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Sorbent impregnated polyurethane foam disk passive air samplers for investigating current–use pesticides at the global scale

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ABSTRACT

A pilot study conducted at a subset of 20 sites operated under the GAPS (Global Atmospheric Passive Sampling) Network compared the performance of two types of passive samplers for measuring air concentrations of currently–used pesticides, during 3–month deployment periods. The conventional polyurethane foam (PUF) disk sampler was able to capture a range of targeted current–use pesticides CUPs (dacthal, trifluralin, chlorothalonil, chlorpyrifos, and pendimethalin) but experienced equilibrium for some compounds (dacthal, trifluralin, and chlorothalonil) during the deployment period. The second sampler type used was a modified PUF disk sampler impregnated with XAD powder [i.e. the SIP (sorbent–impregnated PUF) disk] to increase sorptive capacity. The SIP disk sampler accumulated greater amounts of most targeted CUPs when compared to the PUF disk sampler. Results of the study showed that chlorothalonil was the most abundant CUP reflecting its widespread use, globally; whereas dacthal exhibited greater global distribution, including presence at remote sites, reflecting its high potential for long–range atmospheric transport. A thorough calibration of both the PUF disk and the SIP disk samplers is required to further define uptake profiles and to determine their range of applicability for various CUPs.

Keywords:
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1. Introduction

Current–use pesticides (CUPs) are used worldwide in agriculture. These pesticides were developed to replace some organochlorine pesticides (OCPs), which have numerous undesirable and hazardous properties including: persistence, ability to bioaccumulate in the food chain and potential for long range transport. CUPs are supposed to be less stable than OCPs and less able to bioaccumulate (Chernyak et al., 1996). Elevated air concentrations of CUPs have been reported near application areas (Tuduri et al., 2006; Yao et al., 2006; Yao et al., 2008) and these results have raised questions regarding possible health effects for residents in these areas. Transport from application areas to remote regions has also been demonstrated for some CUPs (Iwata et al., 1994; Halsall et al., 1998; Wania, 2003; Hung et al., 2005) including the arctic region (Muir et al., 2004; Hoferkamp et al., 2010), indicating that some CUPs are sufficiently persistent to be transported long distances. Concern over environmental effects has resulted in closer scrutiny and nomination of some CUPs for international regulations (e.g. UNECE, 1998). For instance, lindane and endosulfan – CUPs that are widely used around the world – were recently listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2001). Trifluralin has been nominated for addition to the UNECE Convention on Long–Range Transboundary Air Pollution on Persistent Organic Pollutants (UNECE, 1998).

In recent years, passive air samplers have proven to be useful and cost–effective tools for investigating the spatial distribution of CUPs in the atmosphere and for identifying compounds that are present in remote environments, indicating their potential for long–range transport in air. For instance Gouin et al. (2008a) used PUF disk samplers to measure the spatial and temporal variations of CUPs in the atmosphere of south–central Ontario. PUF disk samplers were also used to complement high–volume sampling for CUPs under The Canadian Atmospheric Network for Currently Used Pesticides (CANCUP) program with a focus on CUPs in air across agricultural regions in Canada (Yao et al., 2008).

The GAPS (Global Atmospheric Passive Sampling) Network is the only global–scale air monitoring program for POPs and has been operating between 50–60 sites around the world since 2005. The GAPS Network employs PUF disk samplers that are deployed quarterly (every 3–months) (Pozo et al., 2006; Pozo et al., 2009) and XAD samplers that integrate annually. Results from XAD samples deployed during the first four years of the GAPS study (2005–2008) already showed temporal tendencies in air concentrations of some CUPs (Shunthirasingham et al., 2010).

The use of PUF disk samplers under the GAPS Network has been limited by the fact that some CUPs are too volatile to be captured effectively by PUF disks. A recent pilot study conducted under the GAPS Network investigated a modified PUF disk sampler with a higher sorptive capacity that is needed for capturing the more volatile and polar chemicals. The sorbent–impregnated PUF or SIP disk sampler has been shown to generate comparable results to the conventional PUF disk sampler for the legacy POPs – polychlorinated biphenyls (PCBs) (Genualdi et al., 2010) and organochlorine pesticides (OCPs) (Koblizkova et al., 2012) with the added benefit that it is also able to capture more volatile chemical classes such as the polyfluoroalkyl compounds (PFCs) (Genualdi et al., 2010), volatile methyl siloxanes (Genualdi et al., 2011) and penta– and hexachlorobenzenes (Koblizkova et al., 2012).

In the current study, the SIP disk sampler is compared to the conventional PUF disk sampler co–deployed at a subset of 20 GAPS sites during 2009. Samples are analyzed for a subset of CUPs that are known to be persistent enough to be applicable to the passive (time–integrated) sampling approach in that they will not degrade on the sampling medium during the extended deployment period. We have also targeted CUPs that are known to be abundant in the global atmosphere.

2. Experimental Section

Methodology related to the preparation of PUF disks (Pozo et al., 2006) and SIP disks (Shoeib et al., 2008) has been previously described. Detailed Standard Operation Procedures are also available from the GAPS Network (gaps.network@ec.gc.ca).

PUF disk and SIP disk samplers were co–deployed in "flying–saucer" type chambers at 20 sites during April – June 2009 overlapping with the 2nd quarter sampling period of the GAPS Network (see Figure 1). Details on sample collection, preparation and quantification (including quality assurance/quality control measures) were described previously (Genualdi et al., 2010). Genualdi et al. (2010) also present details for the derivation of sample volumes using depuration compounds. These depuration compounds are isotopically labeled compounds or unlabelled compounds that do not normally exist in air, and they are added to the PUF disk samplers prior to deployment. This approach is explained briefly below.

3. Target Chemicals

The list of the CUPs targeted in this study and their key physico–chemical properties is given in Table 1. Many of the targeted CUPs have been recently detected in air samples worldwide including remote areas (Tuduri et al., 2006; Yao et al., 2006; Yao et al., 2008; Shunthirasingham et al., 2010). Some other important CUPs (e.g., lindane and endosulfans) were targeted in a previous paper reporting legacy OCPs (Koblizkova et al., 2012) and are, therefore, not presented here.

The estimated effective air volume for a 3–month sample was calculated for the PUF disk sampler based on an empirical relationship (Equation 1) developed for the non–polar hydrophobic chemicals:

$$V_{air} = (K'_{PSM-A})\ x\ (V_{PSM})\ x\ \left\{1 - exp\left[-\frac{k_A}{K'_{PSM-A}}\ x\ \frac{1}{D_{film}}\right]t\right\} \quad (1)$$

where V_{air} is sampled volume of air (m^3), K'_{PSM-A} is a partition coefficient between the passive sampling media and air (calculated from octanol–air partition coefficient K_{OA}), V_{PSM} is the volume of the passive sampling medium (cm^3), k_A is the air–side mass transfer coefficient (cm/s), and D_{film} is the effective film thickness and t is time. Site–specific k_A values were calculated from the loss of depuration compounds (DCs), which were spiked on each PUF disk prior to deployment. By multiplying the k_A values by the surface area of the PUF disk sampler, it is possible to estimate the sampling rate R (m^3/day). Calculated site–specific sampling rates are listed in Table S1 (see the Supporting Material, SM). The same R values are applied to the SIP disks samplers as discussed in Genualdi et al. (2010). We note that the DCs used in the study did not include any isotopes of the CUPs that were investigated. However, we do not expect to see large differences in the air–side mass transfer rates (i.e. R values) given that the molecules are similar in size to the DCs that were used. Ideally, and for future studies, DCs should include labeled isotopes of the class of compounds that are being investigated.

The template for calculating V_{air} for these CUPs and other POPs is available from the GAPS Network (gaps.network@ ec.gc.ca). Based on their physicochemical properties, particularly the estimated K_{OA} and K_{PSM-A} values (Table 1), we expect that the CUPs investigated here will not reach equilibrium in the PUF disks during the 3–month deployment period and that sampling will be in the linear phase. Equilibrium should occur even later for the SIP disk given that it has additional sorptive capacity compared to the PUF disk alone.

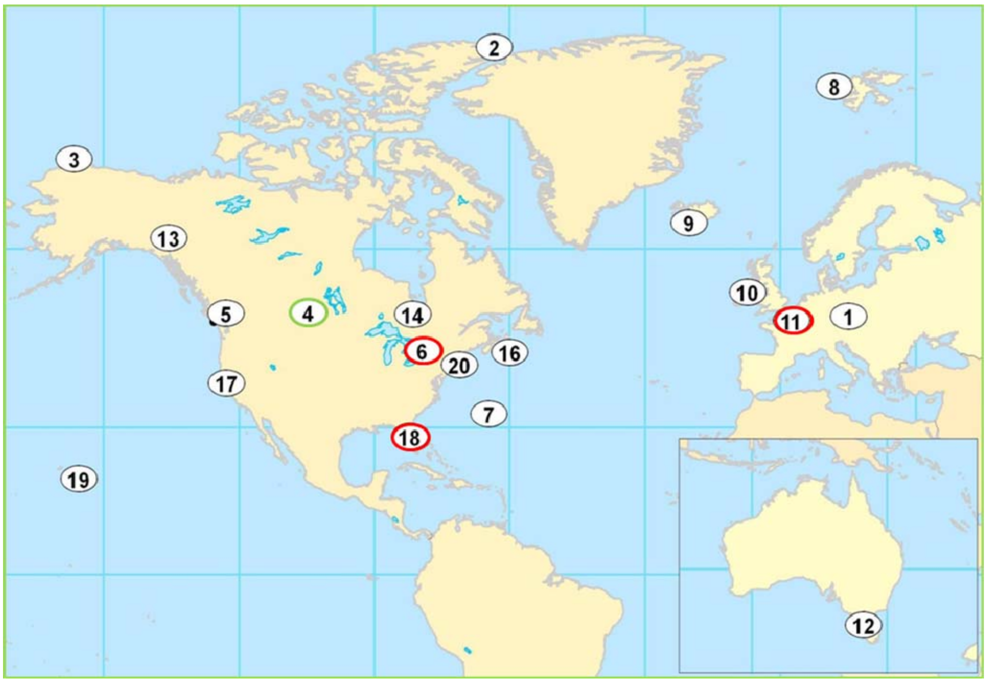

Figure 1. *The map of the sampling sites. Details on sampling sites can be found in the Supporting Material. Background and polar sites are indicated with an oval outlined in black; urban sites are outlined in red and the single agricultural site is outlined in green.*

Table 1. *List of targeted CUPS and their physico-chemical properties. The properties were calculated using SPARC software (http://archemcalc.com) and taken from literature. (NA=not available)*

	Chlorpyrifos	Dacthal	Chlorothalonil	Pendimethalin	Trifluralin
Molecular weight	350.6	332.0	265.9	281.3	335.3
log K_{OW} calc. at 25°C (SPARC, 2011)	6.35	4.62	4.76	5.68	5.33
log K_{OA} calc. at 25°C (SPARC, 2011)	9.38	9.71	8.36	9.84	9.24
log K_{OA} calc. at 25°C (Yao et al., 2007)	8.28	8.45	7.69	NA	7.73
log K_{OA} meas. at 20°C (Yao et al., 2007)	8.88	8.51	8.11	NA	7.93

So far, there have been no long–term calibration studies of the PUF disk or SIP disk samplers for CUPs. This is identified as a future research need that would allow application of Equation (1) with greater confidence.

4. Results and Discussion

4.1. QA/QC

Field blanks for both the PUF and SIP disk samplers were collected at each sampling site. Field blanks were collected by installing the PUF or SIP disk in the chamber for 1 minute and then treating it as a sample. CUPs were below detection limit in all field blanks as well as solvent blanks, and therefore, blank correction of samples was not necessary.

Air concentrations for targeted CUPs in PUF disk and SIP disks are summarized in Tables S2 and S3, respectively. The average extraction recoveries of CUPs investigated in this study are listed in Table S4 (see the SM). The most frequently detected CUP was dacthal (18/20 for PUF disk samples and 16/20 for SIP disk samples). Malathion and metribuzin were below limits of quantification (defined as the lowest calibration point) in all SIP disk samples and detected in only a few PUF disk samplers – 1/20 and 3/20 respectively. Differences in detection frequency of target compounds in PUF disks versus SIP disks may reflect an analytical issue rather than superiority in performance of one over the other. For instance, SIP disks extracts sometimes contain trace amounts of XAD powder which may remove target compound from solution, especially when concentrating extracts down to less than 1 mL. Another source of discrepancy between PUF and SIP disk samples is differences in extraction methods. PUF disks were Soxhlet extracted with petroleum ether for 24 h (following the GAPS Network protocol) followed by 4 hours with methanol. SIP disks, which generally sorb contaminants more strongly compared to PUF disks, were extracted using a more polar solvent mixture comprising acetone/petroleum ether (50:50 v/v) for 24 hours, followed by a 4 hour extraction with methanol (Genualdi et al., 2010).

The resulting air concentrations of CUPs at the 20 global sites are illustrated in Figure 2 for SIP disks, while results for PUF disks are in Table S2 (see the SM). Chlorothalonil is the most abundant CUP in the global atmosphere reflecting its widespread use, while dacthal demonstrates a high potential for transport, with greatest detection frequency at remote sites. This result for dacthal is consistent with empirical evidence used to assess long–range transport of selected CUPs (Muir et al., 2004).

The following section compares results from PUF disks and SIP disks for individual CUPs.

4.2. Comparison of PUF versus SIP

Tables S2 and S3 (see the SM) summarize results for the CUPs which were detected in both PUF and SIP disks. One of the main objectives of the pilot study was to compare the ability of the PUF disk and SIP disk samplers to collect a range of target analytes including CUPs. A similar comparison was previously performed for PCBs (Genualdi et al., 2010) and OCPs and PBDEs (Koblizkova et al., 2012) and showed excellent agreement for the two sampler types with SIP disks also demonstrating greater sorptive capacity for additional, more volatile compound classes.

Figure 3 summarizes the correlations between air concentrations derived from PUF and SIP disk passive samplers. The air concentrations were calculated from amount of compounds captured by the sampler, the average sampling rate (calculated from losses of the depuration compounds) and number of sampling days, as discussed previously.

Correlations were significant (p–values < 0.005) for trifluralin, chlorpyrifos, chlorothalonil, and dacthal. The p–value for the chlorothalonil regression after excluding the highest concentration drops to 0.31. The p–value for the pendimethalin regression was 0.109 and likely due to low number of data pairs (i.e. n = 3).

Dacthal. This herbicide is only registered for use in the United Kingdom, Canada, the United States, New Zealand, and Australia (Ruggirello et al., 2010). In the United States, dacthal underwent re–registration and is still in use (Hoferkamp et al., 2010). Previous studies have documented the long–range transport of dacthal via air and its presence in remote ecosystems such as the Arctic (Muir et al., 2004; Hoferkamp et al., 2010). Dacthal was the most frequently detected CUP in this study with concentrations ranging from below the LOQ to a few pg/m^3 at remote sites to the highest concentration at the site in Sydney, FL of 80 pg/m^3 in PUF and 140 pg/m^3 in SIP. The usage of dacthal in the US is ~10 times higher than in Canada, which is in agreement with our results showing the highest air concentrations at sites in the USA. Air concentrations of dacthal at Canadian sites are consistent with the values detected during previous studies. For instance, Yao et al. (2007) reported dacthal concentrations in air at Canadian agricultural sites under the CANCUP study in the range 0.4–50 pg/m^3 (Yao et al., 2007).

The correlation between air concentrations determined using PUF and SIP disk samplers indicate that for dacthal the SIP generates an air concentration which is on average about two times higher compared to the PUF disk. The underestimation for the PUF disk may be due to approach to equilibrium during the deployment period, which we did not account for (i.e. we assume linear sampling over three months) and this would result in an overestimate of the air sample volume and hence an underestimation of the PUF disk–derived air concentration. Based on the measured log K_{OA} value for dacthal (8.51, Table 1) and previous uptake profiles derived for non–polar hydrophobic chemicals investigated under the GAPS Network, it is likely that dacthal has reached equilibrium in the PUF disk during the three month deployment; whereas the SIP disk should remain in the linear phase for the entire deployment period and have a larger effective air sample volume. Field calibrations (uptake studies) for both PUF disk and SIP disks are required in order to estimate the uptake rate [k_a in Equation (1)] and maximum sorption capacity of these media relative to air (i.e. K_{PSM-A} values) for a range of CUPs that would allow the full uptake profile [(Equation (1)] to be derived.

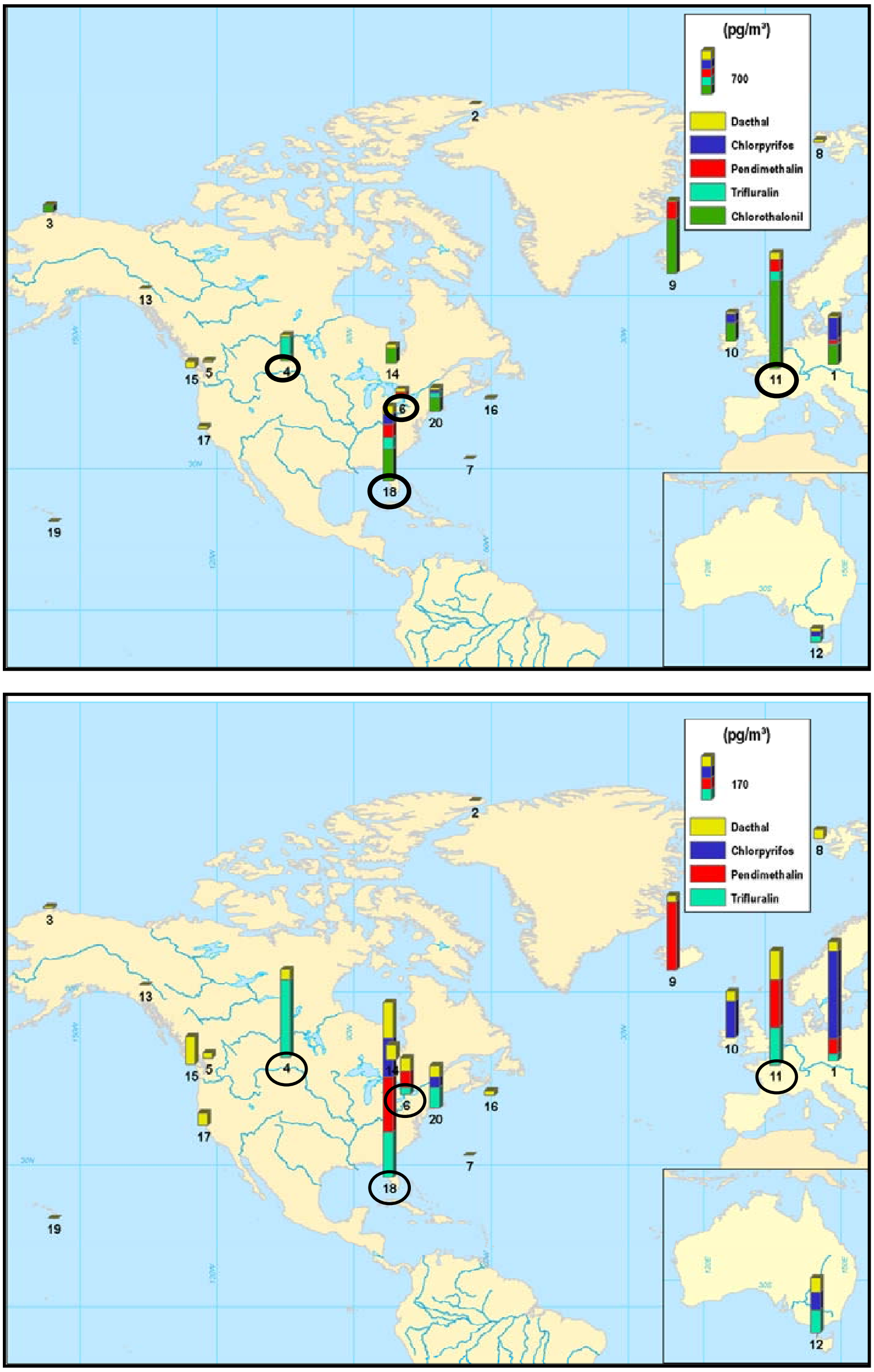

***Figure 2.** Air concentrations of CUPs across 20 global sites derived from SIP disk samplers. Chlorothalonil is included in the top panel and excluded from the bottom panel. Ovals indicate agricultural and urban sites (see also Figure 1).*

Trifluralin. Trifluralin is a fluorinated herbicide, which is mostly used in cotton cultivation (Kannan et al., 2003). Its extended use in North America and Europe, together with its relatively high vapor pressure, make trifluralin a likely candidate for atmospheric transport (Bossi et al., 2008). Air concentrations of trifluralin were fairly low at most background sites (below detection to a few tens of pg/m^3) with the exception of Cape Grim, Australia where the concentration was 110 pg/m^3 based on the PUF disk. Highest concentrations of trifluralin were reported at the three urban–type sites and especially the single agricultural site at Bratt's Lake, SK where the air concentration based on the SIP disk sampler was 300 pg/m^3. Previous air studies at the Bratt's Lake site have also revealed high concentrations of trifluralin averaging 1 600 pg/m^3 during the summer growing season (Yao et al., 2008). Previous measurements of trifluralin at Canadian agricultural sites under the CANCUP study revealed air concentrations in the range 6–90 pg/m^3 (Yao et al., 2006), which are in the range of results from our study.

Similar to the results for dacthal above, the SIP disk sampler generates higher air concentrations compared to the PUF disk. Here again, this is likely due to the lower sorptive capacity of the PUF disk (compared to the SIP disk) as reflected by the relatively low log K_{OA} value for trifluralin (7.93, Table 1, measured value) compared to the other CUPs. The net result is an underestimation of the true air concentration when using the PUF disk under the assumption of linear phase sampling.

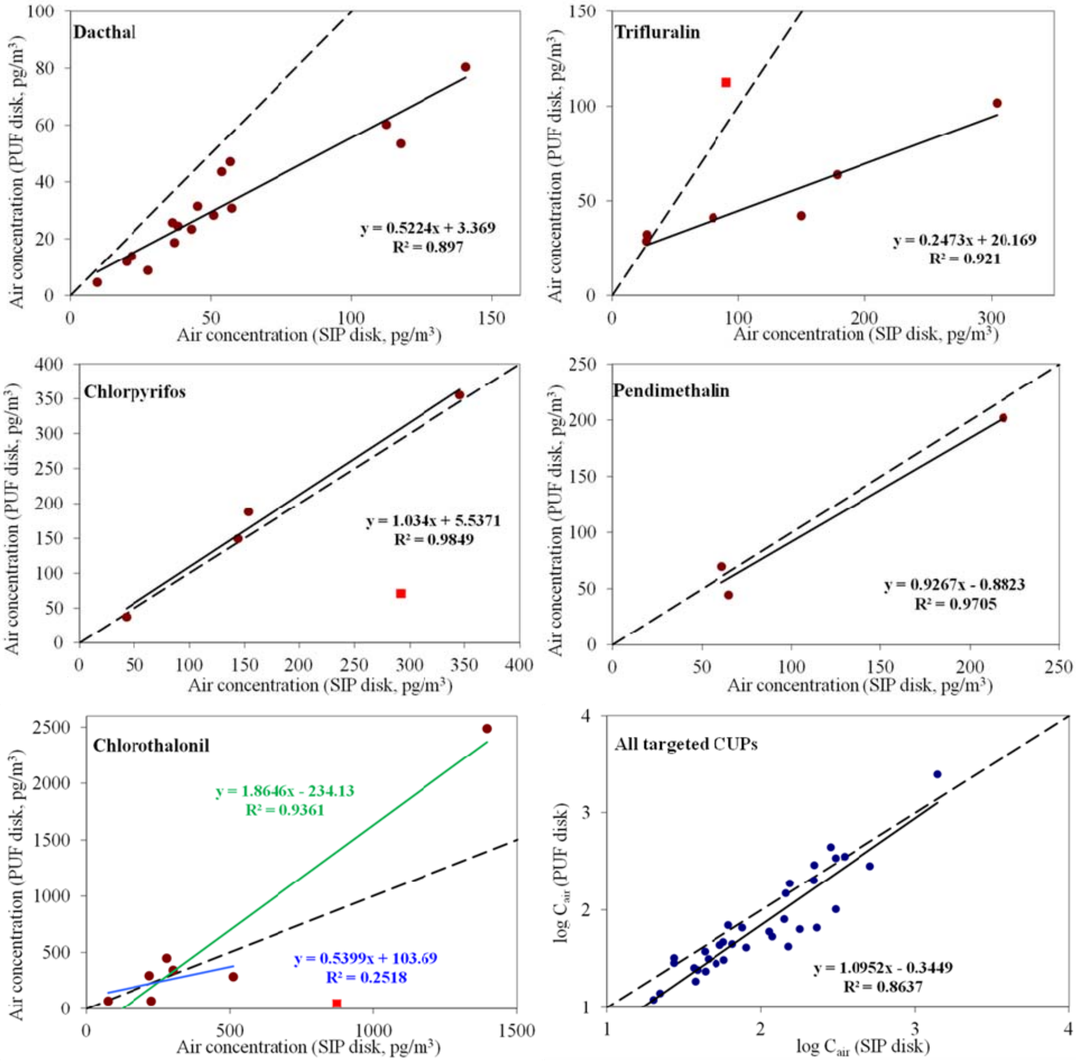

Figure 3. *Comparison between SIP and PUF disk samplers using linear regressions of measured air concentrations of CUPs in pg/m^3. Red squares show outliers, which were excluded from correlations. Chlorothalonil graph (bottom left panel) shows correlations with and without the highest concentrations. The bottom right panel shows correlations of logarithmic values of air concentrations for all targeted CUPs.The 1:1 dashed line represents perfect agreement.*

Chlorpyrifos. Chlorpyrifos was widely used as a broad–spectrum insecticide since 1962 (Ruggirello et al., 2010). In 2000, chlorpyrifos was phased out in the USA for residential and termite use (Hoferkamp et al., 2010). Air concentrations were below detection at most sites. Highest concentrations in air were found at Kosetice, Czech Republic (360 pg/m^3 in PUF and 350 pg/m^3 in SIP).

Air concentrations of chlorpyrifos reported under the CANCUP study were in the range 110–770 pg/m^3 (Yao et al., 2006). With the exception of one data point, the agreement between PUF– and SIP–derived air concentrations for chlorpyrifos was excellent. This is likely attributed to the relatively high log K_{OA} value for chlorpyrifos (8.88, Table 1, measured value) that would help to ensure linear phase sampling over the entire 3–month deployment period for both types of passive air samplers.

Pendimethalin. Pendimethalin is an herbicide used in pre–emergence and post–emergence applications to control annual grasses and certain broadleaf weeds. Similar to chlorpyrifos, air concentrations were below detection at most sites. The highest concentration in air was detected at Sydney, FL in PUF disk sampler (200 pg/m^3) and in Storhofdi, Iceland in SIP disk sampler (270 pg/m^3 in SIP). Detected concentrations are consistent with the concentration levels found in previous studies, e.g. in France (Coscolla et al., 2010) or in Ontario, Canada (Gouin et al., 2008a; Hayward et al., 2010).

There were only three locations where pendimethalin was detected in both PUF and SIP disk. Although the agreement between PUF and SIP is quite good (slope = 0.93, R^2 = 0.97), it is not significant (p = 0.109) due to the low number of data points (i.e. n = 3). Calculated log K_{OA} value for pendimethalin is 9.84 (Table 1, based on SPARC on–line calculator; note: measured value is not available), indicating that there is linear phase sampling for the PUF disks during the deployment period. This is consistent with the good agreement between PUF and SIP.

Chlorothalonil. Chlorothalonil is a broad–spectrum organochlorine fungicide used to control fungi on vegetables, trees, and other agricultural crops. It is the second most widely used fungicide in the USA. The highest concentration in air was found at Paris, France (2 500 pg/m^3 in PUF and 1 400 pg/m^3 in SIP). Other high values included Storhofdi, Iceland in the SIP disk sampler (870 pg/m^3) and in Malin Head, Ireland in the PUF disk sampler (450 pg/m^3). These are consistent with the range of values reported in Ontario, Canada by Hayward et al. (2010) (918±427 pg/m^3) and Gouin et al. (2008a) (1 740 pg/m^3). However, previous measurements of chlorothalonil under CANCUP revealed very high air concentrations in 2003, in the range 3 030–11 900 pg/m^3 (Yao et al., 2006).

The resulting slope of the correlation between air concentrations derived from PUF versus SIP disk sampler is 1.86

(n = 7, R^2 = 0.94). This decreases to 0.540 (n = 6, R^2 = 0.25) after removing the very high value from the site in Paris, which drives the correlation. The slope of 0.540 points to a capacity issue for the PUF disks, similar to what was seen for dacthal and trifluralin. Similar to dacthal and trifluralin, chlorothalonil has a relatively low measured log K_{OA} value (8.11, Table 1) that would result in equilibrium or near–equilibrium in the PUF disk during a 3–month deployment. However, the approach to equilibrium of the PUF disk, does not explain the result for Paris that showed a much higher result for the PUF disk compared to that for the SIP disk. In general, the results for chlorothalonil (as compared to other CUPs) in PUF versus SIP are quite variable. This may be partly attributed to the poor recoveries for chlorothalonil (Table S4, see the SM) which lead to greater uncertainty of the data. Other studies have also reported greater variability for chlorothalonil compared to other CUPs. For instance, Gouin et al. (2008b) observed large variability in experimentally determined sampling rates for chlorothalonil using the XAD–based passive sampler. They suggested that it might be caused by sampling of chlorothalonil in curvilinear region of the uptake curve.

5. Implications

This study builds on previously published results comparing performance of PUF and SIP disk passive samplers for a range of legacy POPs and emerging chemicals which are of interest to research and monitoring activities for POPs. Testing and validation of the SIP disk sampler is important for its future application as a complement to and/or replacement for the PUF disk sampler which has already proven to be very useful in meeting the challenges of the global monitoring plan of the Stockholm Convention on POPs. As shown for other classes of POPs (Genualdi et al., 2010; Genualdi et al., 2011) the SIP disk generates comparable results to the PUF disk sampler and has the advantage of a higher sorptive capacity for the more volatile compounds.

The results of this study show that although the PUF disk sampler is able to capture many of the relevant classes of CUPs, it approaches equilibrium over the 3–month deployment for some compounds having lower K_{OA} values. Approach to equilibrium of the PUF disk is more problematic at higher ambient air temperatures as this results in a reduced sampler capacity.

Future work is needed to characterize the full uptake profile for PUF disk samplers so that accurate air concentrations can be derived that account for approach to equilibrium of the PUF disk. Uptake profiles should also be performed for the higher capacity SIP disk samplers to better define its range of operation for CUPs and other compounds of interest.

Lastly, the detection of CUPs at sites that are far removed from areas of application is indicative of the long–range transport potential of these chemicals.

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Supporting Material Available

Additional details on sample collection, site details and air concentration results for CUPs. This information is available free of charge via the Internet at http://www.atmospolres.com.

References

Bossi, R., Skov, H., Vorkamp, K., Christensen, J., Rastogi, S.C., Egelov, A., Petersen, D., 2008. Atmospheric concentrations of organochlorine pesticides, polybrominated diphenyl ethers and polychloronaphthalenes in Nuuk, South-West Greenland. *Atmospheric Environment* 42, 7293-7303.

Chernyak, S.M., Rice, C.P., McConnell, L.L., 1996. Evidence of currently used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi seas. *Marine Pollution Bulletin* 32, 410-419.

Coscolla, C., Colin, P., Yahyaoui, A., Petrique, O., Yusa, V., Mellouki, A., Pastor, A., 2010. Occurrence of currently used pesticides in ambient air of Centre Region (France). *Atmospheric Environment* 44, 3915-3925.

Genualdi, S., Harner, T., Cheng, Y., MacLeod, M., Hansen, K.M., van Egmond, R., Shoeib, M., Lee, S.C., 2011. Global distribution of linear and cyclic volatile methyl siloxanes in air. *Environmental Science and Technology* 45, 3349-3354.

Genualdi, S., Lee, S.C., Shoeib, M., Gawor, A., Ahrens, L., Harner, T., 2010. Global pilot study of legacy and emerging persistent organic pollutants using sorbent-impregnated polyurethane foam disk passive air samplers. *Environmental Science and Technology* 44, 5534-5539.

Gouin, T., Shoeib, M., Harner, T., 2008a. Atmospheric concentrations of current-use pesticides across south-central Ontario using monthly-resolved passive air samplers. *Atmospheric Environment* 42, 8096-8104.

Gouin, T., Wania, F., Ruepert, C., Castillo, L.E., 2008b. Field testing passive air samplers for current use pesticides in a tropical environment. *Environmental Science and Technology* 42, 6625-6630.

Halsall, C.J., Bailey, R., Stern, G.A., Barrie, L.A., Fellin, P., Muir, D.C.G., Rosenberg, B., Rovinsky, F.Y., Kononov, E.Y., Pastukhov, B., 1998. Multi-year observations of organohalogen pesticides in the Arctic atmosphere. *Environmental Pollution* 102, 51-62.

Hayward, S.J., Gouin, T., Wania, F., 2010. Levels and seasonal variability of pesticides in the rural atmosphere of Southern Ontario. *Journal of Agricultural and Food Chemistry* 58, 1077-1084.

Hoferkamp, L., Hermanson, M.H., Muir, D.C.G., 2010. Current use pesticides in Arctic media; 2000-2007. *Science of the Total Environment* 408, 2985-2994.

Hung, H., Blanchard, P., Halsall, C.J., Bidleman, T.F., Stern, G.A., Fellin, P., Muir, D.C.G., Barrie, L.A., Jantunen, L.M., Helm, P.A., Ma, J., Konoplev, A., 2005. Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: results from a decade of monitoring. *Science of the Total Environment* 342, 119-144.

Iwata, H., Tanabe, S., Aramoto, M., Sakai, N., Tatsukawa, R., 1994. Persistent organochlorine residues in sediments from the Chukchi Sea, Bering Sea and Gulf of Alaska. *Marine Pollution Bulletin* 28, 746-753.

Kannan, K., Battula, S., Loganathan, B.G., Hong, C.S., Lam, W.H., Villeneuve, D.L., Sajwan, K., Giesy, J.P., Aldous, K.M., 2003. Trace organic contaminants, including toxaphene and trifluralin, in cotton field soils from Georgia and South Carolina, USA. *Archives of Environmental Contamination and Toxicology* 45, 30-36.

Koblizkova, M., Genualdi, S., Lee, S.C., Harner, T., 2012. Application of sorbent impregnated polyurethane foam (SIP) disk passive air samplers for investigating organochlorine pesticides and polybrominated diphenyl ethers at the global scale. *Environmental Science and Technology* 46, 391-396.

Muir, D.C.G., Teixeira, C., Wania, F., 2004. Empirical and modeling evidence of regional atmospheric transport of current-use pesticides. *Environmental Toxicology and Chemistry* 23, 2421-2432.

Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C.G., Jones, K.C., 2009. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. *Environmental Science and Technology* 43, 796-803.

Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air: results from the GAPS study. *Environmental Science and Technology* 40, 4867-4873.

Ruggirello, R.M., Hermanson, M.H., Isaksson, E., Teixeira, C., Forsstrom, S., Muir, D.C.G., Pohjola, V., van de Wal, R., Meijer, H.A.J., 2010. Current use and legacy pesticide deposition to ice caps on Svalbard, Norway. *Journal of Geophysical Research-Atmospheres* 115, Art. No. D18308.

Shoeib, M., Harner, T., Lee, S.C., Lane, D., Zhu, J.P., 2008. Sorbent-impregnated polyurethane foam disk for passive air sampling of volatile fluorinated chemicals. *Analytical Chemistry* 80, 675-682.

Shunthirasingham, C., Oyiliagu, C.E., Cao, X.S., Gouin, T., Wania, F., Lee, S.C., Pozo, K., Harner, T., Muir, D.C.G., 2010. Spatial and temporal pattern of pesticides in the global atmosphere. *Journal of Environmental Monitoring* 12, 1650-1657.

Tuduri, L., Harner, T., Blanchard, P., Li, Y.F., Poissant, L., Waite, D.T., Murphy, C., Belzer, W., 2006. A review of currently used pesticides (CUPs) in Canadian air and precipitation: part 1: lindane and endosulfans. *Atmospheric Environment* 40, 1563-1578.

SPARC on-line calculator: http://archemcalc.com/sparc/ October 2011 release w4.6.1691-s4.6.1687.

UNECE, 1998. Protocol on Persistent Organic Pollutants under the 1979 Convention on Long-Range Transboundary Air Pollution: United Nations Economic Commission for Europe. http://www.unece.org/env/lrtap/full%20text/1998.POPs.e.pdf.

UNEP, 2001 Stockholm Convention on Persistent Organic Pollutants (POPs), Interim Secretariat for the Stockholm Convention. United Nations Environment Programme (UNEP) Chemicals, Geneva, Switzerland. www.pops.int, 50 pp.

Wania, F., 2003. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in Polar Regions. *Environmental Science and Technology* 37, 1344-1351.

Yao, Y., Harner, T., Blanchard, P., Tuduri, L., Waite, D., Poissant, L., Murphy, C., Belzer, W., Aulagnier, F., Sverko, E., 2008. Pesticides in the atmosphere across Canadian agricultural regions. *Environmental Science and Technology* 42, 5931-5937.

Yao, Y., Harner, T., Ma, J.M., Tuduri, L., Blanchardt, P., 2007. Sources and occurrence of dacthal in the Canadian atmosphere. *Environmental Science and Technology* 41, 688-694.

Yao, Y., Tuduri, L., Harner, T., Blanchard, P., Waite, D., Poissant, L., Murphy, C., Belzer, W., Aulagnier, F., Li, Y.F., Sverko, E., 2006. Spatial and temporal distribution of pesticide air concentrations in Canadian agricultural regions. *Atmospheric Environment* 40, 4339-4351.