE sheets needed to be constructed into a sampler. The design of the HDPE samplers was optimised for quick field deployment. Deployment would be in a relatively large water body and therefore was secured between floating and gravitational devices. To enhance the sampling efficiency, one standard HDPE sampler contained 12 HDPE sheets, resulting in a total surface area of 60, 000 cm^2 per sampler (see Table 3 for physical characteristics of HDPE).

Table 3. Physical characteristics of high density polyethylene (HDPE) sheets used in field trials

Property	***HDPE***
Weight per sheet (g)	2.12 (SD ±0.01)
Length (cm)	59.09 (SD ±0.29)
Breadth (cm)	43.3 (SD ±0.33)
Total surface area per sheet (cm^2)	5119.46 (SD ±46.26)
Mean sheet thickness (µm)	8 (SD ±0.0)

A total of 600 HDPE sheets were pre-extracted using hexane, washed and dried (see above). These were stored in 500 ml glass jars and sealed tightly in sets of 12, resulting in a total of 50 samplers (12 HDPE sheets per sampler). Each jar was numbered, marked with the total weight of HDPE and wrapped in paper towel to reduce the potential of breakage and stored in a large plastic container ready for transportation to the site.

As well as field blanks, trip blanks were prepared to account for possible contamination during transportation and handling and these accompanied the exposed samples at all times. The HDPE sheets were secured using metal clips which were tied to nylon cord. Each sampler was deployed immediately prior to the spray event. The HDPE sampler design was rugged, easily transportable and ready for swift deployment for the event situation (Figure 1).

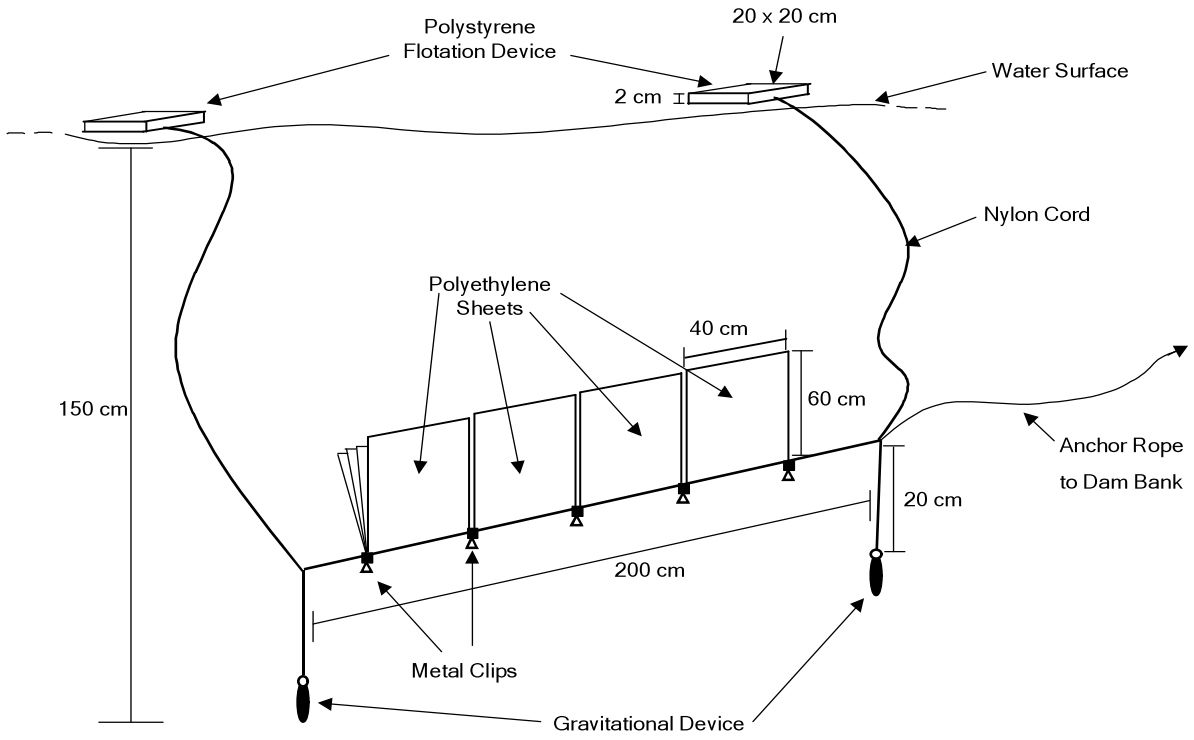


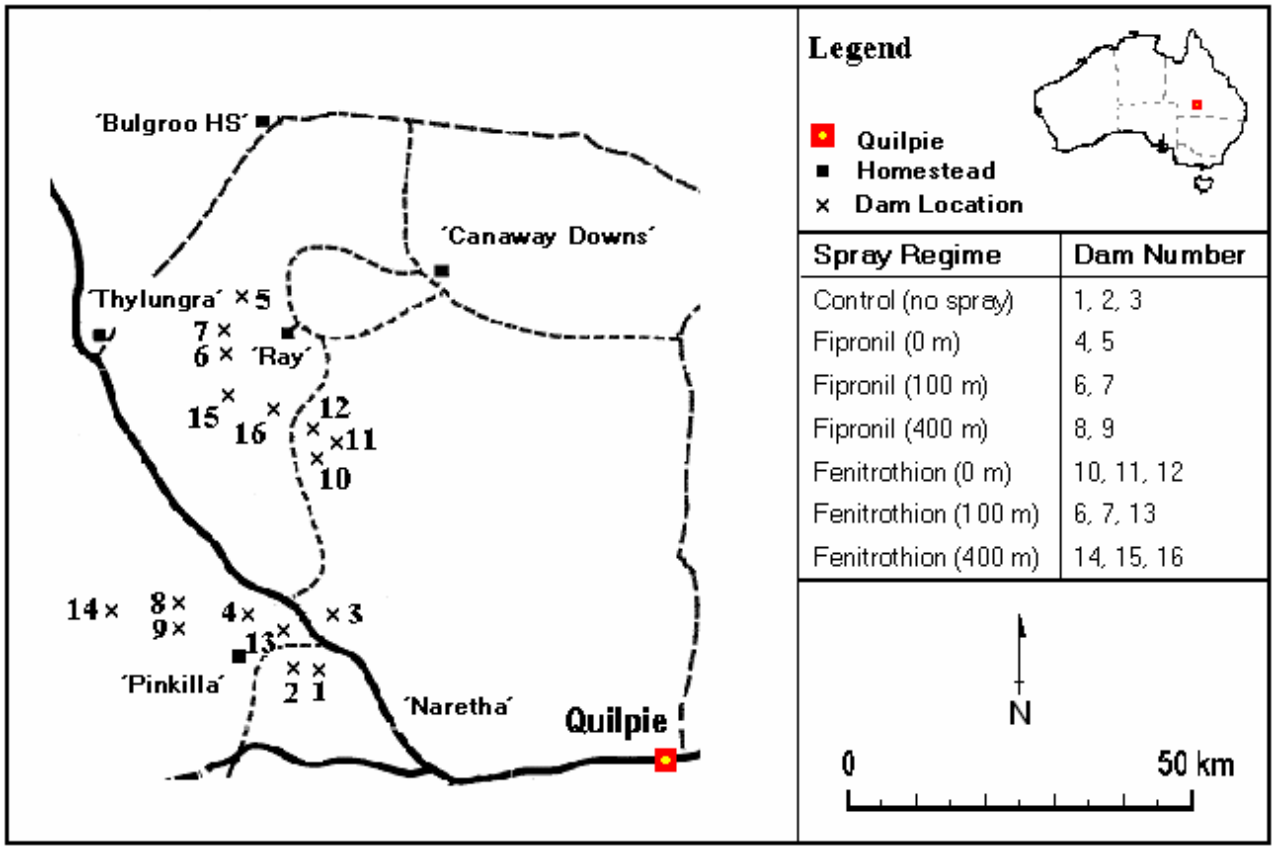
Figure 1. Field deployment of high density polyethylene (HDPE) passive sampler used in the present study

Site description

A flexible study design was prepared as only one set of field experiments could be organised. Furthermore, the movement and hatching of locusts is unpredictable and the field experiment could not be fully planned in advance. Following the detection of locusts near Quilpie in southwest Queensland by the APLC, locust populations were identified and mapped and control operations were organised. During this time, water bodies suitable for PSD deployment were identified. Due to arid conditions in southwest Queensland, finding permanent "natural" water bodies was problematic and it was decided to use cattle dams and borrow pits instead (Figure 2). This was an excellent alternative as the dams and pits served as good replicates being similar in character and lacking riparian vegetation, which could act as a buffer thus creating additional obstacles to pesticide deposition onto the water surface. Sixteen sites were found and following permission from property owners, HDPE samplers were deployed.

Field study design

Variables tested in the field experiment included spray distance from the dam, exposure duration, and insecticide. Three spray distances 0 (a direct over-spray), 100 and 400 m were evaluated. Fipronil and fenitrothion were applied aerially at the APLC's standard operating dose rates of 1 g active ingredient (ai) ha^{-1} and 267 g ai ha^{-1}, sprayed cross-wind by fixed-wing aircraft using a targeted flying height of 10 m and a track spacing of 100 m. Spray aircraft were equipped with two Micronair® AU5000 rotary atomizers (Micron Sprayers Ltd.), one mounted under each wing.



Spray Regime	Dam Number
Control (no spray)	1, 2, 3
Fipronil (0 m)	4, 5
Fipronil (100 m)	6, 7
Fipronil (400 m)	8, 9
Fenitrothion (0 m)	10, 11, 12
Fenitrothion (100 m)	6, 7, 13
Fenitrothion (400 m)	14, 15, 16

Figure 2. Study site showing location and spray regime of all dams sampled

Two sets of HDPE samplers were deployed at each dam, one collected at 24 hours and the other at 7 days post spray. Spray regimes were replicated to result in a total of 2 of each treatment for fipronil and 3 of each treatment for fenitrothion. The experiment included 3 control dams (Figure 3).

Results obtained from chemical analysis were converted to volumetric terms (amount per liter HDPE) as in the laboratory phase of this work. Further data treatment included the estimation of insecticide in the water from the known concentration in the HDPE by simply rearranging equation 3 to solve for the concentration in water as follows:

$$C_W = \frac{C_S}{K_{S/W}} \quad (4)$$

Results from field trials were analysed as follows. Differences in concentration means (log transformed) for the factors time of exposure (time) and spray regime (spray) were analysed for fenitrothion using factorial ANOVA. The effect of interaction between time and distance was also investigated. The statistical model used to describe the factorial ANOVA is given in equation 5.

$$y_{ijk} = \mu + \alpha_i + \beta_i + (\alpha\beta)_{ij} + \varepsilon_{ijk} \quad (5)$$

where,

y_{ijk} is the (log transformed) concentration in the k^{th} replicate of the i^{th} level of spray and j^{th} level of time (k = 1 – 3, i = 1, 2..4, j = 1,2, n = 24);

n is the number of replicates for each of the (time x spray) treatment groups;

μ is the overall grand mean of y;

α_i is the effect of the i^{th} level of spray;

β_j is the effect of the j^{th} level of time;

$(\alpha\beta)_{ij}$ is the effect of interaction between spray and time;

ε_{ijk} is the random effect attributed to the ijk^{th} individual observation.

Results

Laboratory Results

The uptake of fenitrothion by HDPE sheets after 24 hours and 7 days of exposure in water that was spiked with fenitrothion to result in a concentration of 19.92 µg L^{-1} (Figure 3). The equilibrium between HDPE sheets and water was reached around the second day of exposure for the uptake process. The elimination of fenitrothion from pre-loaded HDPE sheets into water was observed by analysing the HDPE following 24 hours and 7 days of being placed into "clean water". The results are also illustrated in Figure 4 and although the number of data points is limited, the trend line suggests that the elimination process of fenitrothion from HDPE was marginally slower than the up-take process.

The residual water from the above experiment was subsequently analysed (Figure 4) showing that the uptake of fenitrothion by HDPE sheets results in a loss of concentration in the spiked-water. Conversely, during the elimination of fenitrothion from pre-spiked HDPE sheets, fenitrothion concentration in water increases over time. Equilibrium between HDPE

sheets and water was reached within 24 hours for the elimination process and soon after for the uptake process.

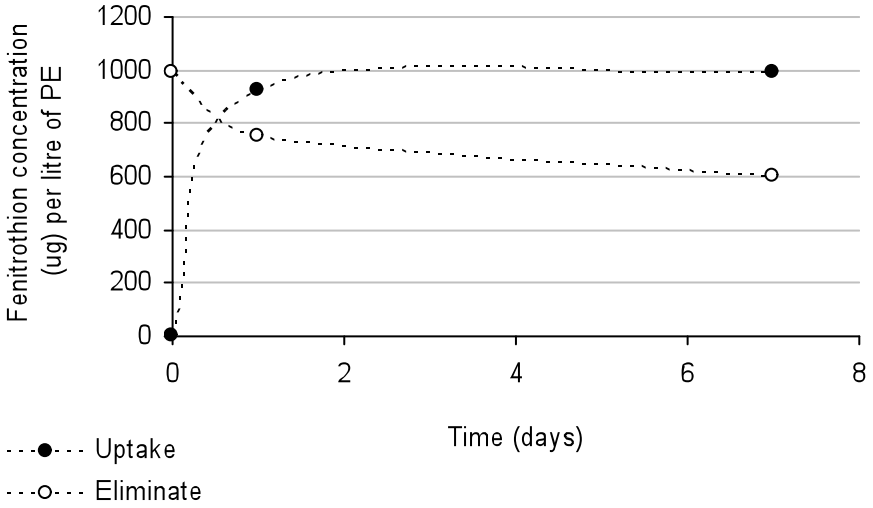


Figure 3. Fenitrothion concentration in high density polyethylene (HDPE) through time as uptake and elimination processes take place

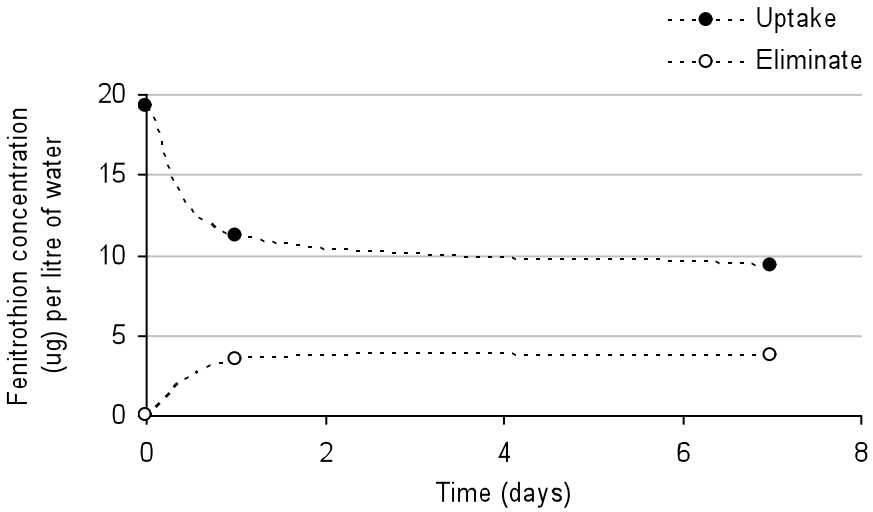


Figure 4. Fenitrothion concentration in water through time during the uptake and elimination processes by high density polyethylene (HDPE)

The uptake of fipronil by HDPE sheets following 24 hours and 7 days of exposure in water that was spiked with fipronil to result in a concentration of 19.296 µg L^{-1} (Figure 5). Over the time period of the experiment, equilibrium between HDPE sheets and water was not reached for the uptake process. The elimination of fipronil from pre-loaded HDPE sheets into water was observed by analyzing the HDPE following 24 hours and 7 days of being placed into

clean water. The elimination of fipronil seemed to approach equilibrium more readily that the uptake process in the HDPE/water system.

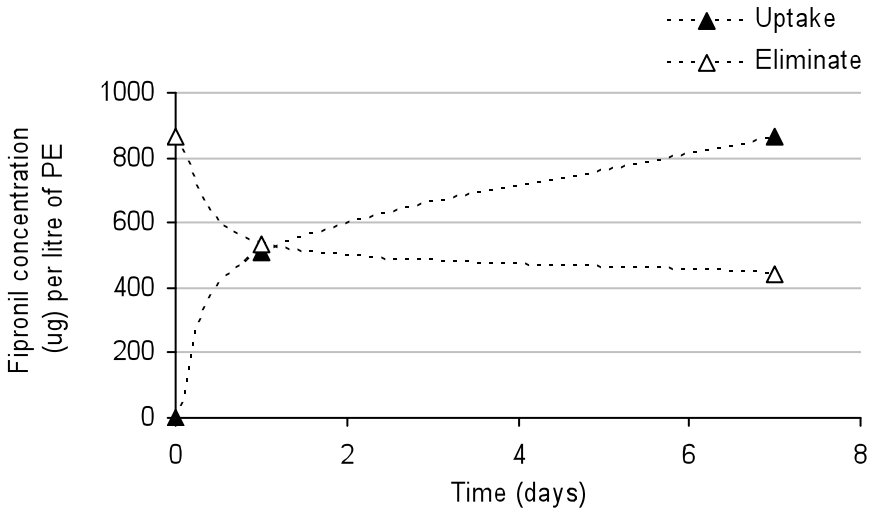


Figure 5. Fipronil concentration in high density polyethylene (HDPE) through time as uptake and elimination processes take place

Residual water from the above experiment was subsequently analysed (Figure 6) showing the uptake of fipronil by a HDPE sheets results in a loss of concentration in the spiked-water. Similarly, the elimination of fipronil by the pre-loaded HDPE sheets results in an increase of fipronil in water overtime. Equilibrium between HDPE sheets and water was reached just after day-1 for both uptake and elimination processes.

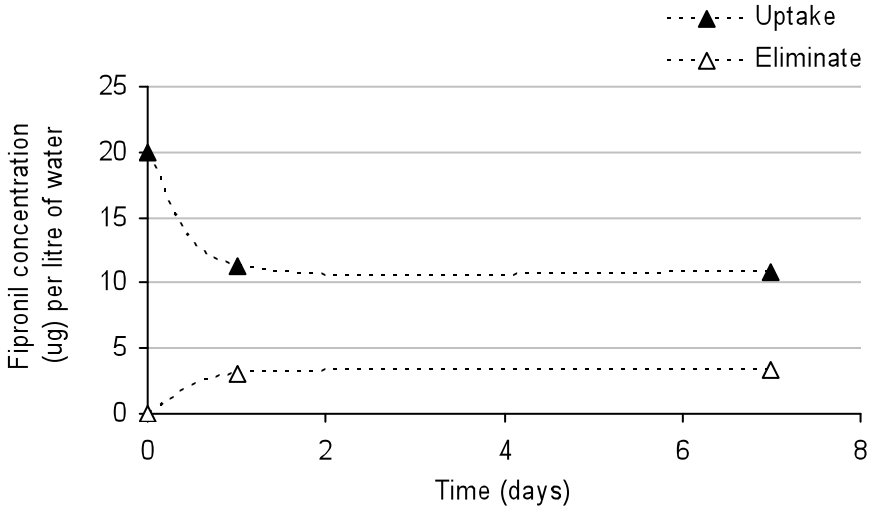


Figure 6. Fipronil concentration in water through time during the uptake and elimination processes by high density polyethylene (HDPE) sampler

HDPE demonstrated an increased time taken for uptake of fipronil from water than the corresponding elimination of fipronil from pre-loaded HDPE into "clean" water. A possible explanation for this could be adsorption of fipronil onto the HDPE surface rather than absorption into the HDPE matrix. We consider it unlikely that the loss of fipronil and fenitrothion resulted from hydrolysis as both pesticides are relatively resistant to this degredation pathway (EPA 1996, Mikami *et al.* 1981, as cited in WHO 1992). Even though the samples were kept covered and away from direct sunlight, some exposure to indoor light did occur during preparation and handling of samples. The degradation of fipronil in water exposed to sunlight is rapid, with a half-life of 3.6 hours (Belayneh 1998, as cited in Tingle *et al.* 2000) and sulphoxide extrusion forms the photodegrade desulphinyl derivative (Fenet *et al.* 2001). Desulphinyl is more hydrophobic than fipronil and would be more readily taken up by HDPE. Therefore, what appeared as equilibrium in the HDPE samplers occurring in the water phase may be due to the degradation of fipronil into desulphinyl.

The results from the uptake and elimination processes of fipronil and fenitrothion in the HDPE/water system were used to calculate the partitioning coefficient ($K_{S/W}$). The C_S/C_W for fenitrothion in the uptake and elimination processes was 2 (Log transformed) and was 2.2 (Log transformed) respectively (Figure 7). The C_S/C_W for fipronil in the uptake and elimination processes was 1.9 (Log transformed) and 2.1 (Log transformed) respectively. The C_S/C_W obtained by the HDPE experiment was much lower compared to the K_{OW} used as a first estimate of affinity of the insecticides for the HDPE.

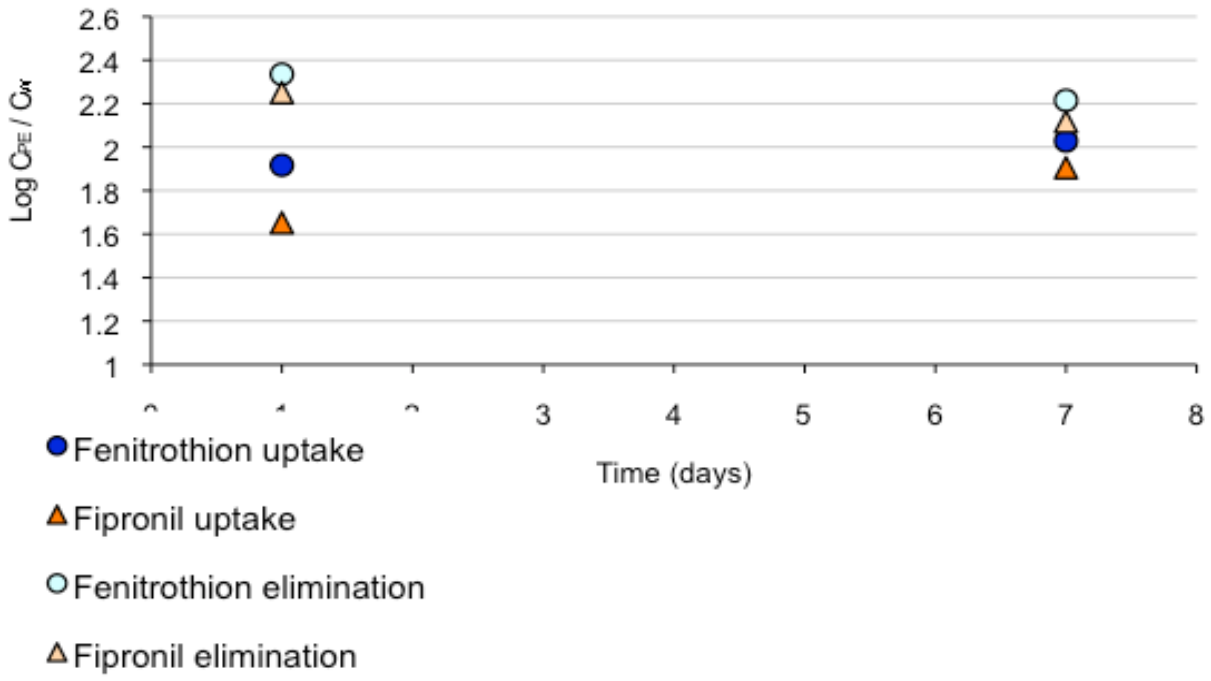


Figure 7. Log C_{PE}/C_W for the uptake and elimination processes of fipronil and fenitrothion

The published fipronil log K_{OW} approximates 4, while the log C_S/C_W obtained by the HDPE experiment was approximately 2. Although, the log C_S/C_W for fenitrothion was higher than for fipronil, it was still much lower than the K_{OW} of 3.43 used as a first estimate of affinity for the HDPE material. The log C_S/C_W for fenitrothion obtained by this experiment was approximately 2.1 (Table 4).

Table 4: Comparison of octanol partitioning coefficients for fipronil and fenitrothion with the results obtained in this study

Pesticide	*Octanol partition coefficient K_{OW} (from Tomlin 2000)*	*HDPE/water partition coefficient $K_{S/W}$*
Fenitrothion	3.43	2.1
Fipronil	4	2

Field results

Following clean-up, the field blanks (which accompanied the exposed samples at all times) were free from detectable levels of fenitrothion, fipronil and the fipronil degradation products, desulphinyl and sulphone, suggesting that contamination did not occur during the field visit.

Fipronil was not detected in any water field samplers. The field application rate of 1 g ai ha^{-1} sprayed directly over a dam (0 m treatment) would result in a water concentration of 100 ŋg L^{-1}. This is low compared to the concentration applied in laboratory experiments (1–10 µg L^{-1}). The majority of dams in this study were very turbid and even though organic matter content was not directly measured, it is not unreasonable to assume that fipronil may have sorbed to the particles in the water column before it had a chance to come in contact with the sampler given fipronil's affinity to adsorb to soils with higher organic matter content (Bobe *et al.* 1997).

Degradation of fipronil under environmental conditions occurs relatively quickly. It was anticipated that if HDPE samplers detected a fipronil degradation product it would be the desulphinyl derivative which exhibits a higher bioaccumulation potential (Tingle *et al.* 2000) and is relatively non-polar thereby increasing it's accumulation potential by the HDPE samplers. The increased polarity of sulphone, another fipronil derivative, would reduce the likeliness of uptake by the HDPE samplers from the water system. Neither the sulphone or desulphinyl degradation products were detected in the water phase of the field experiment.

The application rate of fenitrothion (267 g ai ha^{-1}) resulted in detectable amounts in PSDs. Fenitrothion was detected (3 µg per HDPE sampler) 400 m downwind of application 24 hours after spraying (Figure 8). However, the amount of fenitrothion decreased to undetectable levels by 7 d post exposure at this distance. Sampling at 100 m down wind resulted in a higher fenitrothion concentration 24 h after application, decreasing by 87% by day 7. The direct over-spray of dams resulted in highest levels of fenitrothion 24 hours after application which decreased by 82% 7 days after application. The partitioning coefficient was applied to the fenitrothion concentrations observed in the HDPE to estimate the fenitrothion

concentration present in the dams at 24 hours and at 7 days after fenitrothion application (Figure 10). The estimated fenitrothion concentration in water 400 m downwind from the spray is 0.02 µg/L, 24 hours after application, exceeding the ANZECC fresh water trigger value. As noted before fenitrothion was not detected by day 7 in the 400 m trial. Nonetheless, sampling at 100 m down wind of the dams resulted in a significantly high concentration 24 hours after application (1.2 µg L^{-1}), which remained above the fresh water trigger value even after 7 days. The direct over-spray of dams (0 m) resulted in an estimated water concentration of 5.8 µg L^{-1} 24 hours following application, which fell to 1 µg L^{-1} seven days after application.

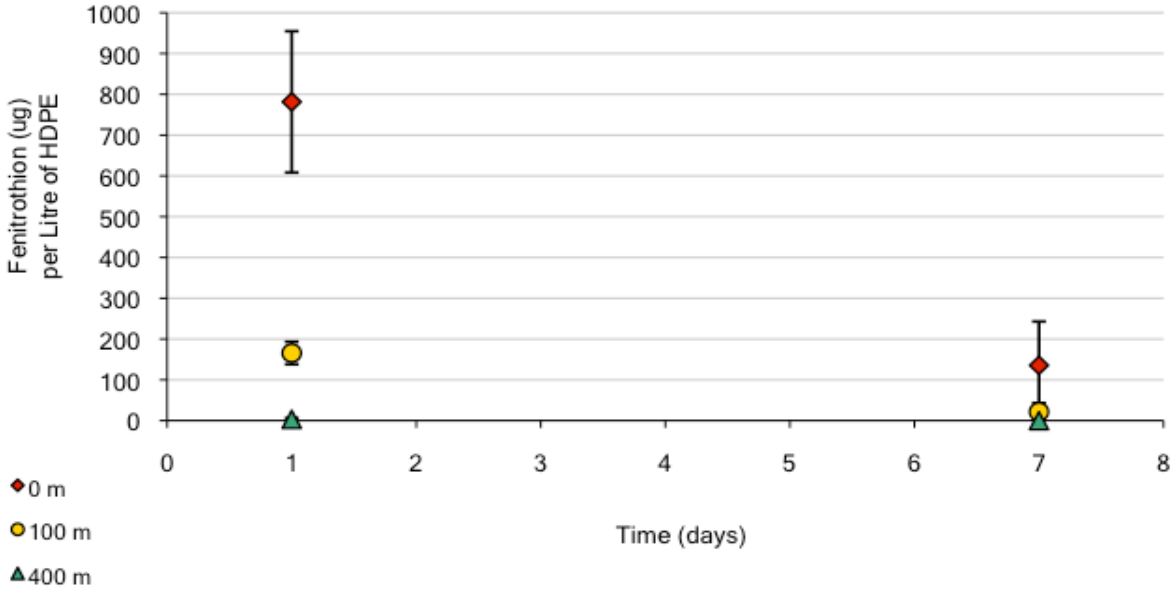


Figure 8. Fenitrothion concentration in high density polyethylene (HDPE) samplers at three distances downwind of the spray target and two time exposures.

Table 5. Multiple t-test involving spray distance and the mean fenitrothion concentration in aquatic high density polyethylene (HDPE) samplers

Distance	*Mean concentration (µg/L of PE)*	*Significant Difference*
0	458.5	A
100	93.6	B
400	1.6	C
Control	0.0	C

Means with the same letters are not significantly different (α = 0.05)

No significant interaction between distance and time for the mean (log transferred) fenitrothion concentration ($F_{7,16}$ = 3.09, p = 0.0569) was evident. Further analysis using ANOVA indicated that there was a significant difference between the four spray distances

($F_{7,16}$ = 27.99, p = 0.0001). Multiple t-tests (or least significant difference test, LSD's) showed which distances were significantly different from one another (Table 5).

ANOVA indicated that there was a significant difference in mean concentration of fenitrothion between 1 d and 7 d post exposure with the mean concentration of fenitrothion at 1 d (237.6 µg L^{-1} PE) significantly higher than that at day 7 (39.3 µg L^{-1} PE) ($F_{7,16}$ = 13.62, p = 0.002).

Conclusion

The major difference between this study and previous research investigating the use of passive sampling devices is the time of exposure of the sampler. In past studies, concentrations of contaminants are relatively constant in the environment and the samplers used are exposed to environmental conditions for extended periods allowing passive accumulation of contaminants. However, in this study the contaminants of interest are relatively short lived and breakdown rapidly after their application.

HDPE samplers developed and calibrated in the laboratory did accumulate fenitrothion. The equilibrium partition coefficient (C_{PE}/C_W) obtained by the laboratory was sufficient to being applied in the field experiment. In the field, HDPE samplers successfully detected fenitrothion in water following spray events. Fenitrothion was detected in the water 400 m downwind of the spray event at above the ANZECC fresh water trigger value, 24 hours following fenitrothion application. This is an important result, suggesting that HDPE samplers may be useful in determining spray drift related water contamination events. However further development of HDPE samplers is needed.

The calibration of samplers for detection of fipronil was problematic in the laboratory study as samplers did not reach equilibrium in the specified time. It was thought that fipronil might have adsorbed onto the polyethylene surface and did not reach equilibrium. This was supported by rapid elimination of fipronil from polyethylene into water. Furthermore, fipronil was not detected during field trials. The major difference between fenitrothion and fipronil is the application rate. Fipronil was applied at a rate of 1 g ai ha^{-1}, compared to a rate of 267 g ai ha^{-1} for fenitrothion. Fipronil has been shown to sorb to particulates readily and therefore may have bound to particulates in the water before it had a chance to come in contact with the sampler.

Processes involving kinetics particularly in relation to the detection of fipronil, were encountered and, assuming equilibrium, presented difficulties both in the laboratory and in the field. The primary disadvantage of using an equilibrium approach is that it underestimates the ambient insecticide concentration when equilibrium is assumed prematurely. The HDPE sampler did show potential as a water sampler. Furthermore, HDPE was a relatively cheap and simple alternative to traditional sampling techniques, highlighting its potential use for future studies, if further developed.

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