Characterization of Polymer-Coated Glass as a Passive Air Sampler for Persistent Organic Pollutants

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The use of thin-film polymer-coated glass surfaces or POGs as passive air samplers was investigated during an uptake experiment in an indoor environment with high levels of gas-phase polychlorinated biphenyls (PCBs). POGs consisted of a micron thick layer of ethylene vinyl acetate (EVA) coated onto glass cylinders. The uptake was initially linear with time and governed by the air-side mass transfer coefficient and surface area of the sampler. This was followed by a curvilinear region and finally a constant phase when equilibrium was established between air and EVA. The high surface area-to-volume ratio of the POGs allowed rapid equilibrium with gas-phase PCBs; equilibration times were on the order of hours for the low molecular weight congeners. The equilibrium concentration was dependent on the EVA-air partition coefficient, K_{EVA-A}, which was shown to be very well correlated to the octanol−air partition coefficient, K_{OA}. When POGs of varying thickness were equilibrated with air, the amount of PCB accumulated increased with increasing thickness of the EVA, indicating that uptake was by absorption into the entire polymer matrix. A wind field of 4 m s^{-1} resulted in an increased uptake rate by a factor of approximately six compared to uptake in relatively still air. This wind speed effect was diminished, however, when POGs were housed in deployment chambers consisting of inverted stainless steel bowls. Relationships based on the air-side mass transfer coefficient and K_{EVA-A} were developed for PCBs that describe the entire uptake profile and allow air concentrations to be determined from the amount of chemical accumulated in the POG. It is believed that these relationships are also valid when POGs are used to detect other classes of persistent organic pollutants.

Introduction

Research on persistent organic pollutants (POPs) would benefit from a simple approach for estimating air concentrations. For the indoor environment, such data are useful for assessing exposure and evaluating risk. Kohler et al. (*1*)

found alarmingly high ΣPCB levels in public buildings in Switzerland in the range 700−4000 ng m^{-3}, 2−3 orders of magnitude greater than typical outdoor concentrations. They attributed this to construction materials such as sealants that may contain up to 30% PCB. Similar studies have investigated indoor concentrations of OCs (*2*), PAH (*3*, *4*), gaseous elemental mercury (*5*), and brominated flame retardants (*6*, *7*). An increasing number of new chemicals are components of conventional construction materials and/or are contained in common household products. Examples include brominated flame retardants (BFRs) which are added to foam materials (e.g. couch cushions, chairs and bed matresses) and electronics and fluorinated chemicals such as PFOS, that are applied to carpets and textiles for stain resistance. These typically "indoor" chemicals have been detected in the remote arctic where they have been shown to accumulate in the food chain (*8*, *9*). Emissions from indoor sources are suspected to be the dominant source to the outside.

A need also exists for a simple approach to sample outdoor air in order to address uncertainties over the sources, long-range transport, and surface-air exchange of POPs. It would be beneficial to have an approach that enables simultaneous sampling of air in different places or repeated sampling events over time. Spatial mapping studies could be on a range of scales, from around a potential point source, across a city or region, or even nationally, regionally, or globally.

The indoor and outdoor sampling needs discussed above are usually not feasible with conventional hi-volume air samplers which are loud and intrusive, in the context of indoor sampling, and expensive and require power which limits their potential for outdoor studies. Hence, there is considerable incentive to develop passive air sampling techniques.

Several interesting studies have made use of "environmental media", such as leaves and pine needles (*10*−*12*), tree bark (*13*), soil (*14*, *15*), and butter (*16*), where POPs concentrations are believed to broadly reflect ambient levels. However, there are often issues of sample comparability, exposure time, uptake kinetics, and potential confounding factors, which can produce uncertainties in data interpretation

It is envisaged that these problems can be excluded if passive samplers can be designed and calibrated, which allow reliable estimates of air concentrations to be made. Several designs are possible and—indeed—are desirable. For example, it would be useful to have samplers which integrate ambient concentrations over time scales as short as hours or as long as months/years. Shorter time scales facilitate studies of contaminant dispersal, fluxes, and transport processes and can provide data for dispersion/transport modeling. Longer time scales allow underlying trends in ambient levels to be investigated. To date, most work on passive samplers has focused on integrating concentrations over weeks/months. Outdoor studies have focused on samplers with a high "capacity" to retain POPs, such as semipermeable membrane devices (SPMDs) (*17*−*22*), polyurethane foam (PUFs) disks (*23*), and XAD resins (*24*). However, exciting possibilities are being developed for short-term sampling. For instance, Koziel et al. (*25*) have used solid-phase microextraction (SPME) to sample formaldehyde in indoor air.

It is also possible to operate on the principle that gas-phase POPs partition from the air onto samplers of "low capacity", reaching equilibrium with the sampler. These

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would require knowledge of the time to attain equilibrium, the influence of temperature on the gas phase-sampler equilibrium partition coefficient, and would need to be coupled with a sensitive and robust extraction and analytical methodology. Examples include SPME, where the analytes can be introduced directly into a gas chromatograph (GC) (26, 27), or thin film coatings which can be extracted, cleaned up, and analyzed by conventional methods, or thermally desorbed (28, 29). Mayer et al. (30) review a variety of "equilibrium sampling devices" or ESDs and discuss strategies for their application for monitoring semivolatile organic chemicals. Wilcockson and Gobas (28) developed a passive sampler consisting of thin films of ethylene vinyl acetate onto glass that was used to measure the chemical fugacities in fish tissues and other solid substrates. This is referred to as a **PO**lymer-coated **G**lass (POG) sampler. The high surface-to-volume ratio that can be achieved with POGs allows rapid equilibration (hours/days) of target analytes, while varying the surface area or coating thickness offers the opportunity to vary the sensitivity and sampling time for different analytes and to meet different study objectives.

In this study, the POG sampler is tested and characterized as a passive sampler for measuring elevated concentrations of POPs in indoor ambient air. Uptake rates are determined for PCBs and related to mass transfer coefficients in air, wind speed, and dependence on film thickness. The application of POGs for outdoor studies is also considered and field deployment chambers, which protect the POG from precipitation, sunlight, and wind effects, are designed and tested.

Theory

Compared to the atmosphere, organic phases such as vegetation, soil, and polymers such as EVA have a relatively high capacity (i.e. low activity coefficient) for retaining POPs. Because the EVA film is a single uniform phase, the overall mass transfer coefficient (MTC), k, controlling chemical uptake can be described using the Whitman two-film approach (31)

$$1/k = 1/k_A + 1/(k_{EVA}K_{EVA-A}) \quad (1)$$

where k_A and k_{EVA} are the air-side and EVA-side MTCs and K_{EVA-A} is the EVA-air partition coefficient (no dimensions). In eq 1, only K_{EVA-A} exhibits a strong temperature dependence (23). For nonpolar organic chemicals K_{EVA-A} is likely to be similar in magnitude to the octanol–air partition coefficient, K_{OA}. Furthermore when K_{OA} is large (i.e. $K_{OA} > 10^6$) the term $1/(k_{PSM}K_{PSM-A})$ is insignificant and mass transfer to the passive sampler is air-side controlled i.e., $k \approx k_A$. This is the case for most semivolatile POPs including the PCBs.

The net rate of chemical accumulation in EVA (g d^{-1}) can be described as

$$V_{EVA}(dC_{EVA}/dt) = k_A A_{EVA}(C_{Ao} - C_{EVA}/K_{EVA-A}) \quad (2)$$

where V_{EVA} is the volume of the passive sampling medium (cm^3), C_{EVA} and C_{Ao} are concentrations (ng m^{-3}) in the EVA and air, respectively, A_{EVA} is the planar area of the exposed portion of the passive sampler (cm^2), and k_A has units cm d^{-1}. C_{Ao} is the initial concentration in air which is assumed to remain constant over the integration period. In reality, small changes in C_{Ao} may occur over time in which case C_{Ao} is really the mean air concentration, C_A.

Equation 2 shows that the initial rate of uptake is constant, resulting in a linear increase of C_{EVA} with time; this occurs because C_{EVA} is small and K_{EVA-A} is large resulting in a small value for the loss term C_{EVA}/K_{EVA-A}. Accumulation of chemical during this phase can thus be simplified to

$$(dC_{EVA}/dt) = (k_A A_{EVA}/V_{EVA})C_A \quad (3)$$

In the linear sampling region the amount of chemical, M, sequestered in the EVA is

$$M = k_A A_{EVA} C_A t = bt \quad (4)$$

where t is the sampling time and b is the sampling rate determined by plotting M versus time, i.e., $b = k_A A_{EVA} C_A$. For monitoring studies eq 4 can be used to back-calculate C_A once the mass transfer coefficient (MTC), k_A, has been established for the particular geometry of the sampling device. In this study the MTC is simply $b/(A_{EVA}C_A)$.

Uptake will become curvilinear as C_{EVA} increases and the net uptake (dC_{EVA}/dt) will approach zero when C_{EVA}/K_{EVA-A} equals C_A. At equilibrium

$$C_A = C_{EVA}/K_{EVA-A} \quad (5)$$

If K_{EVA-A} is known (either through a calibration or through a semiempirical relationship involving K_{OA}), eq 5 can be used to back-calculate ambient air concentrations.

The complete uptake profile can be described by integrating eq 2 to yield

$$C_{PSM} = K_{EVA-A}C_A(1-\exp-[(A_{EVA})/(V_{EVA}) \times (k_A/K_{EVA-A})]t) \quad (6)$$

This is a first-order rate equation of the form $C = C_o\exp(-k_e t)$ or equivalently $\ln(C/C_o) = -k_e t$ where k_e is the loss rate constant. Because we are dealing with a uniform phase we assume that the initial uptake and loss rates are the same. The uptake constant k_U (units of time^{-1}) is calculated as

$$k_U = (A_{EVA})/(V_{EVA}) \times (k_A/K_{EVA-A}) \quad \text{or}$$
$$k_U = 1/\delta_{FILM} \times (k_A/K_{EVA-A}) \quad (7)$$

Thus the time to 95% of equilibrium, $t_{95} = \ln(0.05)/k_U \approx 3/k_U$ (28). We also arbitrarily define the upper bounds of the linear uptake phase (i.e. when uptake becomes curvilinear) as t_{25}, i.e., time when the POG has accumulated 25% of the equilibrium value. In this case $t_{25} = \ln(0.75)/k_U = 0.29/k_U$. Equation 6 can also be rearranged to determine the average ambient air concentration C_A, if C_{PSM} is measured and k_A, K_{EVA-A}, and the application time are known.

An important consideration when employing thin-film air samplers is whether to operate in the linear phase (i.e. $t < t_{25}$) or to equilibrate the EVA with ambient air ($t > t_{95}$). From eq 6, the time to equilibrium is proportional to K_{EVA-A} and inversely proportional to A_{EVA}/V_{EVA}, the surface area-to-volume ratio or inverse of the effective film thickness, δ_{FILM}, since $A_{EVA}/V_{EVA} = 1/\delta_{FILM}$. In other words, a longer linear uptake phase will occur for chemicals with large values of K_{EVA-A}. Conversely, the linear phase can be shortened by decreasing the effective film thickness. This adaptability of thin-film samplers such as POGs is an attractive attribute because it allows them to be used over short- or long-term integration periods. When exposure times result in a mixture of linear, curvilinear, and equilibrium uptake for a range of compounds being investigated, eq 6 can be used to calculate the average air concentration for each compound.

Methodology

Preparation of POGs. POGs consist of a thin film of ethylene vinyl acetate (EVA, Elvax 40W, DuPont Canada) coated onto the inside and outside surfaces of a hollow glass cyclinder (70 mm i.d. and 60 mm tall). A coating solution was prepared by dissolving 8 g of EVA pellets in 400 mL of dichloromethane (DCM). The solution was magnetically stirred for approximately 3 h or until there was no visible sign of the pellets.
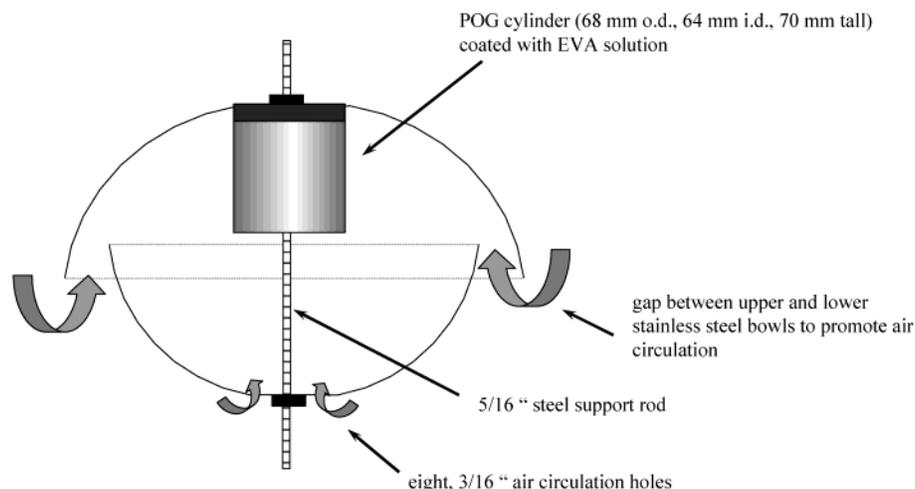
FIGURE 1. Schematic of the chamber system used to deploy polymer-coated glass (POG) cylinders in outdoor studies.

The solution was transferred to a 500 mL glass vessel. The POG cylinders were dipped in the solution covering all but the top 10 mm of the cylinder, resulting in a total coated surface of 300 cm². As the glass cylinder was withdrawn from the solution, the DCM quickly evaporated leaving a micro-layer of EVA. For application of multiple coats of EVA, the dipping step was repeated at intervals of ~30 s. The mean EVA film thickness was calculated as the mass of EVA divided by the surface area of the sampler, recognizing that some variability between samplers and within the same sampler may exist. Prior to and after exposure, POG cylinders were stored in sealed 500 mL glass jars having Teflon-lined lids.

Extraction and Cleanup. The chemical sequestered in the EVA was collected by extracting the entire EVA coating. This was accomplished by repetitive rinsing/soaking with 35 mL of DCM in a closed glass vessel. The resulting solution, containing EVA and all the analytes, was reduced in volume to 2 mL using a gentle flow of nitrogen. This solution was transferred to a centrifuge tube and solvent exchanged into 0.5 mL hexane by sequential volume reduction of DCM to near dryness and addition of hexane. At this stage, 4 mL of methanol was added resulting in the precipitation of the polymer. The polymer was separated by centrifugation at 2500 rpm for 15 min. The supernatant was transferred to a test tube and concentrated to ~1 mL of hexane (again, by sequential volume reduction of DCM) in preparation for the fractionation/cleanup using silicic acid. Extraction efficiency was tested by performing a second extraction on selected samples.

After transferring the supernatant, the wet EVA precipitate was placed under a flow of nitrogen until dryness and then weighed. The mass of EVA was determined by difference, with knowledge of the preweight of each centrifuge tube.

Sample extracts were fractionated using previously developed methodology (32) on a silicic acid-alumina column to separate PCBs from PAHs and polar compounds. The column consisted of 3 g of silicic acid (deactivated with 3% water) (Mallinckrodt Baker, Paris, KY), overlaid with 2 g of neutral alumina (deactivated with 6% water) (EM Science Inc. Glbbstown, NJ), and topped with 1 cm anhydrous sodium sulfate. The column was prewashed with 30 mL of dichloromethane and then 30 mL of petroleum ether. The sample was eluted with 30 mL of petroleum ether (fraction 1, containing PCBs) and then with 30 mL of DCM (fraction 2, containing PAHs, OC pesticides and other polar compounds). Approximately 1 mL of isooctane was used as a keeper for the rotary evaporation of the eluent. Mirex was added as internal standard for volume correction to both fractions. The first fraction was further cleaned by mixing with

TABLE 1. Experimental Details for Uptake Experiments

wind experiment		
EVA mass (g)	0.0146	
exposed surface area (cm²)	267	
EVA volume (cm³)	0.015	
EVA thickness (μm)	0.565	
multiple coating study		
exposed surface area (cm²)	140	
	2X	4X
EVA mass (g)	0.015	0.033
EVA volume (cm³)	0.015	0.034
EVA thickness (μm)	1.08	2.42

concentrated sulfuric acid and then concentrated to ~1 mL in isooctane using a gentle stream of nitrogen.

Analysis. PCBs were determined using a Hewlett-Packard 5890 gas chromatograph (GC) equipped with split/splitless injector and an electron capture detector (ECD). Injector and detector temperatures were kept at 250 °C and 300 °C, respectively. A 60 m DB-5 column (J&W Scientific) with 0.25 mm i.d. and 0.25 μm film thickness was operated with hydrogen carrier gas. The GC oven temperature program was as follows: initial at 90 °C hold for 0.5 min, 15 °C min⁻¹ to 160 °C, then 2 °C min⁻¹ to 260 °C, hold for 10 min. Mirex (U.S. Environmental Protection Agency, Research Triangle Park, NC) was used as internal standard to correct for volume difference and samples were quantified against a 56 component calibration standard (Ultra Scientific, New Kingstown, RI).

Deployment of POG Samplers. The uptake of PCBs by POGs was investigated by exposing them in a large laboratory known to have a high background PCB concentration (23). The effect of wind speed on uptake was tested using a large box fan to generate an air flow field of ~4 m s⁻¹. At the onset of the study 24 unsheltered POGs were exposed to air, 12 were subjected to wind speed of 4 m s⁻¹, and 12 were placed in another part of the lab where the wind field was not detectable. Samples were harvested over a 3-week period, at the following intervals: 0 h (x2), 4, 24 (x3), 48, 72, 120, 168, 336, and 504 h. Details are provided in Table 1. During this time high volume air samples were collected as part of a related study, and PCB air concentrations have been reported (23).

At the same time, a parallel study was conducted to investigate the effectiveness of sampling chambers (Figure 1) used for outdoor deployment of the samplers. Aside from dampening the wind speed effect on uptake rate, the samplers are also intended to protect the sampling media from precipitation, UV radiation, and impaction of atmospheric

TABLE 2. Results of Uptake Study to Investigate the Effect of Wind Speed on Sampling Rate

	PCB congener, amount (ng)						
	18	28	52	49	101	118	153
"No Wind"							
blank A	0.19	0.16	0.13	0.11	0.058	0.026	0.038
blank B	0.33	0.28	0.22	0.17	0.078	0.034	0.018
blank C	0.26	0.28	0.24	0.24	0.083	0.047	0.207
blank D	0.24	0.22	0.19	0.17	0.086	0.040	0.022
blank mean	0.25	0.23	0.20	0.17	0.076	0.036	0.071
blank SD	0.06	0.06	0.05	0.05	0.013	0.009	0.091
4 h	2.37	2.92	2.87	1.50	1.30	0.339	0.212
24 h, A	5.22	7.47	6.91	3.67	3.23	0.87	0.44
24 h, B	4.68	7.13	7.05	3.77	3.44	0.92	0.48
24 h, C	4.11	4.63	5.82	3.21	2.64	0.77	0.40
48 h	4.74	8.85	10.2	5.21	7.07	2.13	1.30
72 h	4.62	11.7	10.9	5.61	8.68	2.12	2.13
120 h	4.88	12.5	11.8	5.94	10.0	2.79	2.62
168 h	5.95	14.3	16.5	8.51	13.8	3.98	3.11
336 h	5.13	10.7	13.7	7.35	16.0	7.75	5.08
504 h	5.52	10.7	13.0	6.98	14.9	7.98	5.38
"Wind" (4 m s^{-1})							
4 h	3.68	5.54	5.88	3.00	3.13	0.86	0.53
24 h, A	7.36	14.0	17.7	9.19	14.0	4.31	2.77
24 h, B	6.00	10.6	13.8	7.45	11.1	3.61	2.20
24 h, C	6.75	12.3	16.0	8.56	12.7	4.08	2.37
48 h	4.86	9.26	13.5	6.98	16.9	8.02	5.03
72 h	7.99	14.6	22.9	11.8	27.7	12.5	7.95
120 h	7.25	15.0	20.2	10.4	28.7	15.1	9.85
168 h	4.81	10.3	16.7	8.59	25.7	16.9	12.3
336 h	4.50	9.26	14.7	7.65	22.3	17.2	12.1
504 h	6.75	12.9	17.8	9.53	24.4	20.6	15.0
Equilibrium Partitioning Results (Using "Wind" Data at 504 h)							
air concentration (pg m^{-3})	6830	4120	3150	832	438	237	87
C_{EVA} (pg m^{-3}) (504 h)	4.47E+11	8.61E+11	1.18E+12	6.31E+11	1.62E+12	1.37E+12	9.97E+11
air sampled (L)	0.99	3.15	5.65	11.5	55.8	86.9	173
log(C_{EVA}/C_{AIR})[a]	**7.82**	**8.32**	**8.57**	**8.88**	**9.57**	9.76	10.1
log K_{OA} (@ 20 °C) (21)	7.80	8.24	8.56	8.60	9.34	10.1	10.1

[a] Values in bold font indicate congeners that have come to equilibrium that were included in Figure 3.

particulate matter. It is envisaged that the use of the chambers in outdoor studies will result in a more uniform uptake rate over the entire duration of the sample and between sites that are subject to different meteorology. Three POGs were placed in chambers and exposed to a wind field for 24 h. Results will be compared to POGs that were deployed in relatively still air over the same time period.

EVA Thickness Experiment. An experiment was conducted to characterize uptake into films of varying thicknesses. Specifically, the study addresses the issue of whether the uptake of PCBs by POGs occurs by adsorption (onto the surface layer) or by absorption, directly into the entire POG matrix. Multiple POGs of two different thicknesses were made by successive dippings in the EVA solution—1.1 μm (2 dippings) and 2.4 μm (4 dippings) (Table 1). Samples were exposed to laboratory air and collected after $t = 0$ (blank), 2, 8, 24, 48, and 60 h.

Quality Assurance/Quality Control. Recoveries were performed in duplicate for PCBs by extracting a blank POG and adding a known quantity of the PCB calibration solution. This spiked sample was then taken through the sample methodology described earlier. Mean recoveries for 13 PCB congeners (2-Cl to 8-Cl) ranged from 71 to 111% with a mean of 77%. These were satisfactory, and no correction was applied to the data.

To test the efficiency of the sample extraction procedure, a second extraction was performed on a sample that was exposed for 504 h in the laboratory. Results showed that the methodology was satisfactory. More than 95% of the analyte was removed in the first extraction for 90% of the PCBs

determined. In one case (PCB 180) approximately 14% was collected in the second extract.

Results and Discussion

Uptake Study: Equilibrium versus Linear Sampling and Wind Speed Effect. The results of the uptake study are presented in Table 2 for several of the dominant 3-Cl to 6-Cl PCBs that are observed in air—congeners 18, 28, 52, 49, 101, 118, and 153. A graphical comparison of the uptake under calm (no wind) and windy conditions (4 m s^{-1}) is shown in Figure 2 for PCB 28 and PCB 153. PCB 28 is typical of the lower molecular weight congeners investigated here. Equilibrium is established for PCB 28 within the time frame of the study under both windy and calm conditions when approximately 10–15 ng has been accumulated in the POG sampler. Under windy conditions the time to achieve equilibrium was reduced by a factor of about five—20 h versus 100 h. This occurs because higher wind speeds reduce the thickness of the microboundary layer above the POG surface, which acts as a resistance to air-side mass transfer. As a result, the air-side MTC (k_A value) increases. These results demonstrate the dominant role of air-side resistance to overall mass transfer to the POG. PCB 153, on the other hand, does not reach equilibrium because it has a larger EVA mass capacity and hence larger K_{EVA-A} (and smaller k_U). For PCB 153, the wind speed effect is demonstrated by a steeper uptake slope (Figure 2).

The effect of wind speed on the uptake rate is an important consideration when designing samplers for outdoor deployment. If the objective is to use POGs as equilibrium samplers,
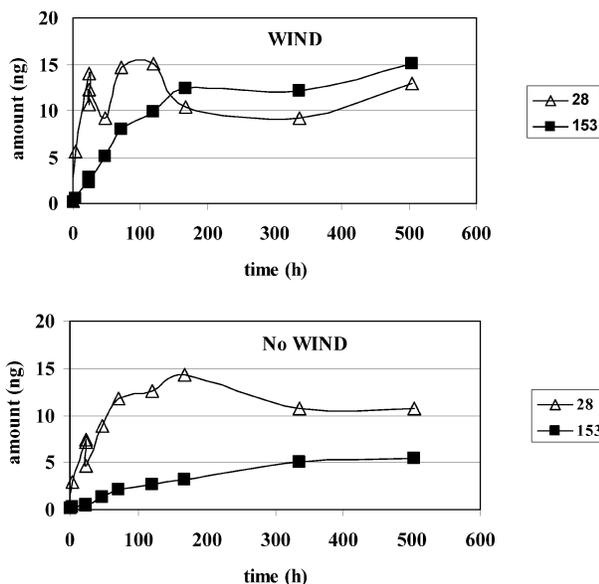
FIGURE 2. Uptake study results showing the effect of wind speed (4 m s^{-1}) on the accumulation of PCB 28 and PCB 153 in POG cylinders coated with 0.57 μm EVA.

TABLE 3. Results for Replicate Analysis of POG and Comparison of Uptake for POG Cylinders in Sheltered Chambers (in wind) Compared to Exposed POG Cylinders at t = 24 h

	PCB congener, amount (ng)						
	18	28	52	49	101	118	153
Exposed (No Wind)							
mean (ng)	4.67	6.41	6.59	3.10	3.10	0.85	0.44
%RSD	11.9	24.2	10.2	8.42	13.4	8.95	9.57
Exposed (in Wind)							
mean (ng)	6.70	12.4	15.9	8.40	12.6	4.00	2.45
%RSD	10.2	13.6	12.2	10.5	11.6	9.02	11.9
factor diff[a]	1.4	1.9	2.4	2.4	4.1	4.7	5.6
Sheltered (in Wind)							
A	6.00	9.37	9.98	6.17	4.97	1.42	0.64
B	6.76	10.8	10.8	5.68	5.71	1.48	0.87
C	5.10	7.86	7.80	4.07	3.80	0.97	0.55
mean (ng)	5.95	9.34	9.53	5.30	4.83	1.29	0.69
%RSD	14.0	15.7	16.3	20.7	20.0	21.5	24.0
factor diff	1.3	1.5	1.4	1.5	1.6	1.5	1.6

[a] Factor difference is relative to the exposed, no wind scenario.

then it may be advantageous to exploit wind speed to reduce the time to reach equilibrium. As discussed earlier, the time to establish equilibrium may also be manipulated by adjusting the thickness of EVA. Reproducibility of the method was tested by performing triplicate analyses for samples collected at 24 h during the wind study. Results in Table 2 show reasonable reproducibility with %RSD values less than 25% for 90% of PCBs analyzed (Table 3).

The results of the triplicate analysis at 24 h (Table 3) can also be used to assess uptake behavior under different deployment schemes. First, comparing exposed POGs (no chambers)—"wind" versus "no wind"; POGs exposed to the wind experienced more rapid accumulation. Enrichment factors relative to the "no wind" case ranged from ~1.4 for PCB 18 and increased to a high of 5.6 for PCB 153. The smaller differences for the lower molecular weight congeners are likely attributed to equilibrium or near-equilibrium conditions for these congeners under both schemes. When equilibrium exists, the amount accumulated is dependent upon K_{EVA-A} and not the uptake rate. Conversely, for a higher

TABLE 4. Results of Multiple Coating Experiment for POGs—1.1 μm versus 2.4 μm EVA[a]

	PCB congener, amount (ng)						
	18	28	52	49	101	118	153
2X (1.1 μm)							
blank	0.29	0.12	0.55	1.10	0.02	0.04	0.090
2	0.63	0.71	1.34	0.61	0.18	0.02	ND
8	2.39	2.81	3.29	1.25	0.80	0.12	0.025
24	2.79	3.92	4.76	1.55	0.95	0.19	0.161
48	2.13	3.96	4.62	2.35	2.52	0.75	0.302
60	2.52	5.03	5.77	3.09	3.73	1.33	0.685
4X (2.4 μm)							
blank	NA	NA	NA	NA	NA	NA	NA
2	1.03	1.20	0.87	0.46	0.19	0.08	ND
8	2.33	3.05	2.93	1.00	0.66	0.16	0.303
24	9.71	5.30	4.54	1.58	1.00	0.29	0.160
48	6.17	10.02	8.66	4.54	3.71	1.25	0.699
60	4.79	8.21	7.46	4.05	3.80	1.35	0.675

[a] NA − not analyzed; ND − not detected.

molecular weight PCB such as PCB 153 that is in the linear phase after 24 h, the enrichment factor of approximately 5.6 may represent the factor increase in the MTC associated with direct exposure to a 4 m s^{-1} wind speed. These results again indicate the air-side control on mass transfer.

For the POGs that were sheltered in chambers and subjected to the 4 m s^{-1} wind, uptake enrichment factors (relative to exposed chambers under "no wind" conditions) ranged from 1.3 for PCB 18 to 1.6 for PCB-153 (Table 3). These factors are not significantly different than unity (*t*-test, *p < 0.05*) and indicate that for the shielded samples, the increased uptake attributed to a higher wind speed (outside the chamber) has a minor effect on uptake and is within the bounds of analytical variability. The wind speed effect can be excluded entirely if POGs are allowed to establish equilibrium.

Multiple EVA Coatings. The objectives of the multiple coating study were 2-fold. First, to confirm whether PCBs are taken up by adsorption onto the outer surface of the EVA film or by absorption (dissolution) into the matrix of the EVA. An absorptive mechanism would be indicated if the equilibrated amount of chemical in the film was proportional to the film thickness. Second, to demonstrate how POGs could be used as air samplers in the linear uptake region and to calculate the corresponding air-side mass transfer coefficient, k_A.

Results are presented in Table 4. The lower molecular weight PCBs, congeners 18 and 28, equilibrate after 60 h for both the 1.1 and 2.4 μm EVA films. The greater amount in the 2.4 μm film (i.e. ~5 ng versus ~2.5 ng for PCB 18 and ~10 ng versus ~5 ng for PCB 28) are consistent with its greater volume (thickness) and indicates that the PCBs are dissolving or absorbing into the entire EVA matrix. These results are consistent with those of Wilcockson and Gobas (*28*) where 0.05 μm and 0.33 μm films were used. Therefore, increasing the thickness (volume) of the EVA will result in smaller uptake rate constant (k_U, eq 7) and a longer time to equilibrium since $t_{95} = 3/k_U$. It is interesting to note that for the PCBs with higher K_{OA} values (e.g. congeners 118 and 153) which have not come to equilibrium, the amount sequestered by the EVA film after 60 h is not dependent on film thickness (i.e. EVA volume or mass). This result is in accordance with theoretical predictions (eq 4) and nicely demonstrates that during the linear uptake phase (which is the case here) the amount of chemical transferred to the EVA is proportional to the surface area of the film (which is the same for both film thicknesses). We recognize that there is likely to be some variability in EVA thickness between similarly coated cylinders
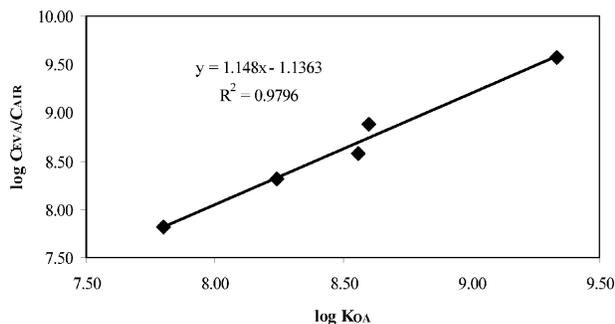
FIGURE 3. Correlation of log K_{EVA-A} and log K_{OA} for PCBs at 25 °C.

and along the surface of the same cylinder. However, this variability was not investigated in this study. For our purposes, the EVA thickness represents the EVA mass divided by the coated surface area. For POGs that have come to equilibrium, it is the total mass (or volume) of the EVA and not the thickness of the film that determines the amount of chemical that can be sequestered.

Calibration: Equilibrium Partitioning. As discussed earlier, the increased sampling rate in the "wind" experiment allowed equilibrium to be established after 504 h for many of the congeners investigated. From Table 2, the results at 504 h are used in conjunction with average air concentrations reported by Shoeib and Harner (*23*) to derive equivalent air sample volumes (i.e. the volume of air that contains an equivalent amount of chemical as trapped by the EVA). This ranges from ~1 m³ for PCB 18 to almost 200 m³ for PCB 153. For congeners that have come to equilibrium, the ratio C_{EVA}/C_{AIR}, is equivalent to the EVA−air partition coefficient, K_{EVA-A}. It should be noted, however, that K_{EVA-A} may exhibit site-specific saturation effects caused by complex mixtures (*33*). This is an area for further study.

Figure 3 shows an excellent correlation between $\log(C_{EVA}/C_{AIR})$ and log K_{OA} for congeners up to PCB101 (log $K_{OA} = 9.57$) (*34*), resulting in the semiempirical relationship describing equilibrium partitioning of gas-phase PCBs between air and EVA

$$\log K_{EVA-A} = (1.148 \pm 0.096) \log K_{OA} - (1.1363 \pm 0.82) \tag{8}$$

This is in good agreement with findings in Wilcockson and Gobas (*28*) who showed a similar linear relationship for a combination of chlorobenzenes and PCBs.

The slope of near unity in eq 8 suggests that octanol is a good surrogate for EVA (i.e. the ratio of the PCB activity coefficient in octanol and EVA is constant over the range of PCBs investigated here). Congeners 118 and 153 fell below the regression line and were excluded from the plot. Because of their higher K_{OA} values they were not yet equilibrated in the EVA after 504 h.

It is likely that K_{EVA-A} will have a strong temperature dependence, similar to ΔH_{OA} (J mol^{-1}), the enthalpy of phase transfer associated with K_{OA}. Thus this correlation can be applied at different temperatures by adjusting K_{OA} accordingly. It would be useful however to derive the temperature dependence of K_{EVA-A} empirically during controlled temperature studies.

Equation 8 can be used to predict K_{EVA-A} for PCBs, and it is likely that this relationship will hold for other classes of nonpolar, semivolatile POPs. With this knowledge, ambient air concentrations can be back-calculated for equilibrated POGs using eq 5. The time to reach 95% of saturation, t_{95}, can be determined as $3/k_U$ (see eq 7), but this requires knowledge of the air-side mass transfer coefficient. This is considered next.

Calibration: Linear Uptake. The thicker 2.4 μm film used in the multiple coating investigation results in an extension of the linear uptake phase (time to equilibrium). These results (Table 4) are plotted in Figure 4 for the time period 0−48 h. As discussed previously, the slope of this plot (*b*) is equal to the sampling rate $k_A A_{EVA} C_A$ which is on the order of ~3 m³ d^{-1} (Table 5). This is a useful value and can be used to assess operational questions such as how many sampling days are required to surpass the method limit of detection (LOD) or conversely, how large an exposure surface area is required for a specific sampling duration to exceed the method LOD. The sampling rate is also used to estimate the air-side MTC, k_A, with knowledge of the exposed surface area of the sampler and the average air concentration in the laboratory (Tables 1 and 2). The resulting values for the MTC are in the range 0.15−0.25 (cm s^{-1}) (Table 5) with an apparent outlier for PCB 49 (0.46). These MTC coefficients are consistent with values for other passive sampling media exposed during a longer term experiment in the same laboratory: 0.1−0.15 for SPMDs and PUF disk samplers and 0.15−0.2 for soil (*23*).

The derived MTCs for EVA (Table 5) and K_{EVA-A} values calculated using eq 8 were used to calculate uptake rate constants (k_U, eq 7) for POGs with different film thickness values ($\delta_{FILM} = 0.1$, 1, and 10 μm). Values of k_U were then
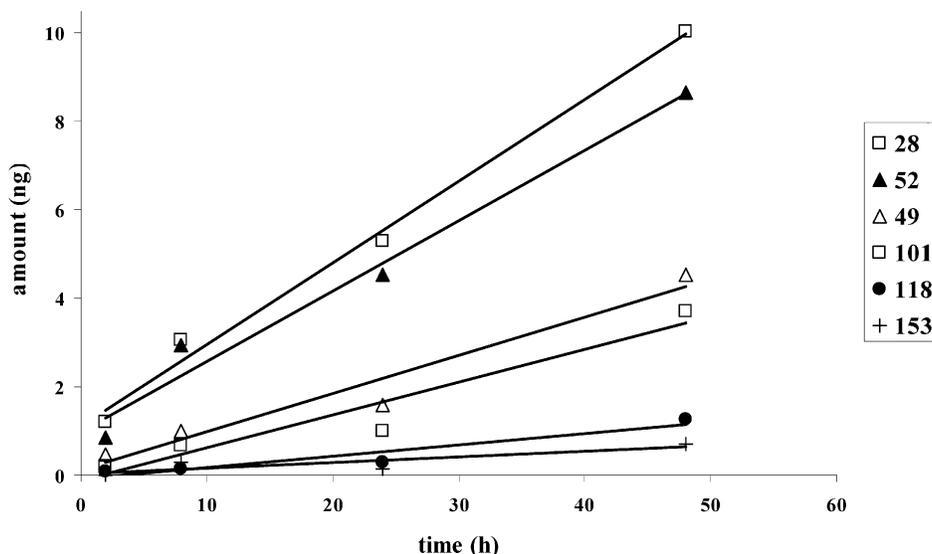
FIGURE 4. Linear uptake of PCBs by EVA (2.4 μm coating) up to 48 h.

TABLE 5. Linear Sampling Rates and Mass Transfer Coefficients for POG Cylinders Based on Uptake Results Using 2.4 μm EVA Coating[a]

PCB	sampling rate, $m^3 d^{-1}$	r^2	MTC, $cm s^{-1}$	linear phase, t_{25} (d)			time to equilibrium, t_{95} (d)		
				$d = 0.1 \mu m$	$d = 1 \mu m$	$d = 10 \mu m$	$d = 0.1 \mu m$	$d = 1 \mu m$	$d = 10 \mu m$
28	2.58	0.99	0.16	0.07	0.7	7.1	0.74	7	74
52	2.46	0.978	0.16	0.11	1.1	11	1.2	12	120
49	7.23	0.949	0.46	0.35	3.5	35	3.6	36	360
101	3.64	0.924	0.23	0.52	5.2	52	5.3	53	530
118	3.51	0.905	0.22	1.3	13	130	13	132	1320
153	3.79	0.752	0.24	2.1	21	210	22	217	2170

[a] t_{25} ($0.29/k_U$) and t_{95} ($3k_U$) are the time to 25% and 95% of equilibrium. k_U is the first-order uptake constant calculated using an average MTC of 0.2 cm s^{-1} (1.7e 8 μm d^{-1}) and K_{EVA-A} values from Table 2.

used to estimate the duration of the linear phase as $t_{25} = 0.29/k_U$ and the time to equilibrium as $t_{95} = 3/k_U$.

For a 1 μm film, values of t_{25} ranged from 0.7d (PCB 28) to 21d (PCB 153) and times to equilibrium (t_{95}) range from 7 days to 217 days, respectively. These estimates will change proportionally with film thickness as demonstrated in Table 5. It is important to understand the relationships when interpreting results from POG samplers and also when preparing POGs for deployment. Ideally, the sampling period duration (t) should be chosen so that linear sampling ($t < t_{25}$) or equilibrium sampling ($t > t_{95}$) exists for the target compounds. Sample durations that fall within the curvilinear portion ($t_{25} < t < t_{95}$) will result in greater complexities/uncertainties for deriving air concentrations. If the intention is to use POGs over short integration periods, the linear phase may be preferred. Linear sampling is limited by the target compound that has the lowest value of K_{OA}. For instance, if the desired integration period is 1 day, a coating thickness of at least ~1 μm is required to ensure linear sampling for PCBs with K_{OA} values greater than about PCB 28 (see Table 5). To target chemicals with lower K_{OA} values a thicker film may be required. If long integration periods are preferred, the required film thickness to ensure that $t > t_{95}$ will also be limited by the compound having the lowest value for K_{OA}. Again, for a 1 μm film, the integration period must be greater than about 7d as defined by the lowest K_{OA} compound, which in this case is PCB 28. One negative aspect associated with "equilibrium sampling" over very long integration periods is that different representative integration periods apply to different target compounds. For instance for a 1-year deployment of a 1 μm POG, a high K_{OA} chemical such as PCB 153 will be accumulated in a linear fashion (i.e. equally weighted) over much of the exposure period before finally establishing equilibrium. Hence, the back-calculated air concentration for PCB 153, based on the amount of chemical sequestered in the POG, is fairly representative of the last year. Conversely, a low K_{OA} PCB such as PCB 28 equilibrates in less than 1 week and will respond relatively quickly to changes in ambient air concentrations. In this case, the back-calculated air concentration is not representative of the entire 1-year integration period.

It is conceivable that passive sampling times on the order of minutes are possible by further reducing the film thickness or increasing the air-side MTC (e.g. by exposing the sampler to the wind or inducing air-flow across the sampler). Such a rapid sample would be especially useful for indoor sampling where concentrations typically show relatively minor temporal variability and a longer time-integrated sample is thus not required. Limitations associated with instrument detection limits can be countered by using analytical techniques such as thermal desorption-GC-mass spectrometry. However, greatly reducing the film thickness may result in contamination issues for low K_{OA} compounds since only a short exposure to contaminated air will result in a new and rapid equilibrium.

Implications

The ability to operate POGs as equilibrium samplers and as accumulators during linear uptake has been demonstrated for indoor air. This flexibility combined with the relatively simple and fast preparation and cleanup methodology makes POG samplers a feasible choice for conducting exposure-type investigations in indoor air.

The potential to use POGs for outdoor spatial mapping campaigns has also been shown (35). These studies require greater control on blanks and enhanced detection sensitivity achievable using gas-chromatography mass spectrometry (GC-MS). Because uptake is sensitive to wind speed, it is essential to use wind-dampening deployment chambers during outdoor studies. These chambers will also serve to protect POGs from precipitation and UV sunlight and reduce the particle impaction onto the EVA surface. However, more work is required to evaluate the contribution from fine particles and soot, particularly in industrial/urban settings. Although the chambers have been shown to be effective for wind fields up to 4 m s^{-1}, it would be useful to extend these experiments to higher wind speeds that may be encountered. The effect of temperature on K_{EVA-A} also needs to be investigated, although as a first approximation it can be assumed to follow ΔH_{OA}, the enthalpy of phase change from octanol to air. Based on the variability associated with the relevant uptake parameters, we expect that air concentrations that are back-calculated for the integration period will be accurate within a factor of about two.

Literature Cited

(1) Kohler, M.; Zennegg, M.; Waeber, R. *Environ. Sci. Technol.* **2002**, *36*, 4735−4740.

(2) Leone, A. D.; Ulrich, E. M.; Bodnar, C. E.; Falconer, R. L.; Hites, R. A. *Atmos. Environ.* **2000**, *34*, 4131−4138.

(3) Liu, X.; Zhu, L.; Shen, X. *Environ. Sci. Technol.* **2001**, *35*, 840−844.

(4) Naumova, Y.; Eisenreich, S. J.; Turpin, B.; Weisel, C. P.; Morandi., M. T.; Colome, S. T.; Totten, L. A.; Stock, T. H.; Winer, A. M.; Alimokhtari, S.; Kwon, J.; Shendell, D.; Jones, J.; Meberti, S.; Wall, S. J. *Environ. Sci. Technol.* **2002**, *36*, 2552−2559.

(5) Carpi, A.; Chen, Y.-F. *Environ. Sci. Technol.* **2001**, *35*, 4170−4173.

(6) Sjödin, A.; Carlsson, H.; Thuresson, K.; Sjölin, S.; Bergman, A.; Östman, C. *Environ. Sci. Technol.* **2001**, *35*, 448−454.

(7) Wijesekera, R.; Halliwell, C.; Hunter, S.; Harrad, S. *Organohalogen Compds.* **2002**, *55*, 239−242.

(8) Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, P. D.; Helle, E.; Nyman, M.; Giesy, J. P. *Environ. Sci. Technol.* **2001**, *35*, 1593−1598.

(9) Ikonomou, M.; Rayne, S.; Addison, R. F. *Environ. Sci. Technol.* **2002**, *36*, 1886−1892.

(10) Calamari, D.; Bacci, E.; Focardi, S.; Gaggi, C.; Morosini, M.; Vighi, M. *Environ. Sci. Technol.* **1991**, *25*, 1489−1495.

(11) Gaggi, C.; Bacci, E.; Calamari, D.; Fanelli, R. *Chemosphere* **1985**, *14*, 1673−1686.

(12) Tremolada, P.; Burnett, V.; Calamari, D.; Jones, K. C. *Environ. Sci. Technol.* **1996**, *30*, 3570−3577.

(13) Hermanson, M. H.; Hites, R. A. *Environ. Sci. Technol.* **1990**, *24*, 666−671.

(14) Simonich, S. L.; Hites, R. A. *Nature* **1994**, *370*, 49−51.

(15) Meijer, S. N.; Steinnes, E.; Ockenden, W. A.;, Jones, K. C. *Environ. Sci. Technol.* **2002**, *36*, 2146−2153.

(16) Kalantzi, O. I.; Alcock, R. E.; Johnston, P. A.; Santillo, D.; Stringer, R. L.; Thomas, G. O.; Jones, K. C. *Environ. Sci. Technol.* 2001, *35*, 1013−1018.

(17) Petty, J. D.; Huckins, J. N.; Zajicek, J. L. *Chemosphere* **1993**, *27*, 1609−1624.

(18) Ockenden, W. A.; Prest, H. F.; Thomas, G. O.; Sweetman, A.; Jones, K. C. *Environ. Sci. Technol.* **1998**, *32*, 1538−1543.

(19) Ockenden, W. A.; Sweetman, A. J.; Prest, H. F.; Steinnes, E.; Jones, K. C. *Environ. Sci. Technol.* **1998**, *32*, 2795−2803.

(20) Huckins, J. N.; Petty, J. D.; Orazio, C. E.; Lebo, J. A.; Clark, R. C.; Gibson, V. L.; Gala, W. R.; Echols, K. R. *Environ. Sci. Technol.* **1999**, *33*, 3918−3923.

(21) Lohmann, R.; Corrigan, B. P.; Howsam, b.; Jones, K. C.; Ockenden, W. A. *Environ. Sci. Technol.* **2001**, *35*, 2576−2582.

(22) Ockenden, W. A.; Corrigan, B. P.; Howsam, M.; Jones, K. C. *Environ. Sci. Technol.* **2001**, *35*, 4536−4543.

(23) Shoeib, M.; Harner, T. *Environ. Sci. Technol.* **2002**, *36*, 4142−4151.

(24) Wania, F.; Shen, L.; Lei, Y. D.; Teixera, C.; Muir, D. C. G. *Environ. Sci. Technol.* In press.

(25) Koziel, J. A.; Noah, J.; Pawliszyn, J. *Environ. Sci. Technol.* **2001**, *35*, 1481−1486.

(26) Llompart, M.; Li, K.; Fingas, M. *J. Chromatogr.* **1998**, *824*, 53−61.

(27) Potter, D. W.; Pawliszyn, J. *Environ. Sci. Technol.* **1994**, *28*, 298−305.

(28) Wilcockson, J. B.; Gobas, F. A. P. C. *Environ. Sci. Technol.* **2001**, *35*, 1425−1431.

(29) Mayer, P.; Vaes, W. H.; Hermens, J. L. M. *Anal. Chem.* **2000**, *72*, 459−464.

(30) Mayer, P.; Tolls, J.; Hermens, J. L. M.; Mackay, D. *Environ. Sci. Technol.* In press.

(31) Whitman, W. G. *Chem. Metal Eng.* **1923**, *29*, 146−150.

(32) Harner, T.; Bidleman, T. F. *Sci. Technol.* **1998**, *32*, 1494−1502.

(33) Baltussen, E.; Cramers, C. A.; Sandra, P. J. F. *Anal. Bioanal. Chem.* **2002**, *373*, 3−22.

(34) Harner, T.; Bidleman, T. F. *J. Chem. Eng. Data* **1996**, *41*, 895−899.

(35) Harner, T., Shoeib, M.; Farrar, N.; Stern, G.; Ikonomou, M.; Gobas, F. A. P. C.; Jones, K. C.; Diamond, M. L. Society of Environmental Toxicology and Chemistry, 23rd Annual meeting, Salt Lake City, Utah, Nov. 16−20, 2002. Oral presentation.