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Field Evaluation of Solid Sorbents for Ambient Air Sampling of Pesticides

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Abstract: Seven solid sorbents including Amberlite® XAD-2 and XAD-4, Tenax-TA®, Anasorb-747, Chromosorb 102, 108, and 750 were evaluated for the collection of the gas phase fraction of pesticides under field conditions at an agricultural site, Bratt's Lake, SK, located in the Canadian prairies. The polyurethane foam (PUF)/sorbent cartridge consists of two PUF layers which sandwich the solid sorbent and each layer was analyzed separately to determine which portion of the PUF/solid sorbent retained the pesticides and the extent of breakthrough. The pesticides that had high detection frequency throughout the study and ambient air concentrations well above MDL were triallate, trifluralin, ethalfluralin, and chlorpyrifos. All sorbents had improved collection efficiency as compared to a standard 7.6 cm PUF and the improvement varied with each pesticide. The most effective sorbents for trapping gas phase fraction of pesticides were XAD-2, XAD-4, Tenax-TA, and Chromosorb 108. The only sorbent not recommended for use is Chromosorb 750. For selected sampling periods when ambient concentrations were above detection limits a number of other organochlorine and organophosphorus pesticides also showed more efficient collection with PUF/solid sorbent cartridges as compared to PUF cartridge. Shorter sample collection periods of 4-days improved detection frequency of pesticides.

Keywords: ambient air sampling, sorbents, PUF/XAD-2, PUF/Tenax-TA, currently used pesticides (CUPs)

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Introduction

High-volume ambient air sampling methods for semi-volatile organics compounds (SVOCs) utilize a sampling head that contains a filter to collect the particles followed by a glass cartridge containing typically either a 7.6 cm polyurethane foam plug (PUF) or a PUF/solid sorbent cartridge to collect the gas phase fraction. Historically, PUF plugs have been widely used for organochlorines (OCs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo p-dioxins and furans (PCDD/*Fs)* due to their low cost, ease of handling in the laboratory, and adequate collection efficiency.[1–4] PUFs may exhibit breakthrough for more volatile or lower molecular weight compounds of these chemical classes, and this limitation can be reduced by either using additional PUF plugs in series[5] or addition of a solid sorbent that is sandwiched between two PUF plugs or held in place by a metal sieve.[6–10] Solid sorbents such as XAD-2, XAD-4, Tenax-TA or Tenax-GC, and Anasorb 747 have been used in low or high-volume air sampling methods for more volatile or lower molecular weight compounds including alkanes, benzene, two-ring aromatic hydrocarbons, polyfluorinated organic compounds, guaiacols, aliphatic and aromatic nitro compounds, PCBs, PCDD/Fs, and halogenated phenols.[3,11–15] For pesticide analysis extending beyond OCs high-volume air sampling methods generally use two PUFs in series,[16–19] a combination of PUF with XAD-2/Tenax-TA,[20–22] PUF/XAD-2 or XAD-2[23–29] to minimize the potential for breakthrough. However there have been few studies examining breakthrough of pesticides on sorbents. XAD-4 in sorbent tubes with passive sampling methods has also been recently used.[30,31] Based on information from the manufacturer, XAD-2 and XAD-4 differ in surface area, mean pore size, and porosity (XAD-2: 300 m^2/g, 90 Å, 0.41 mL pore/mL bead; XAD-4 750 m^2/g, 40 Å, 0.50 mL pore/mL bead). XAD-4 has 54 to 60% moisture holding capacity with XAD-2 expected to be similar. Tenax-TA may have some advantages as it has a low affinity for water.[11] Other solid sorbents which have been used for selected pesticides in sorbent tubes[32] may also be suitable for high-volume air sampling of pesticides. We wanted to evaluate the effectiveness of existing sorbents for gas phase collection of pesticides under field conditions as pesticides have been less widely studied than other SVOCs. In addition, this study includes a wider range of sorbents other than XAD-2 and Tenax-TA. Due to higher cost of Tenax-TA and availability of XAD-2, alternative or "equivalent" sorbents need to be identified.

The ambient air sampling field site was an agricultural location in the Canadian prairies (Bratt's Lake, SK) and at the onset of this research there was no available usage inventory for pesticides in Saskatchewan. Environment Canada conducted most of the ambient air pesticide studies prior to 2003, and these focused on selected herbicides, and lindane (γ-HCH) an OC insecticide that was applied to canola seed prior to purchase until 2002.[24,33–37] Since that time Environment Canada conducted pesticide monitoring across Canada for selected periods and several studies focused on pre-emergent herbicides at Bratt's Lake.[23,38–43] However, as little information on occurrence of pesticides was available at the time of the study, the research focused on pre-emergent herbicides (triallate, trifluralin, and ethalfluralin), organochlorine pesticides, and organophosporus pesticides. New GC/MS and GC/MS/MS methods with electron impact and negative ion chemical ionization for over 50 pesticides were developed for analysis of air samples.[20] Two co-located high-volume PS-1 samplers were used for this study, one containing a 7.6 cm PUF cartridge while the other contained a PUF/solid sorbent cartridge. Our study also examined sampling duration (1-, 2-, 4-, and 7-days) over 12 consecutive months. Shorter duration sampling periods were selected during spring-fall when higher usage of pesticides for agricultural activity was expected and there was greater potential for breakthrough during sample collection.

Experimental

Materials

Polyurethane foam plugs (PUFs) (6 cm OD and 2.5, 5.1, and 7.6 cm lengths) and glass fibre filters (10.2 cm diameter) were supplied by Pacwill Environmental (Grimsby, ON, Canada). Labx 170 cleanroom filter paper (10.16 cm diameter, 63% abaca, 37% softwood with polymer binders) supplied by Berkshire (Great Barrington, MA) were used to make the loading and unloading of sorbent in the PUF/sorbent cartridge easier and did not impact total air flow. Glass fiber filters were weighed in a glovebox with nitrogen atmosphere before and after sampling to ±0.003 mg with a Mettler

Toledo MX5 microbalance (VWR International, Mississauga, ON, Canada). All filters were heated in a cleanroom overnight prior to usage at 100 °C to remove any possibility of residual volatile organics that may be present from shipment of the filters from the manufacturer. Blank filters were tested and showed no presence of pesticides. The solid sorbents included crosslinked polystyrene divinylbenzene copolymers: Chromosorb 102 (surface area 300–400 m^2/g, density 0.29 g/cm^3, Chromatographic Specialties, Brockville, ON, Canada), and Amberlite® XAD-2 and XAD-4 (both supplied by Supelco, Inc., Oakville, ON, Canada); 2,6-diphenylene oxide polymer, Tenax-TA (surface area of 35 m^2/g and $d = 0.25$ g/m^2) from Mandel Scientific Co. Inc. (Guelph, ON, Canada); beaded active carbon, Anasorb 747, (980 m^2/g, density not available) from SKC Inc. (Eighty Four, PA); and Chromosorb 108 and 750 (Chromatographic Specialties) which were polyacrylic ester polymer and silica (flux calcined diatomaceous earth) with surface areas of 100–200 and 700 m^2/g and densities of 0.3 and 0.4 g/cm^3, respectively.

Individual pesticide standards and deuterated internal and surrogate standard (parathion-d_{10} or diazinon-d_{10}) used for chemical analysis were supplied from Chem Service Inc. (West Chester, PA). Stock solutions of organochlorines and organophosphorus pesticides were purchased from UltraScientific (North Kingstown, RI). Acetone, ethyl acetate, and hexane used for sample extraction, sample or standard preparation were pesticide grade and supplied by Fisher Scientific (Ottawa, ON, Canada). SPE 6 mL tubes with 1000 mg of ENVI-C18 (Supelco Inc) were used for sample clean-up.

Field Sampling Method and Location

The Environmental Canada sampling site at Bratt's Lake, Saskatchewan (latitude 50° 12' 10"N, longitude 104° 12' 15"W) is a field site in the prairie agricultural region where grain and oil seeds such as wheat, barley, oats, canola, and flax are dominant. Environment Canada conducts other monitoring at this site through CAPMoN (Canadian Air and Precipitation Monitoring Network) and BSRN (Baseline Surface Radiation Network). The farmland area surrounding the site is flat to within 5 m over a radius of greater than 20 km. Air samples were collected during April 2, 2003 to March 5, 2004 using two co-located high-volume air samplers (Model PS-1, Tisch) at a flow rate of 225 L/min. Samplers were located approximately 5 m apart. One PS-1 sampler contained a sample head with a glass cartridge with a 7.6 cm PUF, while the other PS-1 sampler contained a sampling head with glass cartridge with PUF/solid sorbent cartridge. Samples were collected for either 1-day, 2-days, 4-days, or 7-days and starting times and flow rates were kept consistent between the two co-located samplers. All winter samples were 7-days in duration as pesticide levels were expected to be lower. For the other sample durations the 1-day, 2-day, and 4-day samples were run in sequence for each sorbent type.

The sampling head consists of a 102 mm diameter borosilicate microfiber filter in front of the glass cartridge containing either PUF or PUF/solid sorbent. The glass cartridge was 60 mm id. by 125 mm long with a stainless steel mesh support screen (Supelco, Sigma-Aldrich Canada Ltd., Oakville, ON, Canada). For the PUF/solid sorbent cartridge a 2.5 cm PUF was placed on the bottom, followed by a 10 cm diameter filter paper (LabX) which was shaped into a cup of diameter 6.0 cm and inserted into the glass cartridge. The solid sorbent (14 g) was poured into the filter paper cup. A second piece of 10 cm filter paper (LabX) which was shaped into a cup of diameter 6.0 cm was placed on top of this sorbent layer. To sandwich the sorbent in the glass cartridge, a top 5.1 cm PUF was inserted carefully into the filter paper cup above the sorbent. Pesticide levels were determined separately for the PUFs and sorbent layer such that the extent of breakthrough and collection on the sorbent could be assessed. The use of the LabX cleanroom filter allowed the sorbent to be more easily removed from the glass cartridge without contact with the PUF layers. The LabX filter paper was extracted with the sorbent layer. Lab and field blank filters and PUF or PUF/sorbents were tested throughout the study and showed no detectable levels of pesticides. In addition particle levels determined from each of the two co-located high-volume PS-1 samplers could be used for evaluation of variability between the samplers.

Analytical Procedures

The GC/MS/MS system consisted of an Agilent HP6890GC coupled to a tandem mass spectrometer (GC quattro micro) from Waters-Micromass (Milford, MA, U.S.A). The GC system was equipped with a split/splitless inlet with a splitless sleeve containing carbofrit (4 mm id., 6.5 × 78.5 mm, Restek, Chromatographic Specialties Inc., Brookville, ON, Canada). The injector temperature was 225 °C. A LEAP technologies (Carrboro, NC) autosampler with a 10 µL syringe was used for injections of 1 µL. The analytical column was DB-5 ms, 30 m × 0.25 mm id. and 0.25 µm film thickness (J&W Scientific, Folsom, CA). GC/MS and GC/MS/MS methods for analysis of pesticides in this study including organochlorines, organophosphorus pesticides, and the three common pre-emergent herbicides (triallate, trifluralin, ethalfluralin) were developed in both selected ion monitoring (SIM) and selected reaction monitoring (SRM) modes with electron impact (EI) and negative chemical ionization (NCI) and have been described in detail elsewhere.[20] The GC-NCI-SIM method was used for pesticides reported in this study and had method detection limits (MDLs) of 1–20 pg μL^{-1}, which is equivalent to approximately 0.001−0.020 ng m^{-3} air concentrations for a 7-day air sample. In NCI the chemical ionization reagent gas was methane (99.999%) at 0.6 mL min^{-1}. The ion source temperature was 130 °C and the interface temperature was 250 °C.

PUFs and solid sorbents were extracted separately and the material in the glass cartridge was loaded or unloaded into 66 or 100 mL extraction cells in a class1000 cleanroom laboratory. Samples were extracted with ethyl acetate using an ASE100 or ASE300 pressurized solvent extraction system (Dionex, Sunnyvale, CA). The extraction method parameters were: temperature 100 °C; static time 30 min at 1500 psi; two static cycles; 60% flush volume; purge time with nitrogen (UHP) of 300 s. Total extraction volume was approximately 1.5 times the extraction cell volume. A second extraction with acetone was also tested and showed no presence of pesticides in the extracts. All solid sorbents and PUFs were also cleaned prior to use with the same extraction procedures. After extraction, samples were concentrated to ~5–10 mL, transferred to 15 mL vial and dried to near drynesss with nitrogen or clean-room air using a solid-phase extraction (SPE) apparatus. C18 (ENVI-18, 6 mL, 1 g) SPE tubes were conditioned with 6 mL ethyl acetate, followed by 6 mL methanol. Sample extract (0.25 or 0.5 mL) was loaded onto the preconditioned tubes, followed by surrogate standard (diazinon-d_{10}, generally 0.1 mL at 1 µg/mL) and methanol such that the total volume was 1 mL. The eluted solvent collected into the F0 fraction contained no pesticides of interest. The pesticides were eluted with 5 mL of ethyl acetate in the next fraction (F1), and the Versiprep drying attachment (Supelco) was used to dry the eluted extracts to near dryness. Dried extracts were dissolved with hexane to a total volume of 1 mL with addition of internal standard (parathion-d_{10}, generally 0.1 mL at 1.0 µg mL^{-1}) such that the concentration of internal standard was 100 pg μL^{-1} in samples for GC-NCI-SIM analysis. Recoveries were on average 86%.[20,22]

The filters used in the PS-1 sampling head were weighed (±1.5 µg) before and after sampling using a Mettler Toledo microbalance housed in a glove box with a UHP nitrogen atmosphere for humidity control. Filters were conditioned in the glove box for a minimum of one day prior to gravimetric analysis. The total suspended particulate concentrations for each sampler were determined by dividing the particle mass collected on the filters by the total air volume sampled.

Results and Discussion

Total suspended particulate levels were determined for the two co-located PS-1 high volume samplers. Variability of total suspended particulate levels between the two samplers was 20.1% for the 91 sampling periods throughout the year which agrees with the variability between paired sampling of <25%.[24] In addition, all field and shipment blanks (50 PUF, and 51 PUF/sorbent) taken throughout the year showed no detectable levels of pesticides or total suspended particulate. For verification of paired sampling for these pesticides for one sampling period both co-located samplers contained a 7.6 cm PUF. This sampling period had levels of the four main pesticides above MDL and showed a percentage difference between the co-located samplers of 0% for ethalfluralin, 9.3% for trifluralin, 12.0% for triallate, 14.0% for chlorpyrifos, and 6.7% for lindane well within the expected 25% variability. Recoveries are tested for all samples throughout the study with average recovery of 86% as previously described.[20] Previous studies with PUF/XAD-2 also observed good collection efficiency from spike air samples.[24,35]

There were 91 sampling periods during the year (April 2, 2003–March 5, 2004) ranging in duration from 1-day to 7-days. It was found that a large number of the samples had most of the detected pesticide on the upper 5.1 cm PUF layer such that pesticide did not breakthrough to the sorbent during the sampling period. Only periods where measurable levels of pesticide were found on the sorbent layer were used in this comparison. Four pesticides were found to have a higher frequency of detection during spring–fall and included the three pre-emergent herbicides (ethalfluralin, triallate, trifluralin) and an OP insecticide, chlorpyrifos. Of the total 91 sampling periods in this study, the number of sampling periods with levels of these four pesticides above MDL for the PUF/sorbent samples was 38, 54, 45, and 45, respectively. The 7.6 cm PUF from the co-located PS-1 sampler had a similar number of sampling periods with detectable levels ranging from 41–55 sampling periods. As the 7.6 cm PUF was analyzed in total as compared to the PUF/sorbent where each layer was analyzed separately there were a few more detections of the lower levels of pesticides near MDL. During the 12 weekly sampling periods in the winter (December–February) only 3 sampling periods showed detectable levels for chlorpyrifos, 1 sampling period for trifluralin, and no detection of triallate or ethalfluralin were observed.

Of the sampling periods with detectable levels where pesticide reached the sorbent layer Table 1 shows that there were only between 10–14 sampling periods most of which were 4-day in duration that could be used for the sorbent comparison. The highest atmospheric concentration of the four pesticides was observed for chlorpyrifos (Table 2). There is a large range in sample concentrations for these sampling periods and a significantly different of average concentrations was only observed for trifluralin (p-value of 0.027). However large variations of concentration for the individual sampling periods occurred which were $>25\%$ expected for co-located samplers. The largest improvement in collection efficiency when a sorbent was used as compared to the 7.6 cm PUF was observed for chlorpyrifos as shown in Table 1. Figure 1A shows the variation of chlorpyrifos levels with majority of sampling periods showing higher amounts on the PUF/sorbent combination as compared to the 7.6 cm PUF. It is expected that the large improvement in collection efficiency for some individual sampling events when PUF/sorbent was used as compared to a 7.6 cm PUF (average percentage difference of 142.9% for chlorpyrifos) can be attributed to breakthrough and loss when using a 7.6 cm PUF. This breakthrough of chlorpyrifos on the 7.6 cm PUF is much larger for the October 24,2003 sampling event than when PUF/Chrom750 was used although the Chromosorb 750 does not perform well either. Movement of chlorpyrifos from the sorbent layer to the bottom 2.5 cm PUF was observed for the PUF/sorbent with an average of 21.5% of the total pesticide concentration on the bottom PUF layer (Table 1). The vapor pressure of the three pre-emergent herbicides is higher than that of chlorpyrifos, however OPs such as chlorpyrifos are detected predominately in the vapor phase.[22] During a 1-day sampling period in 2003 when there was reported local usage of chlorpyrifos, high atmospheric concentrations of chlorpyrifos were observed at 233 ng/m^3 when PUF/XAD-2 was used as compared to only 179 ng/m^3 when only the 7.6 cm PUF was used. The maximum concentration of chlorpyrifos was observed during a 4-day sampling event with 250 ng/m^3 observed on PUF/Tenax-TA and 200 ng/m^3 on the 7.6 cm PUF. Table 3 also shows for three other sampling periods during June–July where a number of other pesticides were also detected, the chlorpyrifos concentrations were higher with the PUF/sorbent than the 7.6 cm PUF. All of the sorbents observed improvements and there was no correlation with atmospheric concentration or time of year to the amount of improvement. These different

Table 1. Percentage difference of PUF/Sorbent from 7.6 cm PUF, and Percentage Pesticide on Each PUF/Sorbent Layer for Sampling Periods with $<98\%$ of pesticide on the upper 5.1 cm PUF.

Pesticide (number of sampling periods)	Average percentage difference	Average % on upper 5.1 cm PUF	Average % on sorbent	Average % on lower 2.5 cm PUF
All sorbents*				
Chlorpyrifos (10)	142.9	55.7	22.8	21.5
Triallate (14)	45.0	67.6	30.0	2.4
Trifluralin (12)	81.7	56.8	30.2	13.0
Ethalfluralin (13)	36.8	67.5	21.3	11.2

Note: *Excludes October 24, 2003 sampling event for chlorpyrifos shown in Figure 1A with significant breakthrough for PUF, and PUF/Chrom750.

Table 2. Number of sampling periods of 4-day duration, and pesticide air concentrations for sampling periods examined for sorbent comparison during 2003.

Pesticide (total number of sampling periods with pesticide on sorbent Layer)	Average pesticide concentrations PUF/sorbent (7.6 cm PUF) ng/m^3	Range in pesticide concentration on PUF/sorbent (ng/m^3)	Range in pesticide concentration on 7.6 cm PUF (ng/m^3)	Number of sampling periods of 4-day duration with pesticide on sorbent layer
Chlorpyrifos (10)	25.9 (20.7)	0.0087–250	0.0065–200	9
Triallate (14)	3.40 (3.22)	0.230–10.8	0.138–12.3	6
Trifluralin (12)	0.190 (0.117)	0.0063–0.560	0.0073–0.341	7
Ethalfluralin (13)	0.281 (0.240)	0.0075–0.840	0.0102–1.03	9

pesticides have different distribution coefficients for the sorbent materials and based upon polarity of pesticides it would be expected that an organophosphorus pesticide (chlorpyrifos) would have less retention on more non-polar sorbents and exhibit breakthrough more readily. The 1-day and 2-day samples showed less movement of chlorpyrifos to the bottom 2.54 cm PUF as compared to the 4-day and 7-day sampling periods (<1% for 1- and 2-day samples as compared to up to 32.3% for 4-day and 7-day sampling periods) as would be expected from the larger air volumes.

Trifluralin also had better collection efficiency on PUF/sorbent than on the 7.6 cm PUF with average percentage difference of 81.7% but had less movement from the sorbent to the bottom PUF layer than chlorpyrifos (Table 1). For these sampling periods the average concentration of trifluralin was significantly higher with the PUF/sorbent (0.190 ng/m^3, Table 2) than the 7.6 cm PUF (0.117 ng/m^3). All sorbents (from PUF/sorbent sampler) showed comparable or higher levels of trifluralin than when just a 7.6 cm PUF was used (Fig. 1B) and there was no trend with atmospheric concentration or time of year of sampling.

Although the average concentrations for triallate and ethalfluralin did not differ between the co-located samplers, a small improvement with the PUF/sorbent as compared to the 7.6 cm PUF were observed of individual sampling periods above the expected variation between paired samplers of 25% with the average % difference of 45.0 and 36.8%, respectively (Table 1). For triallate for most sorbents <3% of the total pesticide was often observed in the bottom PUF layer, but was as high as 67.9% (October 24, 2003 sampling period) when Chromosorb 750 was used indicating that triallate was not as efficiently collected on this sorbent although it still observed higher levels than on the 7.6 cm PUF (Fig. 1C). For ethalfluralin on average 11.2% of total pesticide concentration was on the bottom PUF layer, similar to that observed for trifluralin (13%). The two sampling periods when Chromosorb 102 was used had a higher portion of pesticide on the bottom PUF between 17.2%–28.4%, however total pesticide concentrations were still higher than when the 7.6 cm PUF was used (Fig. 1D). Overall accounting for the percentage difference in pesticide concentrations, the fraction of pesticide on the bottom PUF layer, and the easy of use of the different

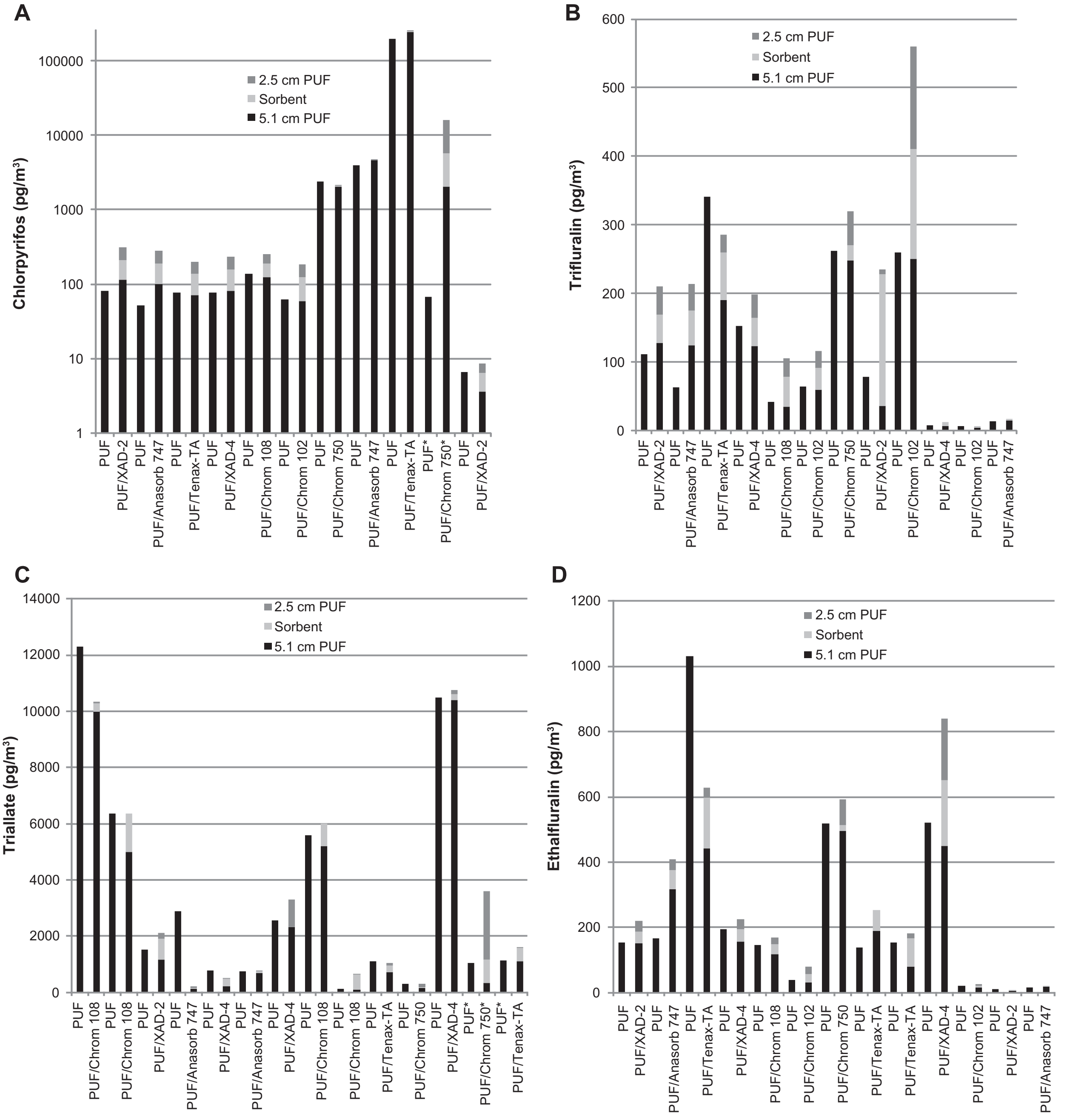

Figure 1. Atmospheric concentration of pesticides obtained from two co-located PS-1 samplers for sampling periods where pesticides reached sorbent layer. Pesticides: **A**) chlorpyrifos; **B**) trifluralin; **C**) triallate; **D**) ethalfluralin. PUF refers to PS-1 sampler containing 7.6 cm PUF, and PUF/Sorbent refers to PS-1 sampler containing 5.1 cm PUF/14 g sorbent/2.5 cm PUF with sorbent specified.
Note: *October 24, 2003 1-day sampling event. Shown are sampling periods where pesticides reached sorbent layer.

sorbents we found that XAD-2, XAD-4, Tenax-TA, and Chromosorb 108 were the best sorbents. The only sorbent we do not recommend for use in high-volume air sampling due to a high percentage of pesticide found in the bottom PUF for some sampling periods was Chromosorb 750, however even this sorbent was better than the standard 7.6 cm PUF. Although not part of this research there may be some advantage in using sorbents which are more tolerant to high humidity conditions such as Tenax-TA so that removal of water is not required from the extract. XAD-2 and XAD-4 both exhibit water in air extracts for sampling periods when humidity was higher or precipitation occurred. The water in extracts must be removed prior to GC/MS analysis and can lead to loss of pesticide during drying.

Table 3. Pesticide concentrations for pesticides with PUF/sorbent and 7.6 cm PUF for selected 4-day duration samples.

Sampling Period	**June 21, 2003**		**July 15, 2003**		**July 21, 2003**	
Pesticide	**7.6 cm PUF (ng/m^3)**	**PUF/XAD-2 (ng/m^3)**	**7.6 cm PUF (ng/m^3)**	**PUF/XAD-4 (ng/m^3)**	**7.6 cm PUF (ng/m^3)**	**PUF/ Chromosorb 108 (ng/m^3)**
α-Chlordane	0.167	0.314	0.162	0.162	0.182	0.556
Alachlor	0.195	0.332	ND	ND	ND	ND
Aldrin	ND	ND	0.005	ND	0.004	0.016
γ-Chlordane	0.073	0.213	0.074	0.217	0.085	0.258
Chlorfenvinphos	1.68	2.57	ND	ND	ND	ND
Chloroneb	8.37	15.8	ND	ND	ND	ND
Chlorothalonil	0.203	0.592	0.202	0.601	0.235	0.724
Chlorpyrifos	4.67	6.06	22.3	38.7	61.6	77.3
Dacthal	0.133	0.385	0.134	0.395	0.154	0.468
Demeton-S	5.33	9.65	ND	ND	ND	ND
Dieldrin	ND	0.032	0.033	0.033	ND	ND
Endosulfan I	0.101	0.189	0.102	0.299	0.116	0.341
Ethalfluralin	0.184	0.508	0.189	0.615	0.176	0.536
Azinphos methyl	18.0	47.2	ND	ND	ND	ND
α-HCH (hexachlorocyclohexane)	0.343	0.587	ND	ND	0.334	0.989
γ-HCH	0.220	0.366	ND	ND	0.205	0.679
Heptachlor	0.153	0.299	0.156	0.461	0.183	0.550
Heptachlor epoxide	0.068	0.129	0.069	0.137	0.074	0.205
Mirex	ND	0.020	ND	ND	ND	ND
Nitrofen	0.045	ND	ND	ND	ND	ND
Pentachloronitrobenzene	ND	ND	0.150	0.445	0.175	0.553
Sulfotepp	0.084	0.161	ND	ND	ND	ND
Sulprofos	0.214	0.482	ND	ND	ND	ND
Trans-nonachlor	0.006	0.010	0.112	0.111	0.129	0.391
Triallate	0.903	1.33	0.536	2.14	0.320	1.29
Trifluralin	0.302	0.880	0.158	0.490	0.170	0.530

Abbreviation: ND, non detect (<MDL).

There were a few selected sampling periods with a number of other OCs and OPs detected above MDL and Table 3 shows that PUF/sorbent samples also had higher air concentrations than the 7.6 cm PUF. Most of these OCs and OPs were rarely detected particularly with 7-day sampling with the exception of DCPA, α-HCH, and γ-HCH. Heptachlor epoxide and dieldrin were detected in only one 7-day sampling period throughout the year. The majority of detections were observed when the sampling period length was of 4-day duration. DCPA, α-HCH, and γ-HCH along with chlorothalonil, endosulfan I, α-chlordane, γ-chlordane, heptachlor, and heptachlor epoxide were detected 9 to 17 of the 20 sampling periods of 4-day duration during the year. The concentrations shown for the 3 sampling periods in Table 3 are above average levels for most pesticides. Azinphos methyl was only detected on the 4-day sampling event on June 21, 2003. This higher detection frequency of pesticides with the shorter sampling duration of 4-days rather than 7-days accounts for higher atmospheric concentrations of some pesticides such as chlordane, heptachlor, heptachlor epoxide, and HCHs observed as compared to other Canadian studies which used weekly sample collection.[40–43]

Conclusions

The present study investigated the role of sorbents in gas phase collection of pesticides in the atmosphere. The use of a sorbent in a PUF/sorbent combination provided improved collection efficiency for pesticides as compared to just using a standard 7.6 cm

PUF for gas phase sampling. If sampling is of longer duration than 7-days then an additional PUF or higher amounts of sorbent should be considered to minimize the potential for breakthrough, however air flow rate restrictions also limit this consideration. Sorbents recommended for future use include XAD-2, XAD-4, Tenax-TA, and Chromosorb 108. These sorbents can also be used in combination with each other and we have used a combination of XAD-2 or XAD-4 with Tenax-TA to take advantage of Tenax-TA tolerance to high humidity conditions so that sample extracts have lower water content.[20–22]

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Disclosure

This manuscript has been read and approved by all authors. This paper is unique and is not under consideration by any other publication and has not been published elsewhere. The authors and peer reviewers of this paper report no conflicts of interest. The authors confirm that they have permission to reproduce any copyrighted material.

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