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Comparison of Active versus Passive Atmospheric Samplers for Some Current-Use Pesticides

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Passive samplers are chemical accumulators that can be used to assess ambient atmospheric concentrations of target chemicals. They are increasingly employed in investigations of persistent organic pollutants (POPs) (Shen et al. 2004, Shoeib and Harner 2002). A number of different media have been used for passive sampling such as polyurethane foam (PUF) disks (Jaward et al. 2004a, 2004b, Shoeib and Harner 2002), semipermeable membrane devices (SPMDs) (Ockenden et al. 2001, Prest et al. 1995), XAD-2 resin (Wania et al. 2003), and polymer coated glass (POGs) (Wilcockson and Gobas 2001). Passive sampling provides an advantage over conventional high-volume (active) sampling in that it is relatively inexpensive and requires no electrical power. PUF disks are particularly attractive samplers because they are cheap, easy to handle and have a high capacity for POPs enabling longer sampling periods (Jaward et al. 2004b). Passive atmospheric samplers employing PUF disks have been reported to operate in the "kinetic phase" where uptake of gas-phase compounds occurs at a constant rate (linear) for a period of at least 42 days (Shoeib and Harner 2002). Thus they were considered acceptable for the 28-day sampling periods used in the current study.

The objective of this study was to investigate the sampling rate of passive samplers using PUF disks for ten currently-used herbicides as well as lindane [γ-1,2,3,4,5,6-hexachlorocyclohexane]. These herbicides were dicamba [3,6-dichloro-o-anisic acid], MCPA [(4-chloro-2-methylphenoxy)acetic acid], bromoxynil [3,5-dibromo-4-hydroxybenzonitrile], 2,4-D [2,4-dichlorophenoxy acetic acid], ethalfluralin [*N*-ethyl-α,α,α-trifluoro-*N*-(2-methylallyl)-2,6-dinitro-*p*-toluidine], trifluralin [α,α,α-trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine], atrazine [6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine], triallate [*S*-2,3,3-trichloroallyl di-isopropyl (thiocarbamate)], alachlor [2-chloro-2',6'-diethyl-*N*-methoxymethylacetanilide], and metolachlor [2-chloro-6'-ethyl-*N*-(2-methoxy-1-methylethyl)acet-*o*-toluide].

MATERIALS AND METHODS

Pairs of passive air samplers were installed at two heights, 10 m and 30 m, on a tower located approximately 35 km south-west of Regina, SK, from June 18 to

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August 13, 2003. The samplers were set up approximately five meters apart at the two elevations. One high-volume air sampler was also installed at each elevation.

Passive samplers consisted of precleaned circular PUF disks (14 cm diameter by 1.35 cm thick; density 0.0213 g cm^{-3}) located within a protective housing consisting of two hemispherical stainless steel bowls, following the design of Shoeib and Harner (2002). With one exception, all passive PUFs were exposed to the air for 28 days from June 18 to July 16 and July 16 to August 13, 2003. One passive sampler from the 30 m elevation was damaged during the first week of sampling and was replaced resulting in an exposure time of 21 days.

High-volume samplers (Model PS-1, General Metal Works, Village of Cleves, OH), one at each elevation, were co-located the passive samplers. Sampling methods have been previously described by Waite et al. (2002) and are summarized here. The air flow through the samplers (12.5 m^3 h^{-1}) was calibrated in the field using a Sierra-Misco (Berkeley, CA) orifice head and was monitored in the field during daily operation by integral Venturi/Magnahelic assemblies. Samplers were operated 24 hours a day for 7 days each week for a total air flow of approximately 2100 m^3 wk^{-1}.

The high-volume sampling unit consisted of a 102 mm diameter borosilicate microfibre filter (Pacwill Environmental, Beamsville, ON) to collect solid particles preceding a cartridge containing 25 mL of XAD-2 resin (Caledon Laboratories Ltd., Georgetown, ON) sandwiched between 50 mm (upstream) and 25 mm (downstream) polyurethane foam (PUF) plugs to trap gaseous residues and particulates not trapped by the microfibre filter. Samples were acquired weekly from the high-volume units and shipped for analysis. The high-volume samplers were operated for 8 weeks to coincide with the sampling period of the passive samplers.

The method for extraction has been described previously by Waite et al. (2002) and references therein. An aliquot (1 mL) of surrogate (2,4-D-d_5 or 2,4-dichlorophenoxy-3,5,6-d_3-acetic –d_2 acid) in acetone was spotted onto the surface of the upstream PUF plug in each PUF/XAD-2 resin cartridge prior to extraction. The PUF/XAD-2 resin cartridge and filter were Soxhlet extracted simultaneously with acetone for at least 8 hours. The acetone extract was concentrated to <1 mL and methylated with ethereal diazomethane. The methylated extracts were exchanged into hexane and taken to volume (10 mL) prior to gas chromatographic analysis. The PUFs from the passive samplers were similarly extracted.

All extracts were analysed using an Agilent Technologies (Palo Alto, CA) model 6890 gas chromatograph (GC) interfaced with the model 5973 mass selective detector (MSD). A 30-m x 0.25-mm internal diameter GC column [Agilent Technologies: 5% phenyl-95% methyl polysiloxane (DB-5MS), 0.25 μm film thickness] was used with a helium carrier gas flow rate of 1 mL min^{-1}.

Extracts were analysed for the pesticide lindane, the methyl derivatives of the herbicides dicamba, MCPA, bromoxynil and 2,4-D, and for the neutral herbicides triallate, trifluralin, ethalfluralin, atrazine, alachlor, and metolachlor.

RESULTS AND DISCUSSION

Samples were analysed for 11 chemicals but quantifiable amounts were found, on the passive samplers, of only dicamba, 2,4-D, triallate, lindane, bromoxynil, and MCPA so only these will be discussed. During the first passive sampling period one of the 30 m pair of samplers was lost. It was replaced and the following three weeks, June 26 to July 16, were sampled (21 days). All other passive samples represent 28 day exposures.

Qualitatively, there was generally a good correlation between the high-volume and the passive samplers (Table 1). Chemicals in complete agreement for all samples included bromoxynil, 2,4-D, trifluralin, and triallate. These chemicals were generally present in the atmosphere in higher concentrations than the other chemicals (e.g. 2,4-D 0.68 ng m^{-3} and triallate 0.66 ng m^{-3}). Chemicals present in lower concentrations (e.g. atrazine, alachlor), while occasionally found in the high-volume samplers, were not detected in the passive samplers. Over the range of chemicals tested, the high-volume samplers were able to detect lower atmospheric concentrations of chemicals than the passive samplers. In cases where a chemical was measured in one passive sampler but not the paired sampler (i.e.- lindane, 10 m, July 16 – August 13), it was present in quantities close to the detection level.

Table 1. Qualitative results of high-volume (Hi-Vol) and passive air samplers (PAS).

	June 18 - July 16						July 16 - August 13					
	10 m			30 m			10 m			30 m		
Chemical	Hi-Vol	PAS A	PAS B	Hi-Vol	PAS A[1]	PAS B	Hi-Vol	PAS A	PAS B	Hi-Vol	PAS A	PAS B
2,4-D	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Bromoxynil	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Triallate	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Trifluralin	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Dicamba	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	ND	Y
MCPA	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	ND	ND
Lindane	Y	Y	Y	Y	Y	Y	Y	Y	ND	Y	ND	ND
Atrazine	Y	ND	ND	Y	ND	ND	Y	ND	ND	Y	ND	ND
Ethalfluralin	Y	ND	ND	Y	ND	ND	Y	ND	ND	Y	ND	ND
Metolachlor	ND	ND	ND	ND	ND	ND	Y	ND	ND	Y	ND	ND
Alachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	Y	ND	ND

[1] 21 day sampling period.

(Y indicates presence of chemical, ND indicates non-detection.)

The ability of a passive sampler to quantitatively measure atmospheric concentrations of pesticides can be calculated by comparing the quantity of each pesticide present on the passive sampler with the atmospheric concentration of the corresponding chemical as measured by a high-volume (Hi-Vol) sampler as follows:

Sampling Rate (*R*)
= Passive mass (ng) ÷ [Average Hi-Vol conc. (ng/m3) × Days sampled]

Atmospheric concentrations (high-volume samplers) of dicamba, 2,4-D, bromoxynil and MCPA were higher during the first sampling period than the second as were the quantities collected by the passive samplers (Table 2). These herbicides are typically applied in mid to late June on the prairies, coinciding with this sampling period. The calculated sampling rates of the passive samplers also tended to be much higher during the early sampling period with the highest being 38.8 m^3 d^{-1} (MCPA, average of the two samplers, 10 m elevation). For these four chemicals the greatest variation in passive sampling rates between the first and second sampling periods was for dicamba at the 10 m elevation with average rates of 31.7 m^3 d^{-1} (first period) and 5.2 m^3 d^{-1} (second period) (Table 2).

Average atmospheric concentrations of triallate and lindane were similar for both sampling periods (Table 2). Triallate is applied as a pre-emergent herbicide, usually in early to mid May with peak atmospheric concentrations occurring at that time (Waite et al. 2002). Atmospheric concentrations in mid June to mid August tend to be much lower and relatively consistent. Lindane use on the Canadian prairies, primarily as a treatment of canola seed, was discontinued after 2002 and atmospheric concentrations in 2003 probably represent volatilisation of residues from previous years' applications. Thus, relatively consistent atmospheric concentrations were expected, dependent on soil moisture, temperature, tillage and other factors affecting volatilisation from soil. Unexpectedly, however, the quantities of triallate and lindane collected in the 21-day sample (period 1, 30 m) were much greater than those in the corresponding 28-day sample for the same elevation and also greater than the quantities in the corresponding 28-day samples collected at 10 m. As a result the calculated sampling rates for the 21-day sample for both chemicals were much higher than those of the corresponding 28-day samples (30 and 10 m heights). We currently have no explanation for this anomaly as the values for the other four pesticides analysed from this sample were comparable to the 28-day samples. Accordingly, the 21-day values for triallate and lindane will not be included in any calculations reported in this paper.

While the calculated sampling rates varied widely, from 43.6 m^3 d^{-1} (MCPA, 10 m, period 1) to 1.2 m^3 d^{-1} (lindane 30 m, period 2) (Table 2) the reproducibility of the pairs of passive samplers was generally good, regardless of the chemical or the sampling period. The variability of the pairs, expressed as percent of the mean of each pair, can be calculated by dividing half the difference between the

Table 2. Quantities of pesticides collected by passive samplers, average atmospheric concentrations (Hi-Vol) for each passive sampling period and calculated sampling rates of the passive samplers.

Chemical	Elevation	Sampling Period	Passive (ng)	Hi-Vol (ng m^{-3})	Sampling Rate, *R* (m^3 d^{-1})	Chemical	Elevation	Sampling Period	Passive (ng)	Hi-Vol (ng m^{-3})	Sampling Rate, *R* (m^3 d^{-1})
Dicamba	10 m	1	330	0.32	37.3	Lindane	10 m	1	60	0.20	10.7
			230	0.32	26.0				30	0.20	5.4
		2	10	0.07	5.2			2	10	0.13	2.8
			10	0.07	5.2				10	0.13	2.8
	30 m	1	120[2]	0.18	32.4		30 m	1	120[2]	0.14	40.2
			200	0.23	31.7				80	0.15	18.8
		2	10	0.04	8.3			2	10	0.30	1.2
			10	0.04	8.3				10	0.30	1.2
2,4-D	10 m	1	330	0.68	17.4	Bromoxynil	10 m	1	390	0.45	30.9
			280	0.68	14.8				340	0.45	26.9
		2	20	0.07	10.3			2	30	0.07	16.0
			20	0.07	10.3				30	0.07	16.0
	30 m	1	190[2]	0.63	14.3		30 m	1	250[2]	0.42	28.2
			350	0.67	18.7				430	0.47	33.0
		2	10	0.07	4.8			2	20	0.04	17.2
			20	0.07	9.6				20	0.04	17.2
Triallate	10 m	1	240	0.66	12.9	MCPA	10 m	1	590	0.48	43.6
			200	0.66	10.8				460	0.48	34.0
		2	180	0.72	9.0			2	10	0.03	10.5
			160	0.72	8.0				10	0.03	10.5
	30 m	1	370[2]	0.38	46.4		30 m	1	120[2]	0.35	16.1
			130	0.46	10.1				250	0.38	23.4
		2	120	0.30	14.1			2	10	0.03	12.1
			130	0.30	15.3				10	0.03	12.1

[1] Sampling periods are June 18 July 16 (1) and July 16 - August 13 (2)

[2] 21 day sample from June 26 - July 16

two sample values by the mean of the sample pair and multiplying by 100 as in the following equation (Waite et al. 2000):

$$\% \text{ Variability} = [(A - B) \div 2] \div [(A + B) \div 2] \times 100$$

where A and B are the chemical sampling rates (m^3 d^{-1}) for the individual samplers of the pair

By combining the sampling rates for all the chemicals, except for triallate and lindane, 30 m, period 1, it can be seen that the variability was less than ±15 % of the mean of the pairs (Table 3). This is comparable to the reproducibility of pairs of high volume PUF samplers reported by Cessna et al. (2000) for the same group of herbicides.

Table 3. Percent variability between passive PUF samplers, combined sampling rates for all chemicals, excluding triallate and lindane, 30 m, period 1.

		Sampling Rate (m^3 d^{-1})		
Elevation	Sample Period[1]	Sampler A	Sampler B	% Variability
10 m	1	25.47	19.63	13
	2	8.97	8.80	1
30 m	1	22.74[2]	22.62	0.3
	2	9.62	10.62	5

[1] Sampling periods are from June 18 – July 16 (1) and July 16 – August 13 (2)

[2] 21 day exposure from June 26 – July 16

Jaward et al. (2004b) suggested that passive samplers can be designed and calibrated to allow reliable estimates of air concentrations to be made or to allow semi-quantitative comparison of the levels and patterns of POPs. The calculated sampling rates found in the present study, however, were different for each chemical and also varied from sampling period 1 to period 2 (range 1.2 to 43.6 m^3 d^{-1}). Shoeib and Harner (2002) reported a theoretical sampling rate of about 3.5 m^3 d^{-1}, based on depuration studies. Tuduri and Harner (2004), however, reported sampling rates varying from 3.5 to 4.8 m^3 d^{-1} in still air, for a range of PCBs (polychlorinated biphenyls). Sampling rates were, however, greatly affected by wind speed with rates >50 m^3 d^{-1} at wind speeds of 1.8 m sec^{-1}. Tuduri and Harner (2004) also found that sampling rates varied from congener to congener, being generally higher for the more chlorinated congeners. The pesticides in the present study are quite different from PCBs and represent a wide range of chemical and physical characteristics including volatility and the potential to bind to particulates (Waite et al. 2002, 2004). These characteristics may affect their rates of adsorption by the medium of passive samplers. High winds, in excess of 30 km h^{-1} (8.3 m sec^{-1}) are not unusual on the Canadian prairies and wind speed may be a factor in the high sampling rates obtained in the current study.

These passive samplers, then, are useful tools to qualitatively sample current-use pesticides in the atmosphere, especially in remote areas where electricity is not available. They collect reproducible samples with acceptably small variation in the results from sampler pairs. Further studies are needed, however, to enable their use to quantitatively measure atmospheric concentrations of current-use pesticides.

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