



Envirolink

Spray Drift Monitoring Systems

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EXECUTIVE SUMMARY

Lincoln Agritech Limited (LAL) has conducted a review of technologies available for establishing a Spray Drift Monitoring Programme for the Marlborough District Council in New Zealand (MDC). This document presents an overview of those technologies and suggestions for future research that could develop a viable solution. At present, the only systems scientifically validated by peer-reviewed literature for long-term spray drift monitoring, as required by the MDC Air Quality Plan, are high-volume air samplers. Recommended hardware systems and operating procedures are presented.

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1. REVIEW OF PESTICIDE AIR SAMPLING PROGRAMMES

The objective of this project is to provide recommendations to the Marlborough District Council on scientifically proven accurate measurements to measure the concentrations of pesticides in the air, in order to determine if they pose a significant risk to humans.

1.1 Current Air Sampling Programmes

There were three continuous multi-year programmes that are currently running that could be found: in the state of California in the United States, in Canada, and in France.

1.1.1 California

The first monitoring started in 1986. A key milestone was the Parlier study in 2006, which was a year-long study that monitored air at three locations around the town, taking samples 3 days each week. The key finding from the Parlier study was “It is likely that sampling at one location in each community, one day each week, will provide adequate data to characterise seasonal and long-term exposure.”

The California Department of Pesticide Regulation (DPR) established the nation’s first Air Monitoring Network to sample community air for pesticides in 2011. The goals are:

- Identify common pesticides in the air and determine seasonal annual and multi-year concentrations
- Compare concentrations to sub-chronic and chronic screening levels
- Track trends over time
- Estimate cumulative exposure to multiple pesticides
- Correlate concentrations with use and weather patterns

The Air Program collects one 24-hour sample each week in each community. Based on the Parlier study, this provides enough data to estimate long-term concentrations.

Currently, the (DPR) and California Air Resources Board (CARB) monitor 40 chemicals (35 pesticides + 5 breakdown products), sampling one day per week.

Other features and findings from the California studies:

- Public buildings such as schools and fire stations were selected as monitoring sites. Samplers typically placed on roofs of buildings for security.
- Flow rates from 1-65 L/min. 24 hour samples.
- Greatest potential health risk not from pesticides but from other air pollutants.
- All levels below screening levels.
- Samples were immediately placed on dry ice after collection. Samples had 28 day storage stability.
- Some chemicals may come from both agricultural and non-agricultural sources.
- In investigating complaints of drift, California DPR will take material wiped from surfaces such as cars or windows for analysis to detect drift, as well as air, water, or soil samples.

1.1.2 Canada

The Centre for Atmospheric Research Experiments (CARE) based in Ontario conducted air monitoring for agricultural pesticides. Atmospheric samples were collected at eight locations across the country - six agricultural sites, one receptor site, and one urban site). They used high-volume air samplers (250 LPM¹) from Tisch, collecting samples either for 1 day (24 hour) exposures, resulting in a 372 m³ sampling volume, or 1 week exposures, resulting in a 2500 m³ sample volume. Gaseous compounds were collected with polyurethane foam (PUF)/XAD-2/PUF sandwiches, while particulates were trapped on glass fibre filters (GFF).

1.1.3 France

There have been a few studies across Europe, but the work in France has the most sites and longest terms of studies. European research on pesticides in air is best documented in the papers of Yusa, Coscolla, and co-workers from Spain (e.g.: Lopez et al., 2017). In France rural areas the Official Air Quality Monitoring Associations

¹ litres per minute

(AASQA) has conducted monitoring campaigns on pesticides in the air since 2001. The main French agricultural regions have been monitored. Some of the key features are:

- More than 100 sampling sites in 16 regions, mostly in urban and suburban areas, and in rural places surrounded by cereals or vine, both representing the major French crops.
- Active air samplers use filter followed by solid absorbent, so that both gaseous and particular phases are collected and analysed together by liquid and/or gas chromatography equipped.
- Both low-volume ($1 \text{ m}^3/\text{h} = 16.7 \text{ LPM}$) and high-volume samplers ($13\text{-}40 \text{ m}^3/\text{h} = 220\text{-}667 \text{ LPM}$) were used.
- Pesticides in the atmosphere were in concentrations from 0.1 pg/m^3 to 10 ng/m^3 .

1.2 Historical Air Sampling Programmes

In addition to the three long-term studies in the previous section, there has been occasional monitoring in other countries as well.

1.2.1 Washington State, United States

A series of air monitoring studies were conducted in the mid-to-late 2000's. 24-hour samples taken every other day for 28 days during peak use, later every 3rd day for 60 days. Air samplers were used with a range of flow rates from 2 to 25 LPM. Samplers were located within 100 m of orchards likely to be sprayed and at 2 m above ground level, and they were secured, fenced or locked, daily access for staff, low foot traffic.

Washington State also monitors pesticide-related illness reported to medical authorities, including those caused by spray drift, and this is an on-going project since 2000. Data are available in reports from 2008 and 2013.

1.2.2 Australia

A previous experiment in Australia for 23 weeks coinciding with aerial spraying of a banana plantation near the town of Coffs Harbour, NSW (Beard et al., 1995) used only absorption tubes for volatile pesticides and was criticized for possibly under-collecting the mass by not collecting particulate phase. They used a low volume sampler at 1 LPM with samples taken for 24 hours, daily for 23 weeks at 4 sites. The experiment looked for a total of 46 organochlorine and organophosphate pesticides.

1.2.3 New Zealand

There is very little work in New Zealand on risk to humans of air exposure to pesticides. Holland et al. (1997) focused mostly on drift from kiwifruit orchards. They took air measurements in urban areas 500-1000 m from orchards and found levels of chlorpyrifos and diazinon of $5\text{-}40 \text{ ng/m}^3$. They used a specially constructed sequential sampler system mounted on a trailer with a retractable mast, with sampling taking place 2 m above ground level. They used XAD-4 filters at either 140 L/min or 21-24 L/min.

Geoghegan et al. (2014) tested feasibility of using passive air samplers for vapour drift near vineyards near Blenheim. They found that the passive samplers could be used near the field when winds were sufficient. Passive samplers have the advantage over active samplers of not requiring electricity to power the air pump. They were able to source their PUF foam sampler/filters from Nexus Foams in Christchurch.

1.3 Human Exposure Risk

There were a few studies on pesticide drift-related illnesses in the United States. Namulanda et al. (2016) found from 2007-2011 there were 5795 documented cases of spray drift exposure. Human illnesses and injury were most commonly caused by insecticides, but there were 38 cases of illnesses caused by sulfur exposure. The older but more thorough study of Lee et al. (2011) found 2945 cases of exposure to pesticide drift from 1998-2006, using data from 11 states. They note that agricultural pesticides are often detected in rural homes and 31% of acute pesticides illnesses in U.S. schools were attributed to drift exposure (as opposed to exposure from pesticides used directly in the schools for pest control). 44% of the drift cases occurred at private residences, 37% on farms, 6% on roads, and 4% in schools. Most cases experience ocular (58%) or neurological (53%) symptoms, and 48% had respiratory symptoms, 42% gastrointestinal, and 15% dermal (such as skin rash). Again, insecticides were far more likely as causing human health effects than fungicides. 39% of drift cases were from aerial application and 40% from ground tractor application. Common contributing factors for drift events were application carelessness, unfavorable weather, and poor communication. Residents in agricultural-intensive regions in California have a 69 times higher risk of pesticide poisoning from drift compared to other regions. 34% of drift cases occurred within 0.25 miles (400 m) of the application site, 35% from 0.25-0.5 miles (400-800 m) from the application site, 16% from 0.5-1.0 miles (800-1600 m), and 15% were more than 1 mile (1.6 km) away.

The Washington State Dept. of Health has collected pesticide exposure and acute injury data since 1990 in a Pesticide Illness Monitoring System. 24% of the cases were among children. Most common symptoms were eye irritations, headaches, dizziness, nausea, and skin irritation. From 2007-2011 Washington State averages 25 drift complaints involving human health per year, most of which were insecticide exposures. Those most affected tended to be workers on a nearby farm. Airblast sprayers were the type of application equipment most commonly associated with the drift incidents (51%). During interviews some workers reported they could feel the droplets of spray on their face and arms. In most of these events the distance from worker to sprayer was less than 50 m.

Butler-Ellis et al. (2017) developed a BROWSE model for predicting human exposure to pesticide drift. There is currently no model available that can be used to predict airborne spray drift downwind of an orchard airblast sprayer in a regulatory context, so they have used an empirical approach. For the BROWSE model they looked at exposure to humans in an area 2-20 m downwind of the spray zone, and model dermal exposure and spray inhalation. The model results indicated the dermal exposure was more significant than the inhalation exposure, and acute exposure effects are more significant than chronic effects, and effects are more strongly felt by children than adults. Note this is different from the Washington state field data, where inhalation symptoms were more prevalent. The Washington data may be indicative of more long distance exposure.

Table 1 lists the chemicals identified as the primary ones used in vineyards that would be important to measure.

Table 1: Pesticides commonly used in NZ vineyards (Sources and details: see text)

CAS #	Active Ingredient	Product	Type	Notes
69327-76-0	buprofezin	Applaud	Insecticide	1-2 per season max between bud break and capfall more use in the North Island
112410-23-8	tebufenozide	Mimic	Insecticide	1 per season max precapfall
91465-08-6	lambda-cyhalothrin	Karate Zeon	Insecticide	November spot treatments; headland areas typically for grass grub
1071-83-6	glyphosate	RoundUp	Herbicide	1-3 per season
7704-34-9	sulfur		Fungicide	5-10 applications per season all through
188425-85-6	boscalid	Pristine	Fungicide	Is part of a two component product with a strobilurin - is being phased out
658066-35-4	fluopyram	Luna Sensation	Fungicide	Maybe one per season - is a two product mix with a strobilurin
118134-30-8	spiroxamine	Impulse, Spiral	Fungicide	many vineyards will use up to once per season
124495-18-7	quinoxifen	Proxima, Quintec	Fungicide	One or two applications per season
189278-12-4	proquinazid	Talendo	Fungicide	One or two per season
180409-60-3	cyflufenamid	Flute	Fungicide	Up to one per season
121552-61-2	cyprodinil	Switch	Fungicide	Typically one or two per season over flowering usually
53112-28-0	pyrimethanil	Scala	Fungicide	Typically one per season
203313-25-1	spirotetramat	Movento 100SC	Insecticide	No more than 2 applications per season- usually November and again pre-flowering December
29232-93-7	pirimiphos-methyl	Attack	Insecticide	No more than two applications per season
161050-58-4	methoxyfenozide	Prodigy	Insecticide	Apply pre- 80% capfall – usually single application at or before 80% capfall
121-75-5	Maldison (malathion)	Fyfanon	Insecticide	Apply pre-capfall

Table 1 was compiled from the list of chemicals in the New Zealand Plant Protection Society (NZPPS) working group on chemical resistance, with input from industry consultant David Manktelow and Sustainable Winegrowing NZ. Table 2 lists the health screening levels identified in Table 1, obtained from the EU database <http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.selection&language=EN>

ADI is the Acceptable Daily Intake, and AOEL is the Acceptable Operator Exposure Level. Toxicity data for vineyard fungicides in units of mg/kg body weight/day. These levels can be used as a screening threshold for the maximum air concentrations (ng/m³) for health concerns.

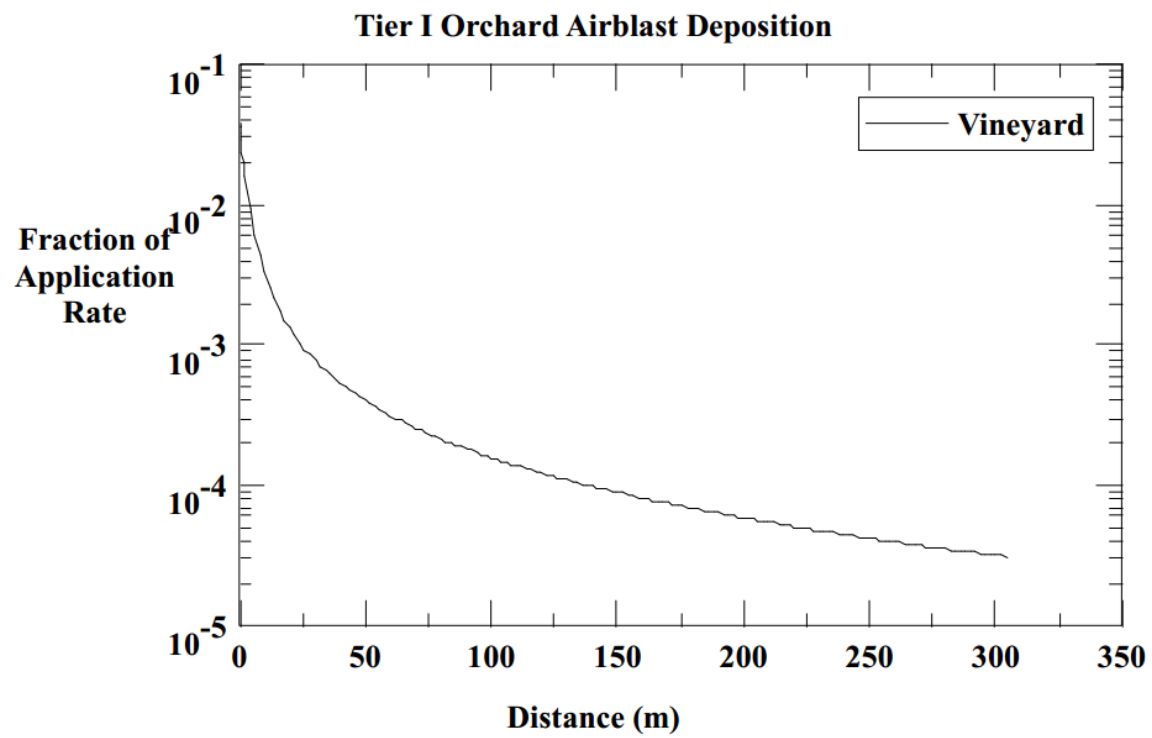
So for example considering a 70 kg male adult, nominal air breathing rates are normally taken as 0.3 m³/hr for children and 0.625 m³/hr for adults. For an adult male, buprofezin at an ADI of 0.01 mg/kg/day = 0.7 mg per day allowed. At breathing rate 0.625 m³/hr for adults, in 24 hours 15 m³ of air is consumed. So the maximum allowable ambient concentration would be 0.047 mg/m³ = 47 ng/m³.

Table 2: Screening levels for health effects of pesticides. (Sources and details: see text)

Pesticide	ADI (mg/kg/day)	AOEL (mg/kg/day)
sulfur	na	na
glyphosate	0.30	0.20
quinoxifen	0.20	0.14
pyrimethanil	0.17	0.12
methoxyfenozide	0.10	0.10
spirotetramat	0.05	0.05
boscalid	0.04	0.10
cyflufenamid	0.04	0.03
cyprodinil	0.03	0.03
malathion	0.03	-
spiroxamine	0.025	0.015
tebufenozide	0.02	0.008
Fluopyram	0.012	0.05
buprofezin	0.01	0.04
proquinazid	0.01	0.02
pirimiphos-methyl	0.004	0.02
lambda-cyhalothrin	0.0025	0.00063

There are very few field experiments that have been conducted from which we can reliably estimate human exposure to bystanders. Besides physical drift, post-application volatilization can be a significant source of drift and air pollution. Figure 1 shows the AgDRIFT curve for downwind deposition of spray material that is used by the US EPA and Australian Pesticides and Veterinary Medicines Authority (APVMA) for spray drift risk assessment. The work of O'Donnell et al. (including Rory Roten, former Lincoln Agritech employee) shows the AgDRIFT vineyard curve is a reasonable fit to spray drift from an airblast sprayer under Australian conditions, but it is a generic curve, and does not account for specific variations in wind and application equipment. It also does not account for volatilisation drift.

There is insufficient data available to estimate human health effects from pesticide drift in Marlborough, hence the need for a pesticide air monitoring system.



AgDRIFT® 2.1.1

Figure 1: AGDISP standard vineyard spray drift curve.

2. AIR SAMPLING EQUIPMENT

The air samplers used in the studies described in section 1 are either high-volume or low-volume samplers.

2.1 High Volume Air Samplers

An air sampling system consists of two major parts of hardware: the air sampler with a pump and aerodynamic inlet to achieve the desired sample rate, and the sampling media which traps the pesticides.

2.1.1 Air Samplers

Figure 2 shows a schematic for a typical high-volume air sampler.

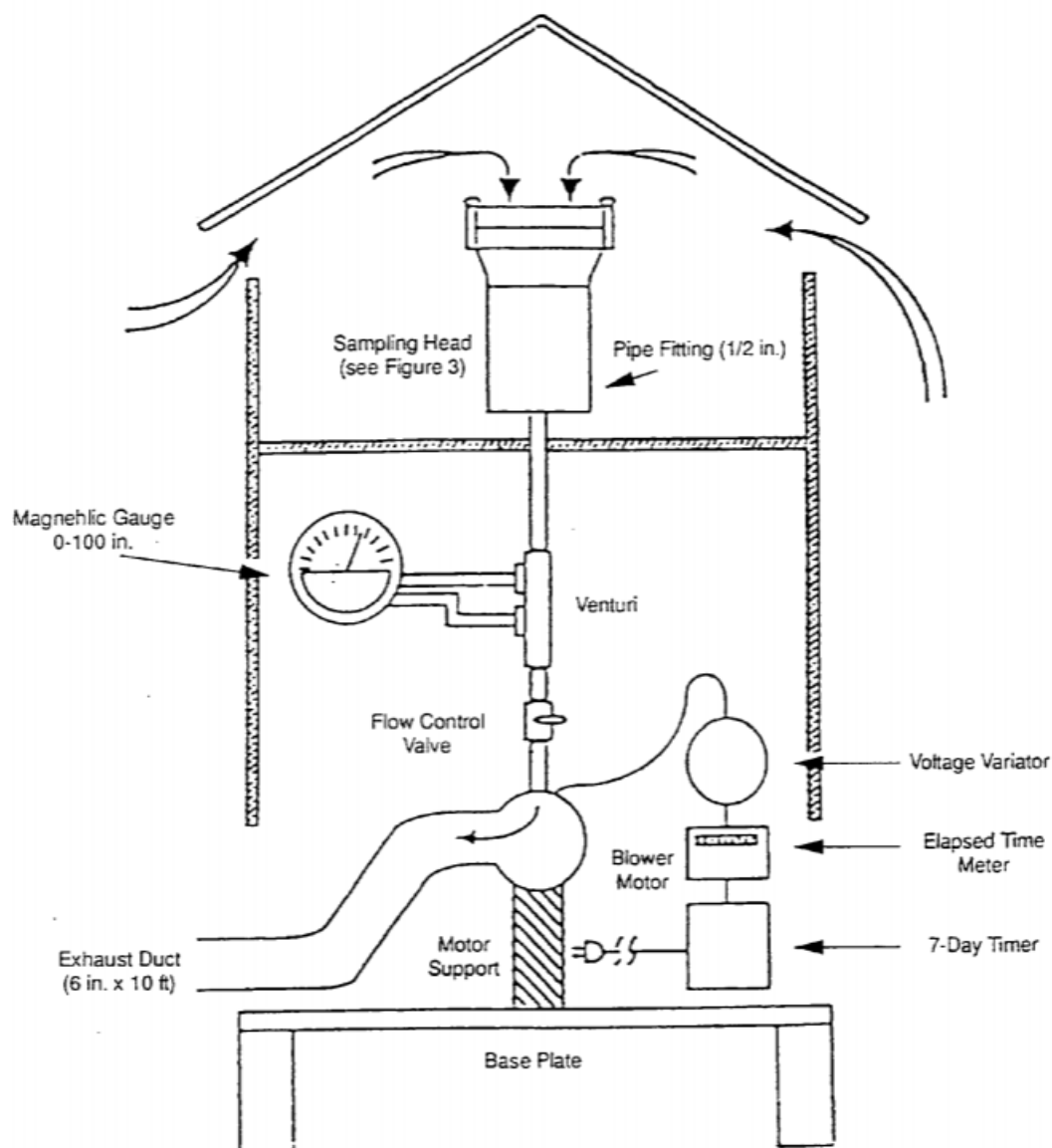


Figure 2: Air sampler sketch

Price quotes for high-volume systems were obtained from two vendors in the United States, as shown in Table 3. Both systems are easy to use, complete installations, with timers and flow rate control, and designed to hold standard sampling media. Information on low-volume samplers are listed in section 2.2.3.

Table 3: Hi Volume Air Sampling Systems

Vendor	Cost	Flow Rate	Flow control	Notes
Hi-Q	US\$4,790+ship NZ\$6,706+ship	60-280 LPM	Seven day mechanical trip timer, an elapsed hour timer	Combination 4" dia. paper & PUF holder; 400 W power
Tisch	US\$4,355+ship NZ\$6,097+ship	125-250 LPM	Control & calculation of flow rate; 7 day timer	Designed to meet US EPA TO-4A; Size 1.55 m tall by 0.7 m wide

2.1.2 Filter Media

It is important that the sample filters be able to capture pesticides in both the vapour phase and the aerosol phase (either as liquid spray drops, dust, or condensates from evaporated drops). The study in Australia was criticized for understating the public health risk by not capturing all phases. For capturing the vapour phase, the three options primarily used in previous studies are: PUF, XAD-2, XAD-4, as well as sandwich combinations of PUF and an XAD resin. For the particulate/aerosol phase, the only two options previously used are glass fibre filters and quartz fibre filters. Table 4 shows price quotes for sampling material from the same two American companies as in Table 3. These fit both Hi-Q and Tisch samplers. XAD Sorbent tubes can also be purchased from SKC (<https://www.skinc.com>; www.skcltd.com). These costs do not include shipping.

Table 4: Sampling filter media

	PUF filters 3" long	4" Diameter Quartz Fiber Filters
Hi-Q	US\$7.90 (NZ\$11.06)	US\$5.95 (NZ\$8.33)
Tisch	US\$4.60 (NZ\$6.44)	US\$4.62 (NZ\$6.47)

2.2 Alternatives to High Volume Air Samplers

Technology currently in development but not yet validated for environmental sampling includes electronic noses and spray deposition sensors.

2.2.1 Electronic Noses

Most electronic noses are based on a metal-oxide gas sensor array, which produces an electronic signal when certain classes of chemicals pass through the sensor. Airsense Analytics produces a Portable Electronic Nose (PEN) which has a maximum flow of 0.4 LPM and sensitivity 0.1 to 5 ppm for gases and organic solvents. This has mostly been used for pesticide residues on fruits, and only once has a client attempted to use for pesticides in the air, so it is not clear if it will work for air monitoring. <https://airsense.com/en/products/portable-electronic-nose>



Figure 3: Air Sense E-nose

Nano Engineered Applications uses a carbon nanotube-based sensor for detecting gases and volatile organic compounds (VOCs) at the parts-per-billion (ppb) in low-power, high-density, multi-gas sensor chips (not on market yet). <http://nanoengineeredapps.com/technology-0>

2.2.2 Spray Deposition Sensors

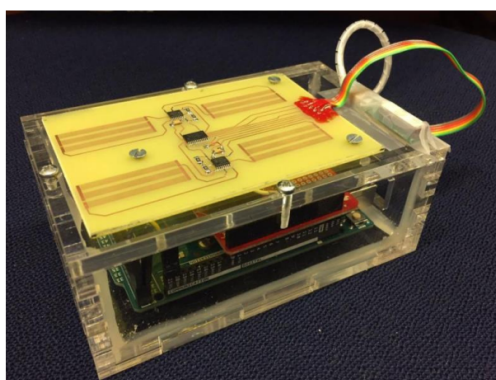
Lincoln Agritech has developed prototype electronic spray deposition sensors (ESDS). The currently tested limit of detection of these sensors is only about 10 m downwind (for a ground boom sprayer in low wind). Further testing would be required to determine the limit of detection for orchard airblast sprayers under typical Marlborough weather conditions. It should also be possible to improve the minimum limit of detection with further electronics development of the sensor. To positively and uniquely identify spray drift events (apart from precipitation or irrigation) it is proposed to add a consumable element adjacent to electronic sensor (some sponge-like element that dries out), and alerts for need for sample collection and delivery to laboratory. The sensor could alert MDC to collect the element only when a spray drift event has been detected.



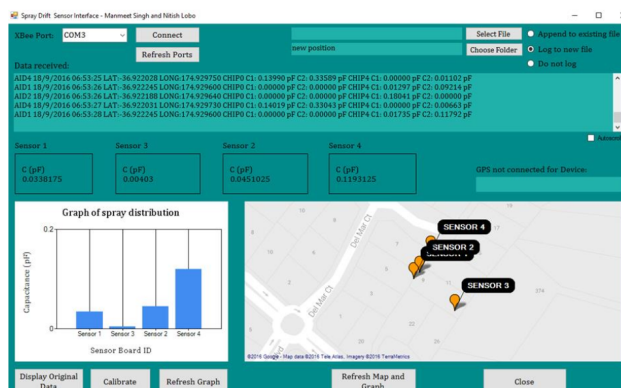
(a): Sensors in field



(b): Spray trial of sensors



(c): Drift station prototype



(d): GUI interface showing sensor locations.

Other electronic spray deposition sensors have been proposed by Luck, Broniowski, and Giles with limited testing, but none are close to being on the market. These all detect water-based sprays and not specific pesticides.

2.2.3 Other types of Air Samplers

The Pesticide Action Network North America (PANNA) has developed a simple air sampler named the Drift Catcher. While this is lower initial cost than the commercial samplers, it has the same limitations. They offer units for a lease cost of US\$200 (NZ\$280) per year and estimate laboratory sample analysis costs at US\$125-255 per sample (NZ\$175-357). There are no peer-reviewed publications validating this sampler, only PANNA internal reports (<http://www.panna.org/resource-library>).

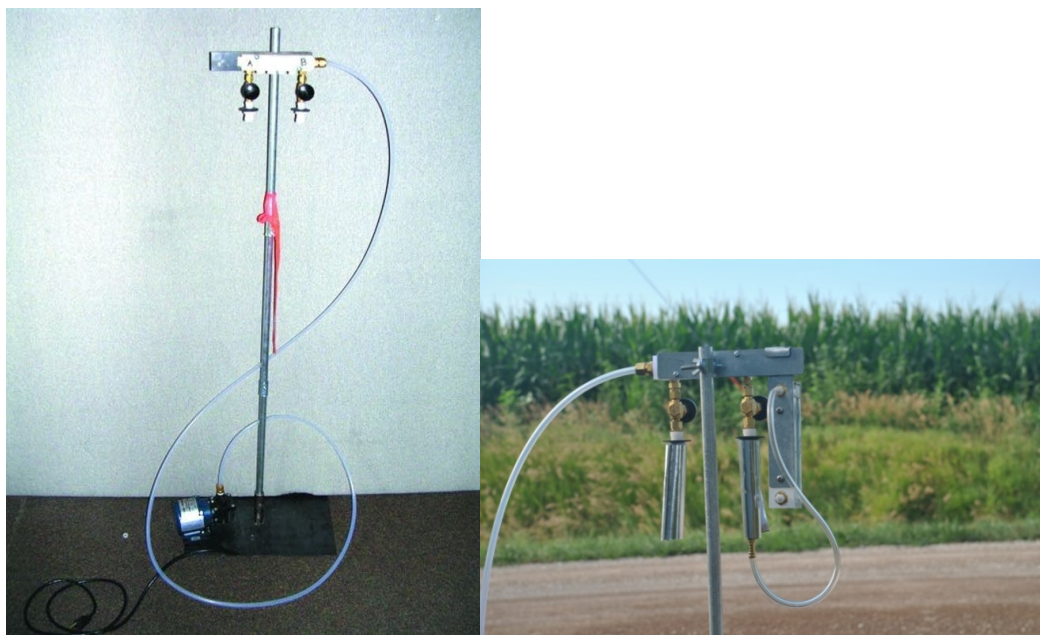


Figure 4: PANNA drift catcher

There are also Passive Air Sampling (PAS) techniques that do not require AC power, but take longer to record a sample and have greater variability in results, as the air sample volume depends on the wind. Passive samplers typically have sampling rates of 0.5-10 m³/day, compared to 200-500 m³/day for high volume samplers. Typically passive samplers are deployed for weeks at a time to obtain a sufficient sampling volume. PAS often sample only the gas phase.

Currently either Water-Sensitive Papers (WSP) or collector plates used with a fluorescent tracer dye are used for quantifying spray drift in a research setting for a single event. These approaches are labour-intensive and too expensive for long-term monitoring, and also require the cooperation of the sprayer operators.

Low-volume air samplers are similar to high-volume samplers, except that they have lower flow rates, and usually do not come as a single ready-to-use unit, but rather require construction of a sampler holder and may not be as easy to program. BGI/Thomson in Australia offers a unit for AU\$4,997 that can sample from 0-20 LPM.

ThermoFisher Scientific in Auckland can provide low-volume air pumps from SKC. The California Dept. of Pesticide Regulation has used SKC AirChek pumps in some of their monitoring. An AirChek Touch system would cost NZ\$3,873, including a flow rate calibrator and holder for their OVS sorbent tubes, which have a combined XAD-2 resin and Glass Fibre Filter. The combined sorbent tubes cost NZ\$35.40 each. The AirCheck would likely only provide about 2 L/min flow with the attached filters.

3. RECOMMENDED PROCEDURES

Relevant standards consulted include EPA Method TO-4A and California DPR Standard Operating Procedure EQAI001.00.

3.1 Siting and Installation of Air Samplers

The recommended monitoring site criteria (including US EPA ambient air siting criteria) are:

- 2-10 m above ground
- At least 1 m horizontal and vertical distance from supporting structure
- At least 20 m from trees
- Distance from obstacles should be twice the obstacle height
- Unobstructed air flow for 270 degrees
- Assess to electrical outlets
- Secure from tampering or theft
- Accessible to sampling personnel
- Preferring monitoring sites include school, day care centre, or other sensitive site located on the edge of community and adjacent to agricultural fields
- Away from combustion sources

Additional recommendations include:

- monitor meteorological conditions at spray drift sampling site
- obtain pesticide use information within a 5 mile (8 km) distance of the monitored community
- Consider staff safety in siting the air sampler (such as avoid a site that would require the use of an external building ladder)

Most of the California monitoring sites are at ground level, such as at a school or police station. For sites at ground level they have also ringed the monitor with a small fence and danger signs to keep people away.

3.2 Operational Procedures

As discussed previously, it is important to sample both aerosol and vapor phases to ensure the total pesticide mass is captured. Once the water has evaporated from a drop, the active ingredient (a.i.) can remain airborne as an aerodynamically buoyant crystalline flake or small oil drop. So both a vapor absorbing medium (PUF, XAD-2 or XAD-4 resin) and a particulate fiber filter are needed. The filter is also needed for capturing pesticides in the aerosol phase (liquid drops, dusts, and condensed particles formed when the water in the solution evaporates off).

EPA Method TO-4A notes common pesticide concentrations from 1 to 50,000 ng/m³ over 4-24 hour sampling periods. Pesticides are extracted from the sorbent cartridge with 10% diethyl ether in hexane and measured with gas chromatography coupled with another technique (depends on exact chemicals being measured). Since the concentrations of pesticides in the air will be low, a high-volume sampling technique is required to acquire sufficient material for analysis (above the detection threshold), but the volatility of most pesticides prevents efficient capture on filter media. Therefore Method TO-4A uses both a filter and a PUF backup cartridge to provide efficient collection of most pesticides. They define high volume air sampler as 225 L/min, so that over 24 hours a sample volume of 324 m³ is measured. The sampling module should be capable of holding a circular particle filter up to 102 mm diameter, and a borosilicate glass sorbent cartridge containing PUF 60-65 mm diameter and 125 mm long. Samples should be held at 4 °C or below during shipping to the laboratory after collection.

After removal from the air sampler, it is important that the sampling media be handled correctly to prevent desorption of the pesticides from the filters. They should immediately be placed in a sealed bag and kept cold (stored at ~4 °C) and in the dark until extraction. This is normally done by placing the sample in dry ice as soon as removed from sampler for shipping to lab. The bagged filters can be kept in a refrigerator at the laboratory until analysed. They can be kept for up to 31 days in this manner.

The California Dept. of Pesticide Regulation has stated that testing at one site 1 day per week is sufficient for chronic/sub-chronic exposure, but not for acute concentrations. To test for acute exposures requires a seasonal study to sample 4 days per week during 3-4 months at the height of spraying season.

For quality assurance and quality control (QA/QC), the California DPR has a laboratory create test spikes with known concentrations that are measured, and also blank cartridges that have not been exposed to pesticides are analysed as well.

Airflow rates and/or sample times may need to be adjusted after an initial pilot study to determine optimum flowrate to achieve valid sample amounts. Flowrates need to be high enough mass for accurate measurement, but not too much that saturates the filter and causes chemical breakthrough. Since the concentration of pesticides in the urban air in Marlborough is presently unknown, it is not possible to say at present whether a high-volume sampler or low-volume sampler will be a more appropriate choice. California DPR recommends to determine the minimum level to measure and sample at 10x that. If there is an available air sampler that could be used for the initial pilot study, it would be beneficial to test that during the next spraying season in order to develop estimates of airborne pesticides concentrations to use in selecting a permanent air sampling station.

In summary, recommended procedures are:

- Samples should be taken for 24 hours duration at least once a week, and probably more often during the height of the spraying season
- When the filter media are removed from the sampler, they should be immediately placed in an insulated container filled with dry ice to keep them at 4 C or colder, and shipped to a suitable laboratory as soon as possible
- Samples may be kept in a refrigerator as long as 1 month until they are analysed
- The fibre filter and absorbing cylinder may be extracted together in one procedure to reduce costs, since only the total pesticide loading is of concern and not the partitioning between aerosol and vapour phases
- Extraction of the pesticide from the filters should follow EPA TO-4A or another appropriate standard procedure
- On an on-going regular basis analysis of “blanks” and “spikes” should be performed to ensure extraction procedure is correct and validity of field measured samples

3.3 Data Analysis

The laboratory analysis of filter media from an air sampler will give a sample mass (typically in units of micrograms) for each pesticide measured. This can be converted into an air concentration using the flow rate of the air sampler (LPM) and the sampling time (min), using equation 1:

$$\frac{\text{sample } (\mu\text{g})}{\text{air flow } \left(\frac{\text{L}}{\text{min}}\right) \times \text{sample time (min)}} \times 1000 \frac{\text{L}}{\text{m}^3} \times 1000 \frac{\text{ng}}{\mu\text{g}} = \text{air concentration } \left(\frac{\text{ng}}{\text{m}^3}\right) \quad (1)$$

In this case suitable unit conversions have been employed to obtain air concentration in units of ng of pesticide mass per cubic meter of air. For most chemicals the detection limit is in the range of 1-5 ng/m³. One of the higher concentrations measured in California was in one air sample diazinon was measured at 172 ng/m³, above the human health protection screening level of 130 ng/m³, prompting DPR to move diazinon to the top of the high priority list for risk assessment.

Trapping efficiencies of filter media have been found to be around 80-90%, and are generally considered to be close to 100% for calculation purposes.

3.4 Economic Analysis

For any sampler system purchased, whether high-volume or low-volume sampler, the initial capital cost will be at least about NZ\$5,000 to obtain a system that includes an appropriate sample holder, calibration of air flow rate, and programmable timer.

The primary on-going costs will be the sample media, dry ice for storage, shipping samples to a laboratory, and the cost of the laboratory analysis. Hills lab provided a rough estimate of \$350 per sample, if quartz filters and PUF plugs are extracted together.

So if one sampler per week is taken for 6 months, the cost of sample media will be at least \$20 per sample, so the costs of sample media and lab analysis over 6 months would be NZ\$9,620 (\$20+\$350x26), excluding shipping, labour, and dry ice.

4. REFERENCES

- Armstrong, J. L. (2012). Passive and Active Air Sampling for Residential Exposures to Airborne Organophosphorus Pesticides and Oxygen Analogs ("Oxons") in Central Washington State (Doctoral dissertation, University of Washington).
- Baker, L. W., Fitzell, D. L., Seiber, J. N., Parker, T. R., Shibamoto, T., Poore, M. W., ... & Duncan, D. W. (1996). Ambient air concentrations of pesticides in California. *Environmental science & technology*, 30(4), 1365-1368.
- Beard, J., Westley-Wise, V., & Sullivan, G. (1995). Exposure to pesticides in ambient air. *Australian and New Zealand Journal of Public Health*, 19(4), 357-362.
- Bui, Q. D., Womac, A. R., Howard, K. D., Mulrooney, J. E., & Amin, M. K. (1998). Evaluation of samplers for spray drift. *Transactions of the ASAE*, 41(1), 37.
- Butler-Ellis, M. C., van den Berg, F., van de Zande, J. C., Kennedy, M. C., Charistou, A. N., Arapaki, N. S., ... & Jacobs, C. M. (2017). The BROWSE model for predicting exposures of residents and bystanders to agricultural use of pesticides: Comparison with experimental data and other exposure models. *Biosystems Engineering*, 154, 122-136. <https://secure.fera.defra.gov.uk/browse/software/>
- California Dept. of Pesticide Regulation (2017) A Guide to Pesticide Regulation in California: 2017 Update.
- California Dept. of Pesticide Regulation (2011) Air Monitoring Network Study: Long-Term Ambient Air Monitoring for Pesticides in Multiple California Communities.
- California Dept. of Pesticide Regulation(2001?) SOP EQAI001/00 – Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps.
- Geoghegan, T. S., Hageman, K. J., & Hewitt, A. J. (2014). Testing flow-through air samplers for use in near-field vapour drift studies by measuring pyrimethanil in air after spraying. *Environmental Science: Processes & Impacts*, 16(3), 422-432.
- Hengel, M., & Lee, P. (2014). Community air monitoring for pesticides—part 2: Multiresidue determination of pesticides in air by gas chromatography, gas chromatography–mass spectrometry, and liquid chromatography–mass spectrometry. *Environmental monitoring and assessment*, 186(3), 1343-1353.
- Holland, P. T., Maber, J. F., May, W. A., & Malcolm, C. P. (1997). Drift from orchard spraying. *Journal of the New Zealand Plant Protection Society*, (pp. 112-118).
- King, K., Vidrio, E., Wofford, P., Segawa, R. (2017) Air Monitoring Network Results for 2016. California Dept. of Pesticide Regulation.
- Lee, S. J., Mehler, L., Beckman, J., Diebolt-Brown, B., Prado, J., Lackovic, M., ... & Moraga-McHaley, S. (2011). Acute pesticide illnesses associated with off-target pesticide drift from agricultural applications: 11 states, 1998–2006. *Environmental health perspectives*, 119(8), 1162.
- Lopez, C. (2009) Organophosphorous Pesticide Air Monitoring Project. University of Washington.
- López, A., Coscollà, C., & Yusà, V. (2017). Selection of sampling adsorbents and optimisation and validation of a GC-MS/MS method for airborne pesticides. *International Journal of Environmental Analytical Chemistry*, 1-16
- Namulanda, G. (2016). Acute nonoccupational pesticide-related illness and injury—United States, 2007–2011. *MMWR. Morbidity and mortality weekly report*, 63.
- Short, K. (1996). Monitoring pesticides in ambient air. *Australian and NZ journal of public health*, 20(2), 219-220.
- Tolbet, L. (2007) Ambient Concentrations of Organophosphorous Pesticides. M.S. Thesis. University of Washington.
- U.S. EPA (1999) Method TO-4A. Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic /Multi-Detector Detection.
- Washington State Dept. of Health (2013) Pesticide Data Report: 2010-2011 Agency Data.
- Washington State Dept. of Health (2008) Pesticide-Related Illness and Injury.
- Wofford, P., Segawa, R., Schrieder, J. (2009) Pesticide Air Monitoring in Parlier, California.
- Yao, Y., Harner, T., Blanchard, P., Tuduri, L., Waite, D., Poissant, L., ... & Sverko, E. (2008). Pesticides in the atmosphere across Canadian agricultural regions. *Environmental science & technology*, 42(16), 5931-5937.

