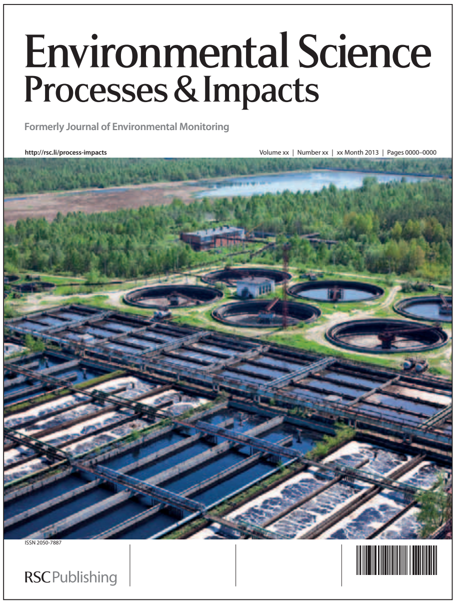
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ENVIRONMENTAL IMPACT STATEMENT

Pesticide vapour drift is increasingly being recognised as a potential environmental and human health issue. Most current field studies designed to measure pesticide vapour drift use active air samplers, such as high-volume air samplers, and these samplers are both expensive and require network electricity. This limits the number of samplers that can be used and where they can be placed. The flow-through sampler is a wind-driven passive sampler and our work shows that it is a viable alternative to high volume samplers in near-field vapour drift studies. This technology thus makes multi-sampler, transect or grid-based sampling designs considerably more practical.

Testing flow-through air samplers for use in near-field vapour drift studies by measuring pyrimethanil in air after spraying

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GRAPHICAL ABSTRACT:

ABSTRACT (350 words max)

Pesticides volatilisation and subsequent vapour drift reduce a pesticide's efficiency and contribute to environmental contamination. High-volume air samplers (HVSs) are often used to measure pesticide concentrations in air but these samplers are expensive to purchase and require network electricity, limiting the number and type of sites where they can be deployed. The flow-through sampler (FTS) presents an opportunity to overcome these limitations. The FTS is a wind-driven passive sampler that has been developed to quantify organic contaminants in remote ecosystems. FTSs differ from other passive samplers in that they turn into the wind and use the wind to draw air through the sampling media. The main objective of this work was to evaluate the FTS in a near-field pesticide vapour drift study by comparing the concentrations of pyrimethanil in air measured using one HVS and three FTSs placed in the same location. Pyrimethanil was sprayed onto the vineyard as part of normal pest management procedures. Air samples were collected every eight hours for 48 h. The volume of air sampled by the FTSs was calculated using the measured relationship between ambient wind speed and the wind speed inside the sampler as determined with a separate wind tunnel study. The FTSs sampled 1.8 to 40.5 m^3 of air during each 8-h sampling period, depending on wind speed, whereas the mean volume sampled by the HVS was 128.7 m^3. Pyrimethanil concentrations ranged from 0.4 to 3.2 $\mu g\ m^{-3}$ of air. Inter-sampler reproducibility, as represented by percent relative standard deviation, for the three FTSs was ~20%. The largest difference in FTS-derived versus HVS-derived pyrimethanil concentrations occurred during the lowest wind-speed period. During this period, it is likely that the FTS predominately acted like a traditional diffusion-based passive sampler. As indicated by both types of sampler, pyrimethanil concentrations in air changed by a factor of ~2 during the two days after spaying and these changes were not correlated with temperature or wind speed in a consistent way. This work shows that the FTS has good potential for use in near-field vapour drift studies and that FTS technology could make multi-sampler experimental designs more feasible.

INTRODUCTION

Pesticides are a common tool in modern crop management; however, they can adversely affect non-target organisms if they move off the target area, for instance, via vapour drift. Vapour drift occurs when volatilised (gas phase) pesticides are transported off the target area by the wind. Pesticide volatilisation and vapour drift from agricultural fields are often measured with active air samplers, such as high-volume air samplers (HVSs).[1-4] These samplers have high sampling capacity and are well established; however, they are also expensive to purchase and require network power to operate. Thus, sample design strategies that involve HVSs are limited by the number of samplers that can be used and where samplers can be placed. Without such limitations, large sampling schemes using multi-sampler grids or transects could be employed, enabling key questions about pesticide vapour drift to be better addressed. The flow-through sampler (FTS) (Figure 1) presents an opportunity to employ such sampling schemes. The FTS was recently developed by Xiao et al.[5-10] to measure the long-range transport of pesticides and other organic contaminants to remote areas. The FTS is a wind-driven passive sampler. It uses wind to force air through the sampling medium,[5] resulting in sampling rates comparable to some active samplers.[6] The FTS is relatively simple to construct, making it cheaper to build than a HVS and it does not require electricity.

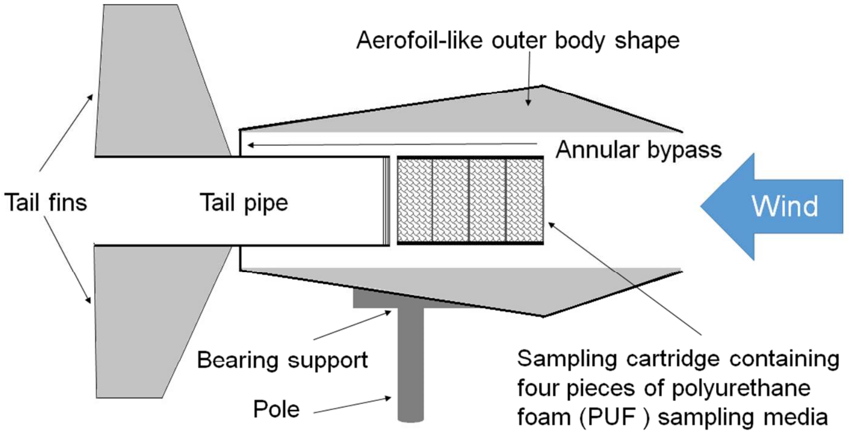

Figure 1. Cross-section of a flow-through sampler. (Image adapted from Xiao et al. 2009.[7])

The FTS sits on a bearing support on top of a pole. The bearing support and tail fins allow the sampler to act like a wind vane, turning into the wind. The body of the sampler is made of two layers of steel, the inner layer being straight while the outer layer is bent outwards to give the body an aerofoil shape that forces air through the sampler.[5] The design of the sampler creates a lower pressure zone in the tail pipe behind the sampling cartridge that helps draw air through the sampling media. The annular bypass (gaps between the tail pipe and the main body of the sampler) prevents eddies, which would block air from moving through the sampling media, from forming in front of the sampling cartridge. The sampling media must be composed of a material with low flow resistance and high up-take efficiency so that air will pass through it and the analytes will be retained. To meet these criteria, low density polyurethane foam (PUF) was used by the original designers and in this study.

Although a passive sampler, the FTS has significantly higher sampling rates than conventional diffusion-based passive samplers.[5] However, it depends on the wind for sample collection; hence, the mass of chemical collected fluctuates with wind speed.[5] The FTS was designed to sample long-range contaminant transport in remote areas using sampling periods of 14-30 days.[7] It has not been tested in short-term (hours per sample) studies at locations where contaminant concentrations are expected to be relatively high. This work examines whether the FTS is suitable for short sampling periods during near-field vapour drift studies by measuring pyrimethanil concentrations in air in a vineyard for two days after spraying.

Pyrimethanil is a fungicide used to treat several species of fungi[11, 12] in a range of fruit, vegetable, nut and ornamental crops.[11] One specific use is for the prevention and treatment of *Botrytris Cinerea* (grape grey mould) on wine grapes.[12] Pyrimethanil is considered only slightly toxic to most terrestrial organisms. For example, the LD_{50} for birds[13] is >2000 mg kg^{-1} and the 14-day acute LC_{50} for earthworms[13] is 313 mg kg^{-1}. Nonetheless, pyrimethanil is considered moderately persistent and moderately mobile in terrestrial environments.[13] Pyrimethanil is used preventatively and can be used on a wide range of crops; therefore, it has the potential to be commonly found in non-target environments. Pyrimethanil has not previously been the subject of a vapour drift study, but it is considered slightly volatile by the Australian Pesticides and Veterinary Medicines Authority (APVMA)[11] and has been measured in ambient air and in greenhouses.[14] The estimated vapour pressure[15] of pyrimethanil is 2.19×10^{-3} Pa and its 24-h cumulative percent volatilisation from soils is 2.5% (at a temperature of 15 °C, relative humidity of 100%, and fraction soil organic carbon of 2%) as calculated by the method of Davie-Martin et al.[16, 17] and using partition coefficients from EPISuite.[15]

In the present study, pyrimethanil concentrations in air were measured for 48 h after it was sprayed on wine grapes. The overarching objective was to test the FTS in a near-field vapour drift study so that its suitability for use in future large-scale grid or transect-type vapour drift studies could be assessed. However, valuable information about pesticide concentrations in air after spraying was also gained and in particular, the effects of temperature and wind were found to less influential than expected based on current understanding. The specific objectives of the study were to (1) compare the concentrations of pyrimethanil in air measured with three FTSs to those measured with a HVS, (2) determine inter-sampler variation between three FTSs operated at the same location, and (3) use meteorological data to understand the observed trends in pyrimethanil concentrations.

SAMPLING METHODS

Sampling Location and Pesticide Application

The field study was conducted in a commercial vineyard near the town of Blenheim, in the Marlborough Region of New Zealand. The Marlborough Region is located in the northeast corner of the South Island and is a major wine-growing area. The dominant land use around the study vineyard is viticulture. The vine height at the time of the study was ~1.5 m. On 9 December 2010 (austral summer), all three blocks of the vineyard (Figure 2) were sprayed with a mixture of *Scala* (pyrimethanil as active ingredient (a.i.); 920 g (a.i) ha^{-1}), *Prodigy* (methoxyfenozide as a.i.; 35.8 g (a.i) ha^{-1}) and *Systane* (myclobutanil as a.i.; 31 g (a.i) ha^{-1}) using a custom-made recapture-recycling sprayer (similar to the FMR R-Series sprayer, FMR Group, Blenheim, New Zealand). Both pyrimethanil and myclobutanil were originally included on the target analyte list; however, only pyrimethanil was detected in the field samples. Myclobutanil may not have been detected because its application rate was ~30 times less than that of pyrimethanil and it is considerably less volatile than pyrimethanil. Myclobutanil's estimated vapour pressure[15] is 2.13×10^{-4} Pa and its 24-h cumulative percent volatilisation from soils is 0.24% (at a temperature of 15 °C, relative humidity of 100%, and fraction soil organic carbon of 2%) as calculated by the method of Davie-Martin et al.[16, 17] and using partition coefficients from EPISuite.[15]

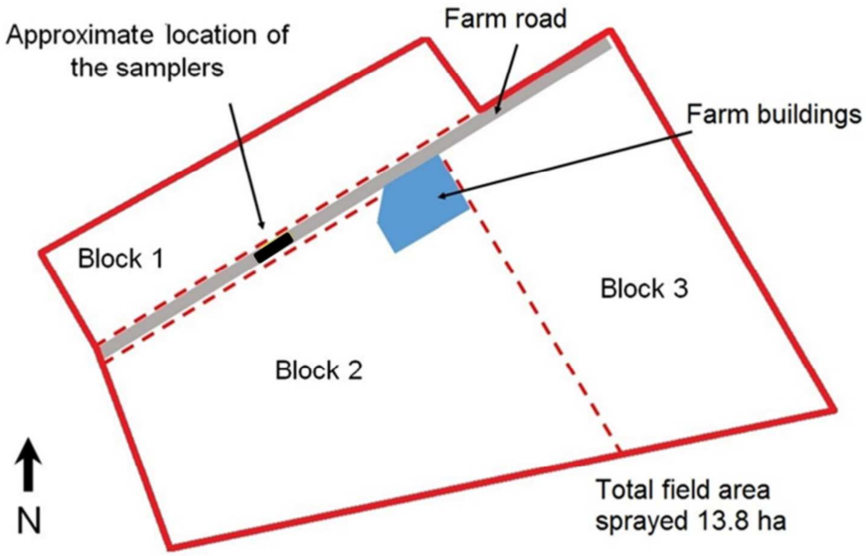

Figure 2. Diagram of the study vineyard, showing the location of the samplers within the three blocks of grape vines.

General Sampling Scheme

One HVS and three FTSs were positioned in a roughly southwest to northeast line between blocks 1 and 2 (Figure 2) ~100 m southwest of the nearest group of farm buildings and were aligned parallel to a row of vines (Figure 3). The FTSs and weather station were placed 2 m apart to minimise interference from each other. The HVS was placed 4 m from the weather station and 6 m from the nearest FTS (Figure 3). A background sample was collected 36 h before spraying using the HVS; the sample was collected, transported and analysed in the same way as the other HVS samples. The samplers were removed from their poles during spraying and stored inside a shed to prevent contamination with spray droplets. The blocks were sprayed in chronological order and the FTSs were deployed immediately after pesticide spraying on block 3 was completed. The vines closest to the samplers (block 1) were sprayed ~3 h before sampling started.

Figure 3. Photograph of the sampling site showing, from left to right, the three FTSs, the weather station and the HVS; photograph was taken the day before spraying and faces approximately north towards block 1 of the vineyard.

Six samples were collected with each sampler during the 48-h period after spraying; sampling cartridges were changed every 8 h. The exact sampling times, rounded to the nearest 5 min, were used to calculate the volume of air sampled and the subsequent mean concentration of pesticide in air during each sampling period.

Sampling with the High-Volume Air Sampler

PUF plugs for the HVS were obtained from Tisch Environmental Inc. (Village of Cleves, OH, USA). They were cleaned before deployment using pressurized liquid extraction (PLE) with an Accelerated Solvent Extractor system (Dionex, Sunnyvale, CA, USA) operated with hexane:acetone (75:25), a temperature of 100°C, a pressure of 1500 psi, static time of 5 min, 2 static cycles, a flush volume of 150% and a purge time of 240 s. The glass cartridges for the HVS were baked at 565 °C for 1.5 h to remove any contaminants, packed with cleaned PUF plugs, sealed in baked aluminium foil bags and finally, placed in clean plastic zip-lock bags for transport and storage.

The HVS used in this study was a PUF-3300BRL/230 Polyurethane Foam (PUF) Outdoor High Volume Air Sampler (HI-Q Environmental Products Company, San Diego CA, USA). The sampler has a height of ~1.4 m. The 51-mm diameter glass cartridges contained two PUF plugs in series; they were 2.5-cm (TE-1012) and 7.6-cm (TE-1010) in length, respectively. The 2.5-cm PUF plug was positioned downstream of the 7.6-cm plug and was used to determine breakthrough. The HVS was operated without a filter paper above the PUF so that the HVS set-up was consistent with that of the FTS. Breakthrough in HVS-PUF plugs was calculated using data from the first sampling period and was determined by extracting and analysing each piece of PUF separately and then dividing the mass of pyrimethanil in the second plug by the total mass in both plugs.

The HVS was calibrated at the start and end of the study using a 10.1-cm adaptor plate (HI-Q Environmental Products Company, San Diego CA, USA) and a digital manometer (Testo 511, Testo AG, Croydon South, VIC, Australia). The flow rate was set to 300 L min^{-1} at the start of each sampling period and the final flow rate was recorded at the end of each sampling period. The change in flow rate over time was assumed to be linear and the calculated air volumes were based on the average calibration-corrected flow rate for each sampling period.

Sampling with Flow-Through Samplers

FTSs require low density sampling media[5] so that air can pass through under ambient wind speeds. Xiao et al.[5] determined that PUF with a density of 0.4 pores per mm was the most effective sampling medium for the FTS.[5] Pre-cut and cleaned PUF disks are not commercially available for the FTS; therefore, sheets of PUF were purchased from a local foam supplier and cut to size. Sheets of 50-mm thick low-density (0.4 pores per mm) PUF (FilterPore reticulated open cell filter foam ME010) were purchased from Nexus Foams (Christchurch, New Zealand). Disks (93 mm in diameter) were cut from the sheets using a drill press and a customised drill attachment in the University of Otago Chemistry Department Workshops. The drill attachment was made from a sharpened section of the stainless steel pipe that was used to construct the sampling cartridge. This produced PUF disks that fit snugly into the sampling cartridges without being compressed or leaving gaps around the PUF through which air could bypass the sampling media.

The PUF disks were washed in soapy water and rinsed in tap and distilled water to remove bulk contaminants associated with their manufacture. Once dry, the PUF disks were cleaned using PLE operated at room temperature (actual operating temperature 20-27°C) with 100% hexane. PLE was conducted with a pressure of 1500 psi, static time of 5 min, 2 static cycles, flush volume of 60% and a purge time of 240 s. This temperature and solvent combination was chosen because higher temperatures and other solvent combinations damaged or distorted the PUF disks. Once dry, four clean PUF disks were loaded into each FTS cylindrical cartridge in series and sealed (Figure 1). The cartridges were then placed in large plastic zip-lock bags for storage and transport.

The FTSs used in this study were constructed by the University of Otago Chemistry Department Workshops according to specifications described in Xiao et al.[5, 6] The FTSs were constructed from stainless steel and mounted on 2.4-m high steel poles, which had a bearing mounted at the top to allow the samplers to turn through 360°. Steel fencing stakes were used to hold the samplers in place. The stakes were driven into the ground and then the sampler poles were attached to them with a series of cable-ties. When deployed in the field, the centre of the body of the samplers sat ~1 m higher than the top of the vines (Figure 3).

Cylindrical sample cartridges (200 mm in length x 93 mm in internal diameter) that held the PUF were constructed from the same stainless steel pipe as that was used for the tail pipe of the sampler (Figure 1). A screw thread at each end of the cartridge was used to attach the cartridge to the sampler, and to fit the screw caps to the cartridge. The caps were composed of a stainless steel ring with a screw thread and a removable Teflon disk. To remove contaminants associated with their manufacture, all parts of the FTS cartridges and caps were washed in soapy water, rinsed in tap and distilled water and then solvent rinsed with HPLC-grade methanol (Thermo Fisher Scientific, Scoresby, Victoria, Australia), ethyl acetate (Thermo Fisher Scientific, Scoresby, Victoria, Australia) and hexane (Merck, Manukau City, New Zealand). Breakthrough in FTS-PUF plugs was determined from one of the samples taken during the first sampling period and was determined by extracting and analysing each of the four pieces of PUF in the sample separately and then dividing the mass of pesticide in the back piece by the total mass of pyrimethanil in the sample.

Flow-Through Sampler Calibration and Calculation of the Volume of Air Sampled

The volume of air sampled by the FTS was calculated from equation 1.[5]

$$V = U_{\text{inside}} \cdot \pi r^2 \cdot t \qquad (1)$$

where V is the volume of air sampled (m^3); U_{inside} is the wind speed inside the sampler (m s^{-1}); r is the radius of the sampler's tail pipe (0.0465 m); and t is the sampling period of each ambient wind speed measurement (300 s). Wind speed measurements taken in the field were logged as 5-min averages; therefore the sample volumes were calculated in 5-min blocks and summed to obtain the volume sampled during each 8-h sampling period.

For calibration, an FTS was placed in a wind tunnel at the University of Otago Physics Department and a rotary turbine anemometer (AVM-03, RS Components, Auckland, New Zealand) was fixed at the back of the tail pipe, flush with the end of the tail pipe. The tail pipe was then extended around the anemometer using a reinforced paper tube to prevent eddies forming around the anemometer and interfering with the readings. The wind tunnel was set to different wind speed settings and the wind speed inside the FTS was measured 50 times at each setting. The rotary turbine anemometer gave a wind speed reading approximately every 5-s. When these measurements were complete, the FTS was removed and the anemometer from the weather station was installed in the centre of the wind tunnel at the same height as the centre of the FTS. Wind speed measurements were obtained with the weather station anemometer 15 times at each of the wind speed settings used to measure the inside wind speed. The weather station anemometer took a reading every 45 s and produced average wind speeds over each 5-min period.

Transport and Storage of Samples and Field Blanks

The HVS and FTS sampling cartridges were prepared in the laboratory, sealed and then transported to the field at ambient temperature. After the samples were collected, the cartridges were placed in insulated containers and packed with ice-packs to prevent volatilisation of pyrimethanil until they were returned to the laboratory. All samples were stored in the dark at -19 °C in the laboratory until being processed.

Field blanks were collected at the start and end of the study and at the start of the fourth sampling period. Field blanks were collected for both types of sampler by inserting a sampling cartridge into the sampler as though it were a new sample, waiting one minute and then removing the cartridge. The HVS was turned off during the blank sample collection. Field blanks were prepared, transported, stored and processed in the same way as the samples.

Weather Station Measurements

An Aercus Instruments WS2083 Professional Wireless weather station (Scientific Sales, Auckland, New Zealand) was mounted at the same height as the FTSs. It recorded temperature, wind speed and direction, maximum gust, rainfall and relative humidity. The weather station took readings every 45 s and logged the average (or maximum for maximum wind gust) values over each 5-min period.

PYRIMETHANIL QUANTIFICATION METHODS

Chemicals

A pestanal® grade pesticide standard of pyrimethanil was purchased from Sigma-Aldrich (Auckland, New Zealand). SupraSolv® grade acetone, hexane, and methanol were purchased from Merck (Manukau City, New Zealand). Alumina (aluminium oxide) (grade 90 standardised, CAS 1344-28-1) was purchased from Merck. Florisil® (magnesium silicate) (100-200 mesh, CAS 1343-88-0) was purchased from Sigma-Aldridge (Auckland, New Zealand). Isotopically labelled standards (d14-trifluralin and d6-*alpha*-HCH), which were used as internal standards, were purchased from CDN Isotopes (Pointe-Claire, Quebec, Canada).

Quantification of Pyrimethanil in PUF from High-Volume Air Samplers

Pyrimethanil was extracted from the HVS-PUF plugs using PLE. The method was based on a previously described method[18] although in the present study, no surrogate labelled compounds were injected before extraction and no recovery correction was performed. PUF plugs were packed into 33-ml extraction cells and extracted using hexane:acetone (75:25), a temperature of 100°C, a pressure of 1500 psi, static time of 5 min, 2 static cycles, a flush volume of 150%, and a purge time of 240 s. Extracts were then solvent exchanged into ethyl acetate and reduced to 300 μl at 30°C using a TurboVap II (Alphatech Systems, Auckland, New Zealand). The extracts were diluted by 10 times and then spiked with an isotopically labelled internal standard solution (500 ng μl^{-1} d_{14}-trifluralin and d_6-*alpha*-HCH) before analysis with GC-MS to monitor fluctuations in instrument response.

The samples were analysed using an Agilent 6890N gas chromatograph (Santa Clara, CA, USA) paired with an Agilent 5975B mass selective detector (GC-MS), which was operated with an electron impact (EI) source in selective ion monitoring (SIM) mode. Analytes were separated using a 30-m TG-5ms (0.25 mm ID, 0.25 μm film) fused silica capillary column (Thermo Scientific, North Shore City, New Zealand). The GC-MS was operated with an inlet temperature of 265 °C and an interface temperature of 280 °C. The oven temperature program started at 50 °C, was held for 1 min, ramped at 25 °C min^{-1} to 170 °C, ramped at 5 °C min^{-1} to 210 °C, held for 5 min, ramped at 50 °C min^{-1} to 310 °C and held for 2 min. The extracts were quantified using an external 6-point calibration curve with a range from 5 ng μl^{-1} to 50 ng μl^{-1} made in ethyl acetate. Spike and recovery experiments indicated that the recovery of spiked pyrimethanil from HVS-PUF was 97% with a percent relative deviation (%RSD) of 8% (*n* = 3).[19]

Quantification of Pyrimethanil in PUF from Flow-Through Samplers

Pyrimethanil was extracted from FTS-PUF disks using the same PLE general settings described above. However, because the total volume of FTS-PUF was much larger, each individual FTS-PUF disk (four per sampling cartridge) was packed into a separate 100-ml extraction cells and a lower flush volume (120% instead of 150%) was used to prevent collection bottles from overfilling. Also, because the FTS-PUF was purchased from a local supplier, it contained unexpected fabric dyes and other matrix compounds. Thus, extracts required more clean-up than those obtained from HVS-PUF. The general approach for the additional clean-up involved adding matrix-sorbing materials (Florisil and alumina) to the extraction cells (i.e., in-cell clean-up), dissolving extracts into water, and then using solid-phase microextraction (SPME). The mean recovery of pyrimethanil from spiked FTS-PUF samples was 80% with a %RSD of 8% (*n* =3). Details regarding the development and validation of this method are described elsewhere.[19]

Each extraction cell contained, from top to bottom (in the order of solvent flow through the cell), one glass fibre filter paper (Microanalytrix, Auckland, New Zealand), acid-washed sand to fill the void volume, one PUF disk, another glass fibre filter paper, 12 g of Florisil, 30 g of alumina and a third glass fibre filter paper. The four extracts from the four PUFs composing each sample were combined in a TurboVap tube and reduced to 400±100 µl at 30 °C. The extract was then transferred to a pre-weighed 4-ml vial (measured capacity 4.8 ml). The vial was weighed again and then 4200 µl of distilled water was added. The samples were refrigerated for at least 18 h at 4 °C and then vortexed for 10 s before a 50-µl subsample was removed and added to 10 ml of distilled water in a 10-ml auto-SPME vial (measured capacity 11.5 ml). Finally, 5 µl of the internal standard solution described above was added.

Quantification was conducted with immersion-SPME-GC-MS with 50/30-µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) SPME fibres (Sigma-Aldrich, Auckland, New Zealand). The sample used for breakthrough analysis was analysed on the same GC-MS as that used for the HVS-PUF analysis using manual injections. The remainder of the samples were analysed with a second GC-MS that was paired with a SPME autosampler. The same column (Zephron 50 m DB 5ms column) (Phenomenex, North Shore City, New Zealand) was installed on both instruments and the same SPME parameters (see below) were used for both manual and autosampler analyses.

The SPME-autosampler GC-MS system was an Agilent 7890A gas chromatograph operated with a CTC Analytics PAL system autosampler and an Agilent 5975C inert XL mass selective detector with triple axis detector under the control of enhanced Chemstation software. SPME extraction was conducted by pre-heating the sample at 60±1 °C for 10 min and then exposing the fibre to the sample for 60 min at 60±1 °C with agitation. The GC-MS was operated with an inlet temperature of 265 °C, an interface temperature of 280 °C, and a fibre desorption time of 5 min. The oven temperature program started at 50 °C, was held for 5 min, ramped at 30 °C min^{-1} to 190 °C, ramped at 5 °C min^{-1} to 250 °C, held for 3 min, ramped at 50 °C min^{-1} to 310 °C, and held for 10 min.

Stock solutions of the pesticide standards were made in methanol (rather than ethyl acetate, which was used for HVS-PUF analysis) for compatibility with the SPME fibre. Calibration standards were made in distilled water in 10-ml auto-SPME vials and contained 5 µl of acetone (which was used as a surrogate for the small amount of solvent in the extracts that originated from the PLE extraction) and spiked with 5 µl of internal standard solution. The extracts were quantified using a 7-point external calibration curve with a range of 5 pg μl^{-1} to 175 pg μl^{-1}.

Before their first use, SPME fibres were conditioned for 60 min at 270 °C (the maximum recommended operating temperature). They were also cleaned for 30 min at the start of each day and for 20 min between samples at 265 °C. A cooler temperature was used for regular cleaning to minimise degradation of the fibre. In addition, a cleaning blank was run between sample sets (e.g. all samples taken during the same sampling period) to prevent carry-over on the SPME fibre. The cleaning blank contained 10 ml of 50:50 acetone:methanol and was run using the same extraction and analysis method as the samples.

Quality Control and Method Detection Limits

Laboratory blanks were taken at several stages during analysis to check for cross-contamination. Because pyrimethanil was not detected in any field or laboratory blank samples, no corrections to measured concentrations were made. Quality control standards were run between each set of three samples and one cleaning blank. The calibration curve was re-run when the calculated pyrimethanil concentration in the quality control standard exceeded 30% of the true concentration. Method detection limits for both methods were calculated using the method described in the United States Environmental Protection Agency (EPA) Method 8280A.[20]

RESULTS & DISCUSSION

Meteorological Conditions

Mean temperature, wind speed, wind direction, rainfall and relative humidity data were logged and averaged over 5-min periods for each sampling period; select data is shown in Figure 4 and Table 1. Overall, the temperature ranged from 7.2 to 29.0 °C and the wind speed ranged from 0 to 6.8 m s^{-1} but rarely exceed 6 m s^{-1}. No rain was recorded during the study although it had rained the day before the first sampling period. The dominant wind patterns in the study area are onshore easterlies and warm northwesterlies. Easterly winds were predominant on the first day of the study and then northwesterlies predominated for the remainder of the study.

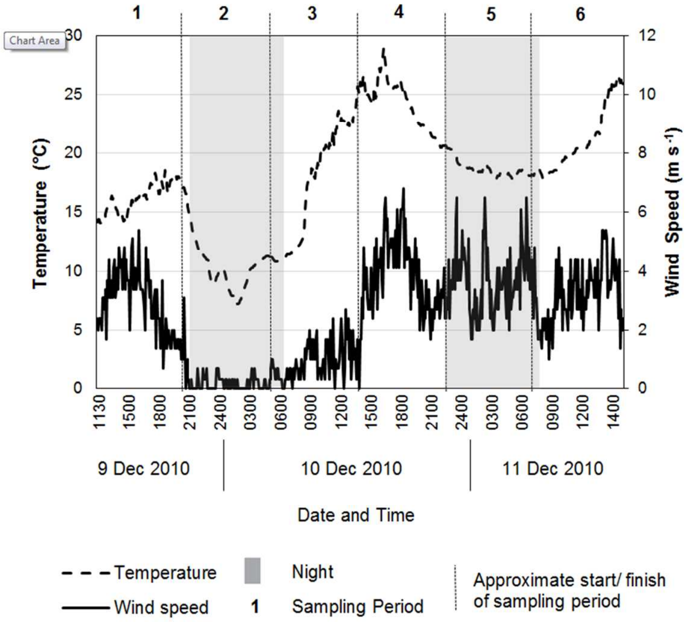

Figure 4. Wind speed and temperature data recorded as 5-min averages over the full study period.

Table 1. Meteorological conditions during each sampling period

Sampling Period		**1**	**2**	**3**	**4**	**5**	**6**
Temperature (°C)	Mean	16.3	10.4	18.0	24.9	19.0	21.2
	Range	14.1 - 18.6	7.2 - 16.2	10.8 - 26.1	20.4 - 29.0	17.8 - 20.3	17.9 - 26.7
Wind speed (m s^{-1})	Mean	2.9	0.2	1.0	3.9	3.7	3.2
	Range	0.4 - 5.4	0 – 1.0	0 – 3.1	1.7 – 6.8	1.7 – 6.5	1.0 – 5.4
Relative humidity, mean (%)		58.4	89.9	66.0	25.3	50.7	66.3

Flow-through Sampler Calibration and Volumes of Air Sampled

A calibration curve depicting the relationship between inside and ambient (outside) wind speeds (Figure 5) was created from data obtained using the wind tunnel. The best relationship between the points was obtained using a polynomial curve forced through the origin (equation 2).

$$U_{\text{inside}} = 0.0025 \cdot U_{\text{ambient}}^{2} + 0.0439 \cdot U_{\text{ambient}} \qquad R^2 = 0.995 \qquad (2)$$

where U_{inside} is the wind speed inside the tail pipe of the FTS and U_{ambient} is the ambient wind speed measured by the weather station inside the wind tunnel. The calibration curve obtained with our FTS sampler was similar, but had a lower slope, than that obtained with the lab study conducted by Xiao et al. (2007),[5] highlighting the importance of calibration for new samplers. However, because the shape and size of the sampler we constructed was very similar to that constructed by Xiao et al., differences are most likely due to differences in the PUF used.

It should be noted that the inside wind speeds shown in Figure 5 represent the maximum speeds that can be obtained for a given ambient wind speed because in the field, the FTS may not always be perfectly aligned with wind direction. This issue was thoroughly investigated by Xiao et al. (2008)[6] and they determined that, for their FTS, the influence of changing wind directions can be ignored above wind speeds of 5 m s^{-1}. Most of the ambient wind speeds measured in our study were below 5 m s^{-1} (Figure 4) and were in the extrapolated range of our calibration curve (Figure 5); however, wind direction was relatively constant during each of our sampling periods and this would have reduced error associated with samplers not facing into the wind. The ideal approach for calculating air sample volumes would involve logging inside wind speeds during sampling; however, high quality anemometers that can measure and log very low wind speeds in the field are very expensive (much more so than the weather station used in this study). Since an anemometer would be required for each sampler, this approach would diminish the usefulness of FTSs.

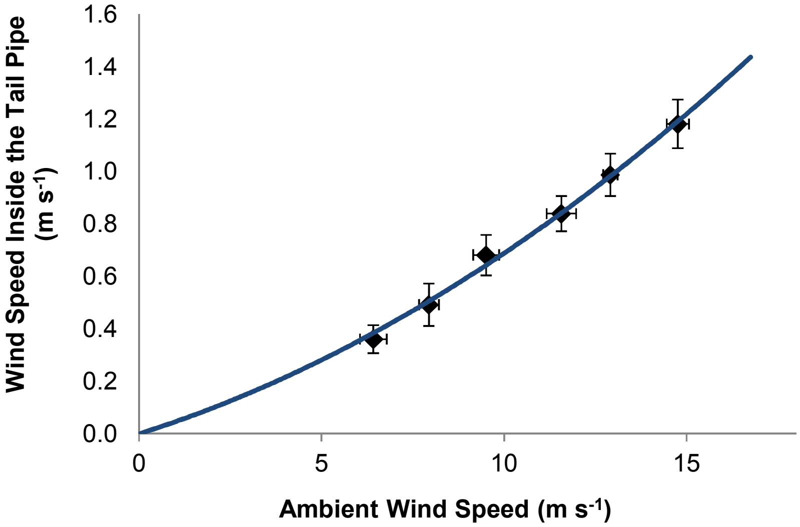

Figure 5. Calibration curve used to represent the relationship between the maximum wind speed inside the tail pipe of the FTS sampler and the ambient wind speed. Error bars represent ±1 standard deviation of the measured wind speeds (n = 50 measurements for each inside wind speed and n = 15 for each ambient wind speed).

The volume of air sampled by each sampler during each field sampling period was calculated using equation 1. The calculated volumes of air sampled by the HVS and FTSs are shown in Table 2.

Table 2. Volumes of air sampled during each 8-h sampling period

Air volume sampled (m^3)						
Sampling Period	1	2	3	4	5	6
HVS	129.7	127.3	121.3	136.9	130.9	126.1
FTS	30.5	1.8	9.0	40.5	39.1	32.9

The variation in the air volumes sampled by the FTS was due to varying wind speeds during the study and is an important characteristic of this wind-driven passive sampler. The relatively minor variations in the HVS air volumes sampled was caused by normal variation in the pump performance.

Breakthrough and Method Detection Limits

The calculated breakthrough for the HVS was 0% because no pyrimethanil was detected in any of the 2.5-cm PUF plugs. The breakthrough for the FTS was 0.8%, which was deemed acceptable and no corrections to measured concentrations were made. The method detection limits for pyrimethanil were 388 pg m^{-3} for the HVS and 27 pg m^{-3} for the FTS. The method detection limit for the FTS was lower than that for the HVS because the FTS samples were analysed with SPME, which concentrated the analytes from the PLE extract. This result demonstrates the power of SPME; however, the SPME method described herein required considerably more effort than the one used for the HVS-PUF so is only recommended when very low detection limits and/or special clean-up is needed.

Masses of Pyrimethanil Collected by FTSs During Different Sampling Periods

The masses of pyrimethanil collected during each sampling period are shown in Figure 6. These values changed significantly during the study due to a combination of changing ambient wind speeds and changing pyrimethanil concentrations in air. The variability, expressed as %RSD, in collected mass between the three samplers for a given sample period ranged from 15% to 28%, with a mean value of 20%. The variability due to the analytical method was 8% (as determined from repeated spike and recovery experiments) and therefore ~12% of this variability was due to differences in collection efficiency between the three samplers. Some of this difference could be due to samplers not facing into the wind at exactly the same angle; i.e this would cause different volumes of air to be sampled. Quantification of inter-sampler variability is useful because it affects the degree to which trends in chemical concentrations over time or space can be discerned with these samplers. The lack of correlation between wind speed and mass collected at the end of the study may have been due to the source material becoming depleted, i.e. a significant proportion of the sprayed pyrimethanil had likely volatilised, degraded, or been absorbed into the plant tissues by the end of the study period.

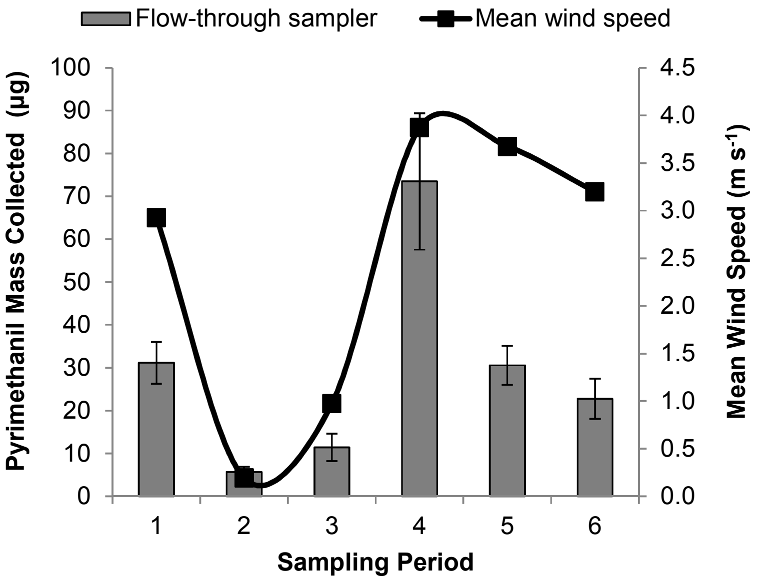

Figure 6. Masses of pyrimethanil collected by the FTSs and mean ambient wind speeds during each sampling period. Error bars indicate ±1 standard deviation of the mean mass of pyrimethanil collected by each of the three FTSs during each sampling period.

Pyrimethanil Concentrations in Air

The overall range for the mean calculated concentrations of pyrimethanil in air for both types of sampler ranged from 0.4 µg m^{-3} to 3.2 µg m^{-3} (Figure 7). Thus, even the highest measured values were more than 1000 times below the occupational exposure limit (time weighted average) for this pesticide (5.3 mg m^{-3})[21] and we can conclude that pyrimethanil vapour drift is unlikely to harm farmworkers exposed to it after spraying. This is mainly due to its low toxicity combined with relatively low volatilisation potential. Although not the focus of the present study, it should also be noted that the total mass of pyrimethanil landing on target plants during spraying was likely lower than normal due to the use of the recapture-recycling sprayer, which was designed to collect and re-use droplets in the air during spraying.

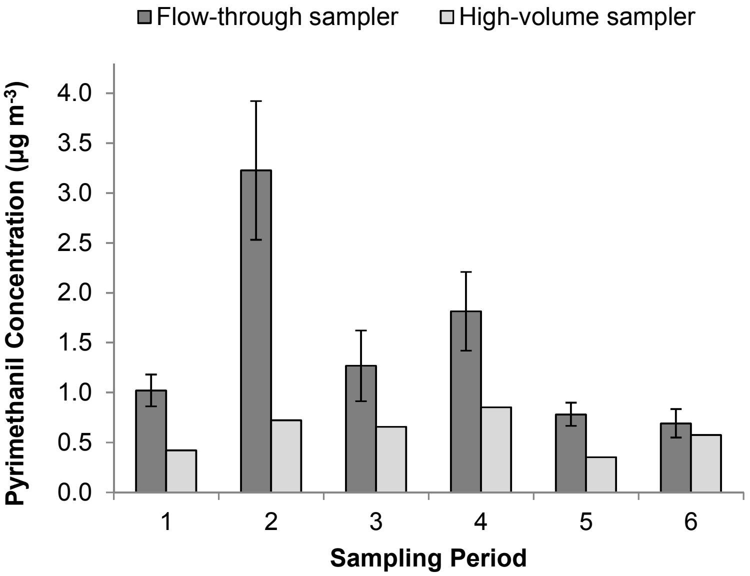

Figure 7. Concentrations of pyrimethanil in air as derived from FTS and HVS data. Error bars indicate ±1 standard deviation of the mean concentration calculated for the three FTSs.

No other studies were identified that have reported pyrimethanil concentrations in air near sprayed fields. However, pyrimethanil has been measured in the air inside greenhouses[14] and in the particulate matter (PM10) fraction of ambient air.[22] The range of concentrations measured in the present study was ~10 times lower than that measured in greenhouses (3.2 to 27 µg m^{-3} between 1 h and 4 days after spraying).[14] However, pesticide concentrations in the air inside greenhouses are expected to be higher than those measured over open fields because the greenhouse structure limits pesticide dispersion in the atmosphere.[14]

Comparison of Concentrations Derived from HVS and FTS Data

The mean pyrimethanil concentrations derived from the FTS data were higher than the HVS-derived ones in all sampling periods (Figure 7). If period 2 is considered separately, mean FTS-derived pyrimethanil concentrations ranged from being 1.2 to 2.4 higher than those derived with the HVS; for period 2, they were 4.6 times higher. As noted earlier, the calibration curve we used for determining inside wind speeds (Figure 5) gives maximum values; however, this is not the source of the observed discrepancy because lower inside wind speeds would result in even higher FTS-derived concentrations. FTS- to HVS-derived concentration ratios commonly exceed a factor of 2, or much more, in the studies conducted by Xiao et al.[5-7] and they have discussed several potential contributing factors. For example, in some studies,[6, 7] 24-h HVS samples were taken at random intervals during 14-day FTS sampling periods. They suggested that the discrepancy between the samplers was related to the timing of the HVS sample periods or the fact that they were not continuous. This explanation, however, does not apply to our study because the two types of sampler were operated in parallel. Another reason for discrepancies that was discussed by Xiao et al. is that atmospheric conditions affect each type of sampler differently[6, 7] and in particular, that sample collection with the FTS was biased towards sampling periods with higher wind speeds during.[7] This could explain discrepancies during some sampling periods in our study but not sampling period 2 when the wind speed was very low.

In our study, the HVS and FTS samplers were positioned at different heights and the micrometeorology of the field could have resulted in different air concentrations at each height. The top of the sampling cartridge in the HVS was ~1.4 m above the ground whereas the centre of the FTS was positioned ~2.6 m from the ground. Thus, the FTS was above the top of the grape vines whereas the HVS was below and this could have contributed to observed differences.

Another explanation may be related to the fact that FTS sampling occurs both via wind-driven active sampling and diffusion-based passive sampling. The pyrimethanil concentrations presented in Figure 7 were calculated using the assumption that the FTS behaved solely like an active sampler, with sampled air volumes sampled being calculated from wind speeds only. However, the FTS can also act like a traditional passive sampler, collecting analytes by diffusion. Diffusive-based sampling could become important during periods of very low or no wind. This effect could have resulted in the sampled air volumes being underestimated and therefore the concentrations being overestimated, especially during low wind periods. In previous reports,[23, 24] investigators have estimated that traditional polyurethane foam passive samplers sample the equivalent of 1.8 - 9.3 m^3 day^{-1} (mean 3.9 ± 1.9 m^3 day^{-1}, $n = 32$) or 0.6 - 3.1 m^3 (mean 1.3 ± 0.6 m^3) per 8-h sampling period, depending on the chemical analysed. Figure 8 shows the concentrations of pyrimethanil in air when recalculated using the assumption that the equivalent of an additional 1.3 m^3 of air was sampled during each sampling period via the passive sampling effect described above.

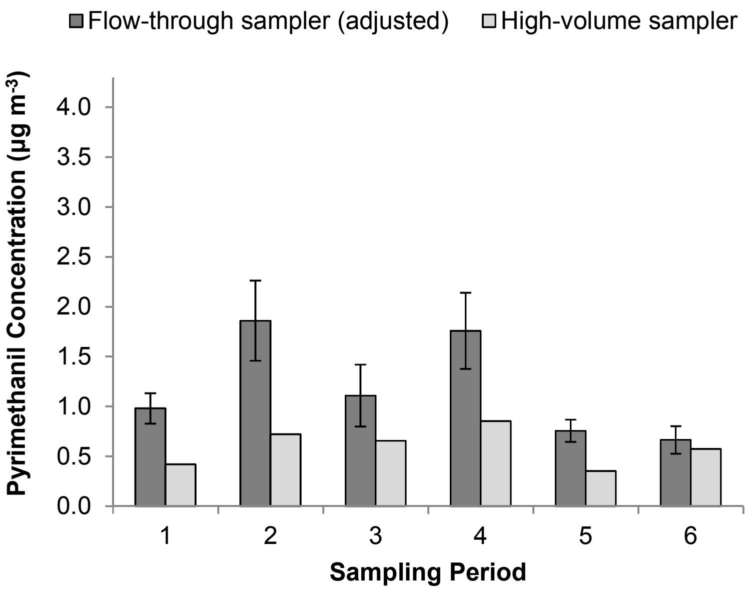

Figure 8. Concentrations of pyrimethanil in air as derived from FTS and HVS data. FTS-derived concentrations were adjusted to account for a passive sampling effect of 1.3 m^3 per 8-h sampling period. Error bars indicate ±1 standard deviation of the mean concentration calculated for the three FTSs.

Figure 8 shows that the difference between FTS- and HVS-derived concentrations for sampling period 2 is greatly reduced (from a concentration ratio of 4.5 to 2.6) when the passive sampling effect is considered. On the other hand, adding 1.3 m^3 of sampled air to the volumes in the other periods had little effect on their calculated concentrations (compare Figures 7 and 8) due to the relatively high wind-based sampling volumes for these sampling periods (Table 2). Even with the passive sampling effect, the FTS-derived concentrations were 2 times higher, on average, than the HVS-derived concentrations. The passive sampling volume may be several times larger than that we used herein, especially because FTSs have larger surface areas and shorter travel distances than traditional passive samplers; thus, more work in this area is needed. However, an additional 45 m^3 of sampled air would be needed to make the FTS-derived concentration equivalent to the HVS-derived concentration in sampling period 1; thus, passive sampling is not entirely responsible for the remaining discrepancy.

<u>Inter-Sampler Variability for Three Co-Located FTSs</u>

It is not common practise to use multiple samplers at the same location during vapour drift or air monitoring studies so there is little reported data about inter-sampler variation that we can use for comparison. Xiao et al. have not reported inter-sampler variation for FTSs; [5-7] however, Cessna et al.[25] calculated the reproducibility for duplicate HVS samples using 40 paired samples. They used percent variability (i.e., the difference between the maximum and minimum concentrations divided the mean and multiplied by 100) to describe the inter-sampler variation.[25]

Two-thirds of the samples from Cessna et al.[25] had a percent variability of <25% and 90% of their samples had a percent variability of <100%.[25] In our study, the percent variability ranged from 27 to 56%, depending on sample period. Thus, this range was somewhat higher than that calculated for HVS by Cessna et al. but the occasional high variability reported by Cessna et al. [25] was also not observed. The variability, as expressed by %RSD, in the concentrations that we report (Figures 7 and 8) is the same as that for the masses measured in the three FTSs (Figure 6) because concentration is mass divided by volume and the volume of air sampled by the three samplers was the same (only a negligible difference was present and it was due to slightly different sampling lengths).

Understanding Observed Trends in Pyrimethanil Concentrations in Air

To investigate the relationship between concentration, temperature and wind speed in the present study, each of these values were normalised to those measured in the first sampling period (Figure 9). Pyrimethanil concentrations only changed by a factor of ~2 during the study and were similar at the end and beginning of the study. In contrast, trends in temperature, and especially wind speed, were more distinct, with both dropping to their lowest levels during sampling period 2. In previous reports, the concentration of volatilised pesticides in air after spray events has been positively correlated with temperature.[26] This was not the case in the present study. However, wind can also play an important role in affecting pesticides and is often described as the major driver of volatilisation processes (evaporation and sublimation).[26, 27] Wind speed affects the distribution and dilution of chemicals in the atmosphere and therefore affects the atmospheric concentration of those chemicals.[6] Thus, the relatively high pyrimethanil concentration observed during sampling period 2 was likely caused by near-still conditions creating an inversion layer and trapping volatilised pyrimethanil near the ground. The amount of pyrimethanil volatilised during this time may have been relatively small but it remained in the field area close to the ground because there was little wind to move it off the field or turbulence to dilute it by vertical mixing.[6, 28, 29] This is an important result because it indicates that concentrations of pesticides volatilised from sprayed fields can be higher than expected during relatively cool, calm conditions.

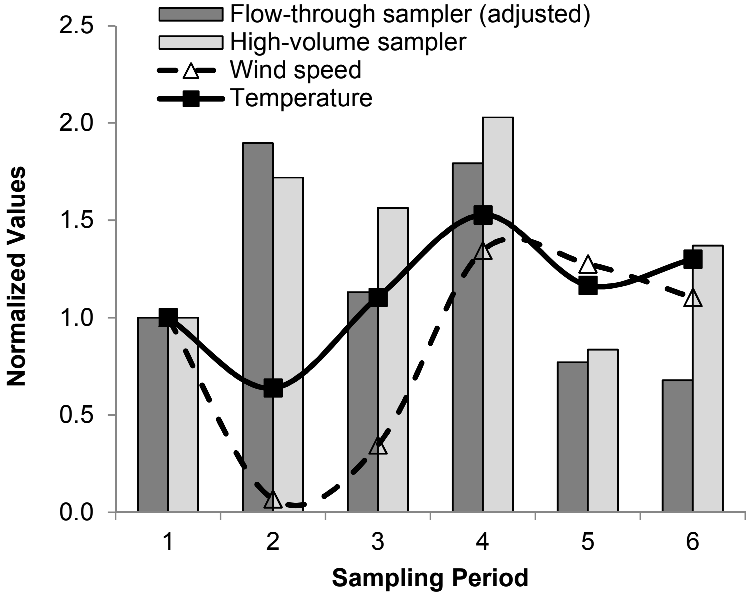

Figure 9. Comparison of values normalized to the first sampling period for FTS-derived concentrations (adjusted for passive sampling effect), HVS-derived concentrations and the mean wind speeds and temperature for each sampling period.

CONCLUSIONS AND RECOMMENDATIONS

This work showed that there is good potential for FTS technology to be used for studies involving short sampling periods when target analyte concentrations are high enough for detection. In particular, FTSs may prove useful for addressing key questions about pesticide drift where sampler grids or transects are needed. For three FTSs situated side-by-side, the variability in derived concentrations was ~20% (%RSD). The quantitation of pesticide concentration in air with FTSs requires accurate determination of inside wind speeds during sampling. This is particularly difficult at low wind speeds and it is more likely that low wind speeds will dominant a particular sampling period when sampling periods are short. Thus, simple yet inexpensive methods for quantifying the relationship between ambient and inside wind speeds are needed if FTS is to become commonly employed.

We found that although FTS-derived concentrations were generally ~2 times larger than those derived from HVS data, this ratio was twice as high during a sampling period when wind speeds were particularly low (mean of 0.2 m s^{-1}). When an adjustment was made to incorporate the effects of passive sampling, the ratio between FTS- and HVS-derived concentrations was significantly reduced during the low-wind sampling period. Thus, further work towards understanding and quantifying the effects of passive sampling on FTS sampling rates may be useful.

An important additional finding of this work was that the highest concentrations of pesticide in the air did not coincide with periods of high temperature, as is the current expectation. This finding could influence decisions about the acceptable time to wait between spraying and re-entering a sprayed field if still or inversion conditions occur within 48 h of spraying.

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