Environ. Sci. Technol. **2008,** *42,* 6625–6630

Field Testing Passive Air Samplers for Current Use Pesticides in a Tropical Environment

TODD GOUIN,*,†,§ FRANK WANIA,† CLEMENS RUEPERT,‡ AND LUISA E. CASTILLO‡

Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, Canada, M1C 1A4, and Instituto Regional de Estudios en Sustancias Toxicas, Campus Omar Dengo, Universidad Nacional, Heredia, Costa Rica

Received March 25, 2008. Revised manuscript received June 11, 2008. Accepted June 12, 2008.

Air was sampled for one year in the central valley of Costa Rica using an active high-volume sampler as well as passive samplers (PAS) based on polyurethane foam (PUF) disks and XAD-resin filled mesh cylinders. Extracts were analyzed for pesticides that are either banned or currently used in Costa Rican agriculture. Sampling rates for PUF-based passive air samplers, determined from the loss of depuration compounds spiked on the disks prior to deployment, averaged 5.9 ± 0.9 $m^3 \cdot d^{-1}$ and were higher during the windier dry season than during the rainy season. Sampling rates for the XAD-based passive sampler were determined from the slopes of linear relationships that were observed between the amount of pesticide sequestered in the resin and the length of deployment, which varied from 4 months to 1 year. Those sampling rates increased with decreasing molecular size of a pesticide, and their average of 2.1 ± 1.5 $m^3 \cdot d^{-1}$ is higher than rates previously reported for temperate and polar sampling sites. Even though the trends of the sampling rate with molecular size and temperature are consistent with the hypothesis that molecular diffusion controls uptake in passive samplers, the trends are much more pronounced than a direct proportionality between sampling rate and molecular diffusivity would suggest. Air concentrations derived by the three sampling methods are within a factor of 2 of each other, suggesting that properly calibrated PAS can be effective tools for monitoring levels of pesticides in the tropical atmosphere. In particular, HiVol samplers, PUF-disk samplers, and XAD-based passive samplers are suitable for obtaining information on air concentration variability on the time scale of days, seasons and years, respectively. This study represents the first calibration study for the uptake of current use pesticides by passive air samplers.

Introduction

Methods for monitoring trace levels of organic pollutants in air typically rely on high-volume (HiVol) sampling pumps that require trained site operators and access to electricity (*1*). Passive air samplers (PAS), on the other hand, require no electricity, minimal maintenance, and are relatively inexpensive and simple to use. They are increasingly used to assess the spatial and temporal trends of a wide variety of organic contaminants from regional to global scales with integration periods ranging from weeks, to months and even years (*2–6*). A PAS takes up organic contaminant from the atmospheric gas phase by diffusion until retrieved or until equilibrium partitioning between the atmosphere and the sampling medium is achieved (*7–12*). Calibration studies for various PAS have yielded sampling rates that can be used to derive temporally averaged volumetric air concentrations within a factor of 2−3 of those measured with conventional techniques (*1*). In applications aimed at the assessment of broad spatial and temporal concentration trends, such uncertainty is generally acceptable.

Virtually all PAS calibration studies have been conducted in temperate and polar areas (*7*) or under tightly controlled indoor conditions (*8, 13*). As a result, stability, performance, and sampling rates of PAS have not been established under the hot and humid conditions prevalent in tropical regions. Yet, PAS appear particularly useful for monitoring organic pollutants in these regions (*14, 15*). Many tropical countries rely heavily on agriculture to sustain their economies. Extensive pesticide use aimed at enhancing agricultural productivity increases the risk of exposing humans and the environment to harmful chemicals (*16–19*). Costa Rica, the largest user of agricultural pesticides in Central America, imported nearly 150 000 t of active ingredients between 1977 and 2000, with usage increasing since the late 1990s (*20*). Whereas most industrialized countries possess the resources to monitor use and environmental levels of pesticides, many tropical countries do not have the same capacity, and the inability to enact or enforce regulatory measures may result in the indiscriminant use of registered and banned pesticides (*17*). A network of PAS could provide a cost-effective tool for monitoring levels of pesticides in the atmosphere, identify areas of concern, and inform regulatory measures to control and limit the chemical exposure of local inhabitants and the environment (*15*).

Improving the understanding of how PAS perform under different environmental conditions would also enhance the reliability of PAS as a monitoring tool on the continental or global scale (*9, 21*). When using PAS in large scale networks, e.g., as part of a global monitoring network for persistent organic pollutants (*4, 22*), the PAS are operating under very different climatic conditions. If PAS performance and sampling rates should depend on climatic variables, the comparability of data derived from PAS deployed at different latitudes or altitudes could be compromised. There is thus a need to calibrate PAS under different environmental conditions so that air concentration data can be derived and compared for a broad range of organic compound classes and locations. Here we present results of a field calibration, performed in Costa Rica, aimed at measuring the sampling rates of two different types of PAS for pesticides under tropical conditions.

Materials and Methods

Field Sampling Site. The study was conducted at the Universidad Nacional air monitoring field station in San

---

* Corresponding author phone: 907 474-1966: fax: 907 474-5640; e-mail: fftg@uaf.edu.

† University of Toronto.

‡ Universidad Nacional.

§ Current address: University of Alaska Fairbanks, Department of Chemistry & Biochemistry, P.O. Box 756160, Fairbanks, AK 99775-6160.

10.1021/es8008425 CCC: $40.75

Antonio de Belen (9° 59′ 14″ N, 84° 10′ 39″ W; altitude, 919 m), Costa Rica, between October 10, 2005 and October 24, 2006, jointly operated by the Laboratory of Atmospheric Chemistry (UNA-LAQAT), the Municipality of Belen, Ministry of Health, and the Ministry of Environment. The field site, referred to as the Belen field site, is located in a suburban area about 15 km northwest of Costa Rica's largest city, San José (Figure S1 in the Supporting Information (SI)). Meteorological data were obtained from the Juan Santamaria International Airport, less than 5 km north of the site. Temperatures during the study ranged from 10 to 31 °C, with a mean of 23 °C.

Sampling Procedure. The study design involved the sampling of air using three different methods, namely a pumped HiVol air sampler, the XAD-2 resin PAS (XAD-PAS) by Wania et al. (*7*) and the PUF disk PAS (PUF-PAS) by Shoeib and Harner (*8*). SI Figure S2 illustrates the design and dimensions of the PAS sampling chambers for the PUF-PAS and XAD-PAS used in this study. Because XAD-resin has a higher uptake capacity for organic contaminants than PUF, the XAD-PAS is suitable for extended periods of nonequilibrium sampling up to, and in excess of, one year (*7*), whereas the PUF-based sampler approaches equilibrium for many organic contaminants within a period of a few months (*8*). Reflecting those differences, the design of the calibration study was slightly different for the two PAS.

A total of nine air samples were collected at the Belen field site between October 17, 2005 and September 11, 2006 using a HiVol air sampler. During each 24 h sampling period approximately 820 m^3 of air were first pulled through a precombusted glass-fiber filter (GFF, Whatman, 11 cm diameter) to collect the particle phase, and then through XAD-2 resin (Supelco, Supelpak-2, precleaned Amberlite XAD-2 resin, 20/60 mesh) sandwiched between two PUF plugs (Supelco, precleaned large PUF plug, 6 × 3.8 cm) to collect the gas phase. On October 10, 2005, 12 XAD-PAS (Supelco, Supelpak-2, precleaned Amberlite XAD-2 resin, 20/60 mesh), and two PUF-PAS (14 cm diameter, 1.35 cm thick, 365 cm^2 surface area, 0.0213 $g\cdot cm^{-3}$) were deployed at the sampling site. Each of the PAS was securely mounted to a railing at about 5 m above the ground. A pair of XAD-PAS was collected approximately every two months to monitor the uptake of pesticides with time, with the first pair being retrieved after 4 months of exposure and the last pair being retrieved on October 24, 2006. At the same two month intervals, duplicate PUF-PAS, spiked with a suite of depuration compounds (*2*), were replaced to monitor temporal trends during the year of the study. SI Table S1 provides details regarding exact dates of deployment.

Extraction and Quantification. HiVol air samples were Soxhlet-extracted for 18 h with 250 mL of dichloromethane (DCM). Separate extraction of the GFF allowed for an assessment of gas/particle partitioning. The second PUF plug in the PUF/XAD-2 sandwich was also extracted separately to quantify the extent of breakthrough of target pesticides. The XAD-2 resin from the XAD-PAS was transferred from the mesh cylinder to preextracted extraction thimbles and Soxhlet extracted for 18 h with 250 mL of DCM. PUF disks from the PUF-PAS were Soxhlet extracted for 18 h with 250 mL of petroleum ether. Prior to extraction, all samples were spiked with 10 μL of 100 μg/μL each of deuterated trifluralin (d_{14}-trifluralin) and chlorpyrifos (d_{10}-chlorpyrifos) to assess method recoveries. Extracts were reduced by rotary evaporation and nitrogen blow-down to 500 μL and solvent exchanged into isooctane. Extracts were then filtered through 1 g of anhydrous sodium sulfate to remove excess moisture, reduced to 500 μL, and transferred to GC vials. Mirex (100 ng) was added as an internal standard to all samples and standards prior to analysis. Details regarding instrumental analysis are provided in the Supporting Information.

Quality Assurance/Quality Control. Field, travel, and laboratory blanks were collected for both the HiVol and PAS. Of the pesticides analyzed, only hexachlorobenzene (HCB) was detected in all blanks. The limit of quantification (LOQ), defined as the mean blank value plus 10× standard deviation, for HCB was 15 $pg\cdot m^{-3}$. Dacthal and γ-HCH were occasionally detected, with one field blank having elevated levels of γ-HCH. The LOQ for γ-HCH and dacthal was 146 and 0.9 $pg\cdot m^{-3}$, respectively. Given its high LOQ, no γ-HCH data are presented. Mean method recoveries were 90 and 74% for d_{10}-chlorpyrifos and d_{14}-trifluralin, respectively for the PUF-PAS extracted with petroleum ether; 100% for each d_{10}-chlorpyrifos and d_{14}-trifluralin for the XAD-PAS extracted with dichloromethane; and 90 and 84% for d_{10}-chlorpyrifos and d_{14}-trifluralin, respectively for the high-volume air samples extracted with dichloromethane. Chlorpyrifos, endosulfan I, and HCB were detected on the back PUF of the PUF/XAD-2 sandwich, with chlorpyrifos and endosulfan I being <1% of the concentration in the top PUF/XAD-2, and HCB being <10%, suggesting that sample breakthrough was minimal for these pesticides.

Theory of Uptake by PAS. The uptake of pesticides by a PAS is based on vapor diffusion from the bulk air phase into the sorbent (XAD or PUF), as described by Fick's first law. Assuming that the concentration in air (C_{air}) remains constant with time, the mass in the PAS will increase linearly with time, until equilibrium is approached (*7, 8, 21, 23*). Assuming that during the phase of linear uptake the rate of desorption is negligible compared to the rate of sorption, (i.e., $C_{surface} = 0$), the concentration in the PAS (C_{PAS}) can be estimated as follows:

$$C_{PAS} = C_{air}Rt \tag{1}$$

where C_{air} is the concentration in air averaged over the duration of the sampling period, *t*, and *R* ($m^3\cdot day^{-1}$) is the sampling rate.

To estimate an air concentration, the amount sequestered in a PAS must be divided by an effective air sample volume. If equilibrium between atmospheric gas phase and PAS medium is not approached, this volume is simply the product of the daily sampling rate *R* and the deployment period *t*. Whereas *R* for XAD-PAS is derived from calibration studies such as this one, the *R* for PUF-PAS can be estimated from the recovery of spiked depuration compounds, as described by Gouin et al. (*2*). The depuration compounds added to the PUF-PAS prior to deployment in the field were deuterated γ-hexachlorocyclohexane ($d_6\gamma$-HCH), 2,3,3′,4,5-pentachlorobiphenyl (PCB-107), and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl (PCB-198). Recoveries are reported in SI Table S3. For relatively volatile chemicals with low PUF-air partitioning coefficients ($K_{PUF\text{-}air}$), which may attain equilibrium, eq 1 is no longer a valid basis for estimating effective sample volumes. In such cases, a chemical-specific sampling volume can be estimated based on a relationship between the octanol-air partition coefficient (K_{OA}) and $K_{PUF\text{-}air}$ (*8*). In this instance, effective sampling volumes for HCB and chlorothalonil, the most volatile of the target analytes, were estimated to be 100 and 80 m^3, respectively, for deployment periods of about 2 months and temperatures of about 25 °C.

It is typically assumed that the transfer of chemical to the PAS is limited by molecular diffusion across a stagnant boundary layer adjacent to the sampling resin. The mass transfer coefficient *k* and therefore also *R* should be related to the molecular diffusivity (D_{air}) of the sampled substances in air. D_{air} increases with decreasing molecular size and increasing temperature, suggesting that *R* could vary for different chemicals and for PAS deployed at different temperatures.

Results and Discussion

High Volume Air Concentrations. Air concentrations in all nine HiVol samples are reported in SI Table S2. Several pesticides were detected in nearly all HiVol air samples. Some of these, including HCB, the chlordanes, and dieldrin, have been banned in Costa Rica since about 1988 (*17*), whereas others, such as chlorothalonil, chlorpyrifos, pendimethalin, and endosulfan, are currently in use. The same pesticides were commonly detected in the PAS. The pesticides were primarily observed in the PUF/XAD-2 sorbent, with negligible amounts on the GFF. Consequently our discussion relates primarily to the gaseous phase, and no estimates of the particle-air partitioning are possible.

With concentrations ranging from 60 to 475 pg·m^{-3} and an arithmetic mean of 165 pg·m^{-3}, HCB was the dominant banned pesticide in air. The use of HCB as a fungicide was discontinued in most countries during the 1970s. Current sources to the atmosphere include the use of chlorinated solvents and pesticides containing HCB as a byproduct and HCB volatilizing from contaminated soils (*24*). The average global concentration of HCB is in the range of 50−150 pg·m^{-3} (*25*). Shen et al. (*26*) observed HCB air concentrations ranging from 50 to 133 pg·m^{-3} based on XAD-PAS deployed across North America. The concentrations observed in this study are higher than the annual average of 63 pg·m^{-3} reported previously for Monteverde, Costa Rica (*26*). The difference may reflect differences in local activity. Whereas Monteverde is located in the mountains far from agricultural activity, Belen is in the country's central valley, a densely populated area with extensive agricultural activity. The higher concentrations in the current study thus likely reflect both past usage of HCB and current use of chlorinated fungicides, such as chlorothalonil and quintozene, which contain HCB impurities (*17, 27, 28*), and which are used in the central valley.

Dieldrin air concentrations, ranging from 1.4 to 40 pg·m^{-3} and averaging at 9.5 pg·m^{-3}, are consistent with levels between 20 and 27 pg·m^{-3} derived from XAD-PAS deployed at several sites in Costa Rica's central valley in 2004 (*15*). They are also similar to concentrations in the range of 3.3−31 pg·m^{-3} reported for the Laurentian Great Lakes region (*29*), as well as those observed in Chiapas, Mexico, which were between 2 and 37 pg·m^{-3} (*30*). Chlordanes in the air samples are dominated by *trans*-chlordane (TC), with concentrations ranging from 0.5 to 17 pg·m^{-3}, whereas concentrations of *cis*-chlordane (CC) and *trans*-nonachlor were similar to one another, ranging from 0.3 to 8.2 pg·m^{-3} and 0.2 to 6.3 pg·m^{-3}, respectively. The TC/CC ratios range between 1.8 and 2.3, well above the 1.16 in technical chlordane (*31*). This is consistent with the higher volatility of TC compared to CC (*32*), and also suggests that the chlordane in the atmosphere likely originated from only slightly degraded sources. Mean air concentrations of heptachlor and heptachlor exoepoxide, an insecticide that is similar to chlordane, were 5.5 and 1.7 pg·m^{-3}, respectively. The concentrations of chlordanes, heptachlor, and heptachlor exoepoxide, as well as the TC/CC ratios observed in this study are within a factor of 2 of XAD-PAS data reported by Daly et al. (*15*) for the central valley region.

Concentrations of chlorpyrifos in air ranged from 144 to 1266 pg·m^{-3}, with a mean of 602 pg·m^{-3}. Relatively high levels were also observed for endosulfan I, with concentrations between 49 and 564 pg·m^{-3}, and a mean of 261 pg·m^{-3}. Endosulfan II, the less abundant isomer of the technical mixture, and the degradation product endosulfan sulfate were both observed, with mean concentrations of 65 and 6 pg·m^{-3}, respectively. Chlorpyrifos and endosulfan are used in the control of insect pests, such as the coffee berry borer (*33*). Thus, the elevated levels are consistent with the usage of these two insecticides in the coffee plantations that dominate the agricultural activity in the vicinity of the field site at Belen.

Chlorothalonil, which is a fungicide aerially applied to banana plantations (*34*), and the preemergent herbicide pendimethalin, used in Costa Rican rice and sugar cane production (*35, 36*), were observed at mean levels of 28 pg·m^{-3} and 9.5 pg·m^{-3}, respectively. Bananas, rice, and sugar cane are not important crops in the central valley of Costa Rica, and the relatively low concentrations of chlorothalonil and pendimethalin may reflect the limited use of these pesticides in this region. Trifluralin and dacthal were observed in all samples at concentrations near the instrumental detection limit. Metribuzin and malathion were observed in less than half the samples, with mean air concentrations of 0.5 and 3.1 pg·m^{-3}, respectively. The low concentrations imply limited use of these pesticides in the vicinity of the sampling site. None of the remaining pesticides monitored were detected in any of the samples.

Uptake Rates for PUF-PAS. Sampler specific sampling rates *R* for PUF-PAS determined in this study ranged from 4.8 to 7.8 m^3·d^{-1}, with a mean of 5.9 ± 0.9 m^3·d^{-1}. This is within the range observed for PUF-PAS deployed globally (*22*) (3.9 ± 2 m^3·d^{-1}). Sampling rates were higher during the dry season (i.e., January to May) (6.7 ± 1 m^3·d^{-1}) than during the rainy season (May to December) (5.6 ± 0.6 m^3·d^{-1}). The difference may be related to a doubling of wind speed between the dry and wet seasons, from an average of about 3.2 to 5.9 m·s^{-1}, respectively. It is unclear how differences in relative humidity might have influenced *R*, but we do not believe it to play an important role. Air concentrations for all PUF-PAS were estimated using sampler specific sampling rates and are given in SI Table S3. These sample rates are applied to all pesticides, except HCB and chlorothalonil, for which equilibrium is assumed. Duplicate PUF-PAS showed good agreement (SI Table S3). Averages for the entire sampling period are included in SI Table S5.

Uptake Rates by the XAD-PAS. Similar to duplicate PUF-PAS, duplicate XAD-PAS showed good agreement (SI Table S4), and were collected after 4, 6, 8, 10, and 12 months of deployment. The amounts of pesticides sequestered in each XAD-PAS are given in the Supporting Information. Figure 1 plots those amounts against the length of deployment. The uptake curves for nearly all pesticides are linear, with the notable exception of chlorpyrifos, which shows large variability in the data, and HCB and chlorothalonil, which may be in the curvilinear region of uptake (i.e., approaching equilibrium). Based on eq 1, the slope of these uptake curves equals $C_{\text{air}} \cdot R$ and dividing it by the mean air concentration during the deployment period yields the sampling rate *R*. SI Table S5 lists the slopes and coefficient of determination of the linear regressions, and the estimated sampling rates for each of the pesticides shown in Figure 2. Mean annual air concentrations based on the PUF-PAS are used in the derivation of *R* since they were deployed continuously throughout the deployment period of the XAD-PAS, whereas the data obtained from the HiVol represent <3% of the deployment period of the XAD-PAS.

The sampling rates for all pesticide chemicals fall between 0.8 and 5.4 m^3·d^{-1}, with the exception of an unusually small *R* for chlorpyrifos (0.01 m^3·d^{-1}). Assuming that the sampling rate for chlorpyrifos is an outlier, the average sampling rate of the XAD-PAS for the remaining pesticides is 2.1 ± 1.5 m^3·d^{-1}. This *R* is approximately four times greater than the value of 0.52 m^{-3}·d^{-1} used for pesticides in earlier XAD-PAS based studies (*15, 26*). This lower sampling rate was based on a field calibration performed in the Arctic (*7*), and therefore may not be applicable to tropical environments. Individual sampling rates estimated by Wania et al. (*7*) in their calibration study of XAD-PAS range from 0.42 to 2.25 m^3·d^{-1} for field sites located in Arctic and southern Canada. Indeed, the high

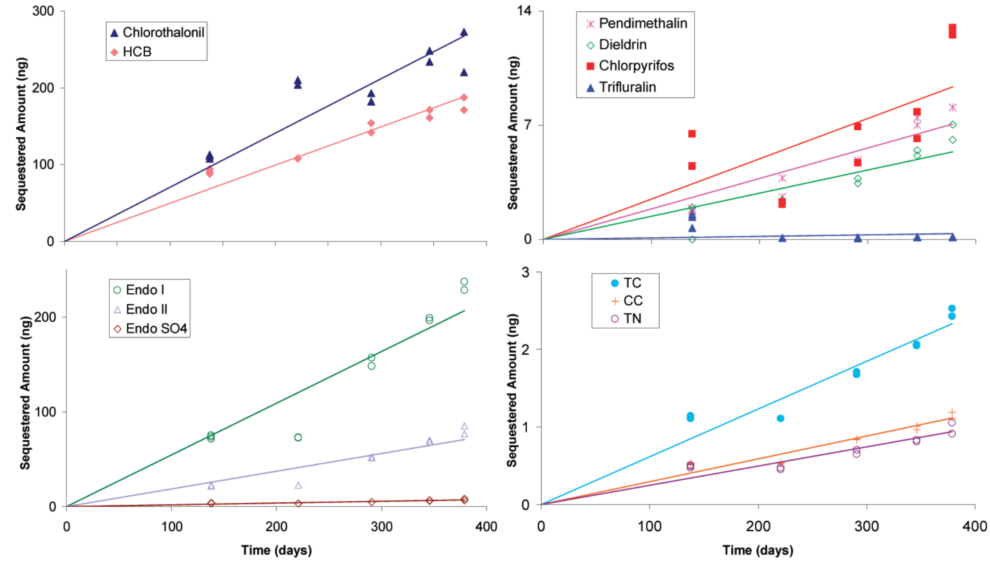

FIGURE 1. Uptake curves of several current-use and banned pesticides in XAD-PAS deployed for periods of up to one year at the field site in Belen, Costa Rica.

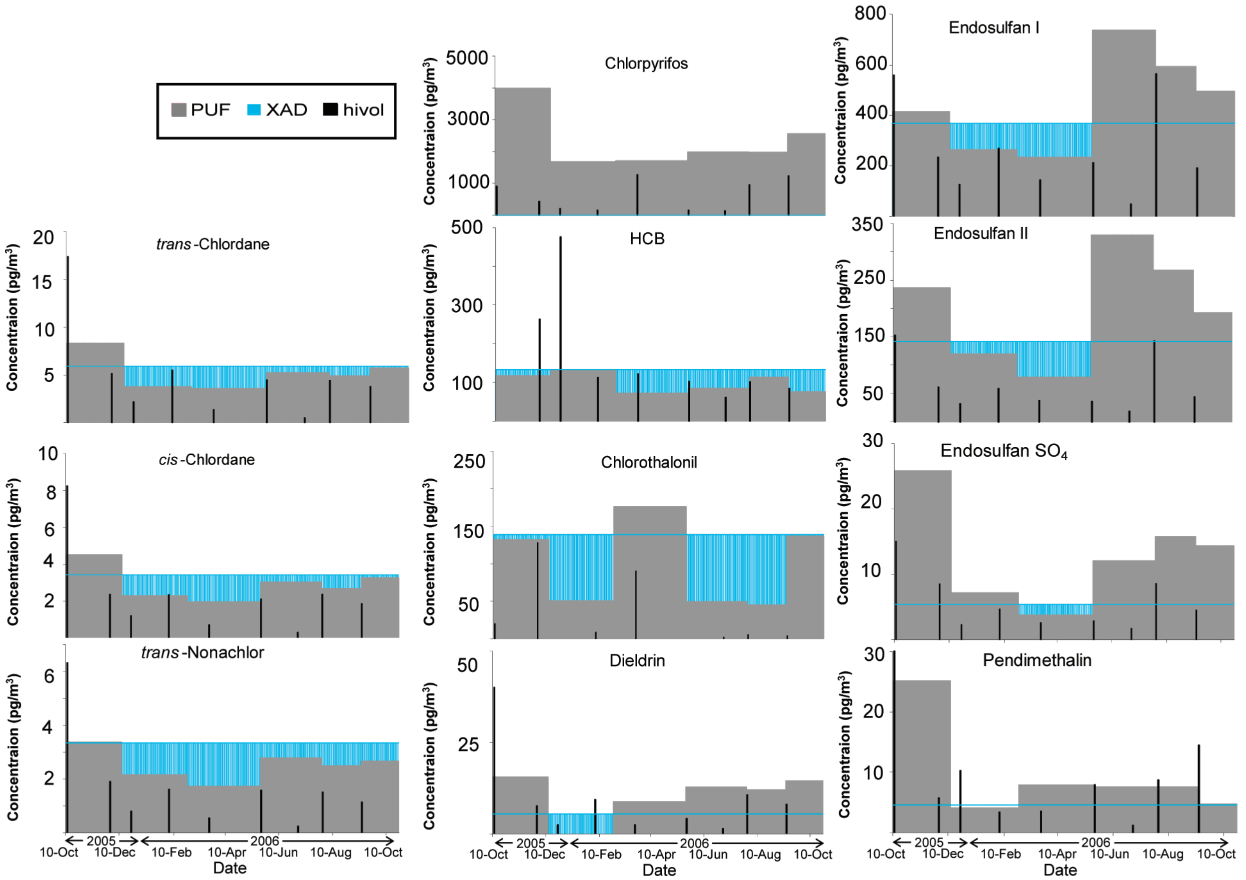

FIGURE 2. Comparison of air concentrations for pesticides measured using three different air sampling methods at the field site at Belen, Costa Rica between October 10, 2005 and October 24, 2005. Data from the XAD-PAS for chlorpyrifos are omitted given uncertainty in its sampling rate.

uncertainty of *R* is acknowledged by earlier authors (*26*, *15*) who express caution when expressing XAD-PAS data in terms of volumetric air concentrations.

Some of the difference in sampling rates between different pesticides may be attributed to the size dependence of D_{air}, calculated using the Fuller, Schettler, Giddings equation:

$$D_{air} = 0.001T^{1.75}(1/M_A + 1/M_X)^{0.5}/P(VA^{1/3} + VX^{1/3})^2 \quad (2)$$

where *T* is temperature (K), *P* is atmospheric pressure (atm), M_A and M_X are the molecular mass of air (28.96 g·mol^{-1}) and pesticide *X*, respectively, and V_A and V_X are the atomic volumes of air (20.1 m^3·mol^{-1}) and pesticide *X*, respectively (*11*). SI Table S5 includes estimates of D_{air} for each of the pesticides at 25 °C. Chlorothalonil, the smallest pesticide had the highest estimated D_{air} of 6.9 mm^2·s^{-1}, and the highest *R* of 5.4 ± 3.2 m^3·d^{-1}, whereas three relatively large chlordane related compounds with an estimated D_{air} below 5 $mm^2 \cdot s^{-1}$ had low R of only 0.9 ± 0.2 $m^3 \cdot d^{-1}$. Intermediate sized pesticides with D_{air} between 5 and 5.3 $mm^2 \cdot s^{-1}$ had an average R of 2.2 ± 0.9 $m^3 \cdot d^{-1}$. Although there is a strong correlation between R and D_{air} ($r^2 = 0.865$, SI Figure S4) the variation of the sampling rates for different pesticides with molecular size observed in this study is much larger (a factor of 3) than can be explained by the effect of molecular size on D_{air} (a factor of 1.3).

The same is true for the apparent temperature dependence of R. For instance, D_{air} for HCB at −17, 8.7, and 25 °C is estimated to be 4.4, 5.2, and 6.4 $mm^2 \cdot s^{-1}$, respectively This means that HCB is diffusing approximately 30% faster under tropical temperature conditions than under High Arctic conditions. If molecular diffusion is the main mechanism of accumulation in XAD-PAS, then it seems reasonable to expect higher sampling rates at higher environmental temperatures, and we would expect R to be higher in Costa Rica than in Canada (*7*), which is indeed the case. However, as with the differences in R between chemicals of different size, the differences in R between cold and warm field sites is much larger than would be expected from the relatively minor effect of temperature on D_{air}. Overall, it appears that the dependence of R on D_{air} is much larger than a direct proportionality would suggest, and implies that some other factor, such as the potential for temperature-induced convection through the PAS chamber, may be influencing sampling rates. Even if we presently have no explanation, it certainly highlights the importance of assessing sampling rates for PAS for a wide range of compounds under different environmental conditions. The same argument can be applied to the PUF-PAS, for which sampling rates are slightly higher than those previously observed. The sampling rates in SI Table S5 were used to estimate average air concentrations from the XAD-PAS deployed at the Belen field site for 12 months (SI Table S6).

The unusually low sampling rate estimated for chlorpyrifos requires some discussion. In the derivation of eq 1 the assumptions were made that air concentration remain relatively constant over the deployment period, and that the rate of desorption is negligible. Factors that might compromise the validity of these assumptions are significant variability in air concentrations, the sampler reaching equilibrium for a particular chemical, or the occurrence of some other loss process, such as degradation in the XAD-PAS. The unreasonably low sampling rate for chlorpyrifos should be considered questionable solely based on the poor linearity of its uptake curve (Figure 2), as indicated by a low r^2 value of 0.47. It is unclear which mechanism may be influencing the lack of linearity for chlorpyrifos, but it is likely attributed to any of the processes described above.

Comparison between Methods and Seasonality of Air Concentrations. Figure 2 compares air concentrations determined by the three different sampling techniques for each of the pesticides. Air concentrations between the three methods are generally consistent, within a factor of 2 of each other, which implies that any of the three methods could be used independently to monitor levels of pesticides in air.

Generally, air concentrations of banned pesticides remained relatively constant throughout the year (Figure 2). The PUF-PAS, which resolve concentrations on a bimonthly basis, show some temporal variability, but in general concentrations do not vary by more than a factor of 2 from one period to another. Such limited temporal variability is expected, since the primary source of these banned compounds to the atmosphere is likely advection from elsewhere or volatilization from historically contaminated soils, and, since temperatures in Costa Rica remain relatively constant throughout the year, the volatilization rates should also remain relatively constant.

Concentrations of the pesticides in current use show much larger variability (Figure 2), which is likely related to seasonally varying usage. While some of this variability is captured by the HiVol, the trends are most evident in the data obtained from the PUF-PAS. It appears that the insecticide endosulfan is more heavily used during the rainy season, which begins in May. This usage is likely associated with chemical control of insects affecting agricultural crops, since this is the period when crops are developing. During the dry season (beginning in December) agricultural crops, such as coffee beans are being harvested, and hence usage is low. Concentrations of chlorothalonil also show a strong seasonal pattern, which indicates that this fungicide is being applied twice a year, coinciding with the beginning and the end of the rainy season. Pendimethalin is a preemergent herbicide that has elevated levels in air during the end of the rainy season. Whereas the PUF-PAS data reveal these seasonal patterns quite clearly, the nine days of HiVol sampling appear to represent too limited a fraction of the entire year to capture the same trends. This suggests that there is considerable short-term variability from day to day in the air concentrations of currently used pesticides and a single day of sampling within a two month period may be insufficient to characterize their average air concentrations.

This observation highlights the strengths and weaknesses of the various air sampling methods. The PUF-PAS provides temporal information that can be used to relate atmospheric levels of current-use pesticides to seasonal usage patterns. The HiVol samples can provide information on short-term variability and transport episodes, whereas the XAD-PAS is most suitable for monitoring long-term trends. All three methods provide air concentration data that complement and are consistent with one another, and that could be used in combination, depending on the resources available and the type of questions being addressed.

Acknowledgments

This study was funded in part by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the United Nations Environmental Programme Chemicals, and through a Canada−Latin America and the Caribbean Research Exchange Grant by the Association of Universities and Colleges of Canada. Access to the field site at Belen was granted by the Liceo de Belen.

Supporting Information Available

Additional tables, figures, and text. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Harner, T.; Bartkow, M.; Holoubek, I.; Klanova, J.; Wania, F.; Gioia, R.; Moeckel, C.; Sweetman, A. J.; Jones, K. C. Passive air sampling for persistent organic pollutants: Introductory remarks to the special issue. *Envrion. Pollut.* **2006**, *144*, 361–364.

(2) Gouin, T.; Harner, T.; Blanchard, P.; Mackay, D. Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes Basin. *Environ. Sci. Technol.* **2005**, *39*, 9115–9122.

(3) Meijer, S. N.; Ockenden, W. A.; Steinnes, E.; Corrigan, B. P.; Jones, K. C. Spatial and temporal trends of POPs in Norwegian and UK background air: Implications for global cycling. *Environ. Sci. Technol.* **2003**, *37*, 454–461.

(4) Harner, T.; Pozo, K.; Gouin, T.; Macdonald, A.-M.; Hung, H.; Cainey, J.; Peters, A. Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. *Environ. Pollut.* **2006**, *144*, 445–452.

(5) Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ. Sci. Technol.* **2004**, *38*, 34–41.

(6) Shen, L.; Wania, F.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Bidleman, T. F. Hexachlorocyclohexanes in the North American atmosphere. *Environ. Sci. Technol.* **2004**, *38*, 965–975.

(7) Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G. Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere. *Environ. Sci. Technol.* **2003**, *37*, 1352–1359.
(8) Shoeib, M.; Harner, T. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36*, 4142–4151.
(9) Bohlin, P.; Jones, K. C.; Strandberg, B. Occupational and indoor air exposure to persistent organic pollutants: A review of passive sampling techniques and needs. *J. Environ. Monitor.* **2007**, *9*, 501–509.
(10) Huckins, J. N.; Petty, J. D.; Lebo, J. A.; Almeida, F. V.; Booij, K.; Alvarez, D. A.; Clark, R. C.; Mogensen, B. B. Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. *Environ. Sci. Technol.* **2002**, *36*, 85–91.
(11) Bland, M. A.; Crisp, S.; Houlgate, P. R.; Llewellyn, J. W. Determination of lindane vapor in air by passive sampling. 1. Development of the passive sampling device and measurement of the diffusion-coefficient of lindane in air. *Analyst* **1984**, *109*, 1517–1521.
(12) Bartkow, M. E.; Booij, K.; Kennedy, K. E.; Muller, J. F.; Hawker, D. W. Passive air sampling theory for semivolatile organic compounds. *Chemosphere* **2005**, *60*, 170–176.
(13) Hazrati, S.; Harrad, S. Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs): Factors influencing sampling rates. *Chemosphere* **2007**, *67*, 448–455.
(14) Santiago, E. C.; Cayetano, M. G. Polycyclic aromatic hydrocarbons in ambient air in the Philippines derived from passive sampler with polyurethane foam disk. *Atmos. Environ.* **2007**, *41*, 4138–4147.
(15) Daly, G. L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Castillo, L. E.; Jantunen, L. M. M.; Wania, F. Organochlorine pesticides in the soils and atmosphere of Costa Rica. *Environ. Sci. Technol.* **2007**, *41*, 1124–1130.
(16) Wesseling, C.; Antich, D.; Hogstedt, C.; Rodriguez, A. C.; Ahlbom, A. Geographical differences of cancer incidence in Costa Rica in relation to environmental and occupational pesticide exposure. *Int. J. Epidemiol.* **1999**, *28*, 365–374.
(17) Castillo, L. E.; delaCruz, E.; Ruepert, C. Ecotoxicology and pesticides in tropical aquatic ecosystems of Central America. *Environ. Toxicol. Chem.* **1997**, *16*, 41–51.
(18) Monge, P.; Partanen, T.; Wesseling, C.; Bravo, V.; Ruepert, C.; Burstyn, I. Assessment of pesticide exposure in the agricultural population of Costa Rica. *Annu. Occup. Hyg.* **2005**, *49*, 375–384.
(19) Wesseling, C.; Corriols, M.; Bravo, V. Acute pesticide poisoning and pesticide registration in Central America. *Annu. Occup. Hyg.* **2005**, 207.
(20) Valcke, M.; Chaverri, F.; Monge, P.; Bravo, V.; Mergler, D.; Partanen, T.; Wesseling, C. Pesticide prioritization for a case-control study on childhood leukemia in Costa Rica: A simple stepwise approach. *Environ. Res.* **2005**, *97*, 335–347.
(21) Tolnai, B.; Gelencser, A.; Gal, C.; Hlavay, J. Evaluation of the reliability of diffusive sampling in environmental monitoring. *Anal. Chim. Acta* **2000**, *408*, 117–122.
(22) Pozo, K.; Harner, T.; Wania, F.; Muir, D. C. G.; Jones, K. C.; Barrie, L. A. Toward a global network for persistent organic pollutants in air: Results from the GAPS study. *Environ. Sci. Technol.* **2006**, *40*, 4867–4873.
(23) Petty, J. D.; Huckins, J. N.; Zajicek, J. L. Application of semipermeable-membrane devices (SPMDs) as passive air samplers. *Chemosphere* **1993**, *27*, 1609–1624.
(24) Breivik, K.; Alcock, R.; Li, Y.-F.; Bailey, R. E.; Fiedler, H.; Pacyna, J. M. Primary sources of selected POPs: Regional and global scale emission inventories. *Environ. Pollut.* **2004**, *128*, 3–16.
(25) Pacyna, J. M.; Oehme, M. Long-range transport of some organic-compounds to the Norwegian Arctic. *Atmos. Environ.* **1988**, *22*, 243–257.
(26) Shen, L.; Wania, F.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Bidleman, T. F. Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America. *Environ. Sci. Technol.* **2005**, *39*, 409–420.
(27) Chaves, A.; Shea, D.; Cope, W. G. Environmental fate of chlorothalonil in a Costa Rican banana plantation. *Chemosphere* **2007**, *69*, 1166–1174.
(28) Ambrus, A.; Hamilton, D. J.; Kuiper, H. A.; Racke, K. D. *Significance of impurities in the safety evaluation of crop protection products (IUPAC technical report). Pure Appl. Chem.* **2003**, *75*, 937–973.
(29) Cortes, D. R.; Hoff, R. M.; Brice, K. A.; Hites, R. A. Evidence of current pesticide use from temporal and Clausius-Clapeyron plots: A case study from the Integrated Atmospheric Deposition Network. *Environ. Sci. Technol.* **1999**, *33*, 2145–2150.
(30) Alegria, H.; Bidleman, T. F.; Figueroa, M. S. Organochlorine pesticides in the ambient air of Chiapas, Mexico. *Environ. Pollut.* **2006**, *140*, 483–491.
(31) Jantunen, L. M. M.; Bidleman, T. F.; Harner, T.; Parkhurst, W. J. Toxaphene, chlordane, and other organochlorine pesticides in Alabama air. *Environ. Sci. Technol.* **2000**, *34*, 5097–5105.
(32) Shen, L.; Wania, F. Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. *J. Chem. Eng. Data* **2005**, *50*, 742–768.
(33) Jansen, A. *Plant Protection in Coffee: Recommendations for the common code for the coffee community-initiative*; Deutsche Gesellschaft für Technische Zusammenarbeit GmbH: Eschborn, Germany, July 2005, *2005*, p 65.
(34) Castillo, L. E.; Ruepert, C.; Solis, E. Pesticide residues in the aquatic environment of banana plantation areas in the north Atlantic zone of Costa Rica. *Environ. Toxicol. Chem.* **2000**, *19*, 1942–1950.
(35) Smith, M. C.; Valverde, B. E.; Merayo, A.; Fonseca, J. F. Integrated management of itchgrass in a corn cropping system: modeling the effect of control tactics. *Weed Sci.* **2001**, *49*, 123–134.
(36) Riches, C. R.; Knights, J. S.; Chaves, L.; Caseley, J. C.; Valverde, B. E. The role of pendimethalin in the integrated management of propanil-resistant *Echinochloa colona* in Central America. *Pestic. Sci.* **1997**, *51*, 341–346.

ES8008425