FINAL REPORT SUMMARY

Development and Evaluation of Passive Samplers for Persistent, Bioaccumulative, Toxic Pollutants (PBTs)

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Until recently air monitoring networks designed to characterize the concentration of persistent, bioaccumulative, toxic pollutants (PBTs) have typically been comprised of a series of high volume samplers deployed at a limited number of sites. Measurements at these sites has increased our knowledge of ambient air concentrations, helped identify the locations of PBTs sources and sinks, and helped researchers understand atmospheric transport of PBTs. To adequately characterize all these factors, considering their spatial and temporal variation, sampling from a large number of sites is required. However high volume samplers are expensive, require significant operator time, and can only be located where power is available.

Passive sampling devices offer an alternative to high volume samplers. They are inexpensive, easy to use, do not require power, versatile and deployable in large numbers over large geographic regions simultaneously (for example see Jaward et al. 2004a and 2004b and Pozo et al, 2006). Passive samplers (also commonly known as diffusion samplers) provide a time-averaged semi-quantitative measurement of the ambient air concentrations and can be designed and calibrated to determine average ambient concentrations (Ockenden et al, 2001, Harner et al, 2002; Shoeib et al, 2002; Harner et al, 2003). Previous passive sampler studies were at used for local scale measurements (Shoeib et al, 2002; Harner et al, 2003), characterized urban-rural gradients (Harner et al, 2002), investigated concentration differences at various latitudes (Meijer et al, 2003; Ockenden et al, 1998) and deployed for continental scale measurements (Jaward et al, 2004; Pozo et al 2006).

Several passive sampler designs have been investigated, including semipermeable membrane devices (SPMDs)(Wennrich et al, 2002), polyurethane foam (PUF) disk samplers (Harner et al, 2002; Pozo et al 2006) and XAD-2 resin ssamplers (Billings and Bidleman, 1980; Wania et al, 2003). These samplers were generally used over time scales of weeks to months as kinetic samplers. A sampler has also been developed to collect gas and particulate phase simultaneously, though at a greatly reduced sampling rate (Tao et al, 2007). A flow through sampler has also been developed that requires a substantially reduced deployment time (Xiao et al, 2007). In all cases knowledge of the sampling rate of the device is necessary for an accurate conversion of the sampled mass to an ambient concentration.

This study focused on the PUF disk passive sampler (Figure 1; Harner et al, 2002), a device that is widely used in the research community, in part because it is easy to handle, operates independently for several months, and is inexpensive. When the PUF disk is operating in the kinetic phase, it is mostly independent of temperature and has the additional positive feature of a having a similar gas-phase sampling rate for various compounds (Shoeib et al, 2002). The sampler was developed by Harner and first used in the analysis of the PCBs, PBDEs and organochlorine pesticides across Europe (Jaward et al, 2004). Calibration of the PUF disk sampler has been performed previously using computational fluid dynamic (CFD) simulations and in indoor experiments (Thomas et al, 2006; Hazrati et al, 2007).

Figure 1: PUF sampler.

The sampling dependence on wind speed must be known to compare results between various sampling sites. The PUF sampler has been previously found to be generally independent of wind speed below freestream velocities of 3.5-4 m/s (Tuduri et al, 2006). But, more recent CFD work shows a linear increase in sampling rate with an increase in wind velocity (Thomas et al, 2006). The work undertaken as part of this project has attempted to better characterize the relationship between external wind velocity and sampling rates inside the sampler. Velocity measurements inside the sampler, flow visualization experiments in a wind tunnel, mercury sampling experiments, and extensive CFD modeling were all conducted. Particle collection by the sampler was also investigated to determine the impact of particle capture on sampling rates. In a previous study wipe samples from inside the sampler housing showed that compounds with higher octanol-air partition coefficients (K_{OA}) were more likely to affect overall sampling rates because they are often particle bound (Hazrati et al, 2007).

Initial CFD simulations were performed in two and three dimensions. Two dimensional (2D) simulations are much simpler to execute and converge must faster than 3D simulations. For complex geometries, like the PUF sampler, 2D simulations can, however, give erroneous results. In order to confirm that CFD simulations are in agreement with the actual flow in the sampler, smoke-based flow visualization experiments were performed in a wind tunnel. In particular these experiments focused on the flow entering and exiting the sampler. The experiments found that the flow passes smoothly passing over the top and bottom portions of the sampler (Figure 2). In addition smoke was seen to exit the back of the sampler and a small recirculation region developed immediately behind the sampler, similar to what was predicted in the 3D simulations.

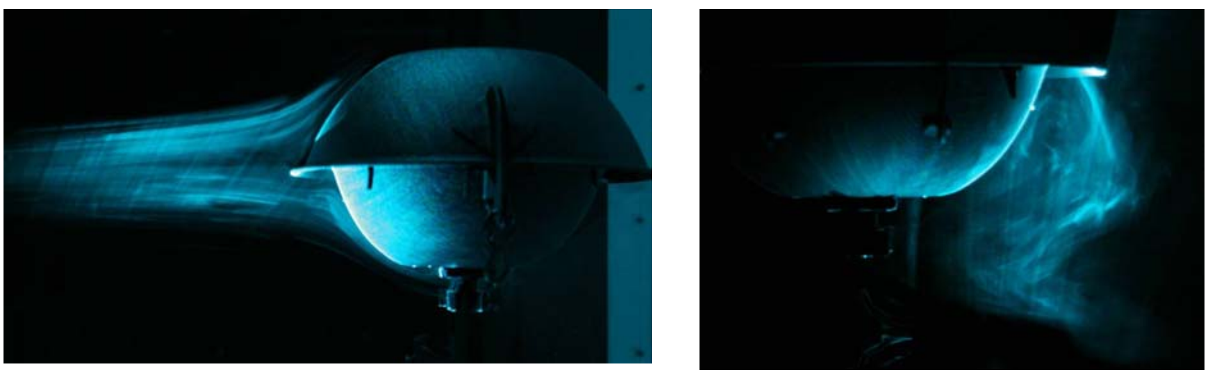

Figure 2. Pictures of flow visualization experiments characterizing flow entering and exiting the PUF sampler.

To further validate CFD simulations air velocity measured inside the sampler were compared to predicted values. Overall the 3D velocity simulations match experimental observations fairly well (Figure 3), particularly for the region above the PUF. The poorer agreement for the region below the PUF may be due to the hinges on the bowl which were not included in the simulations.

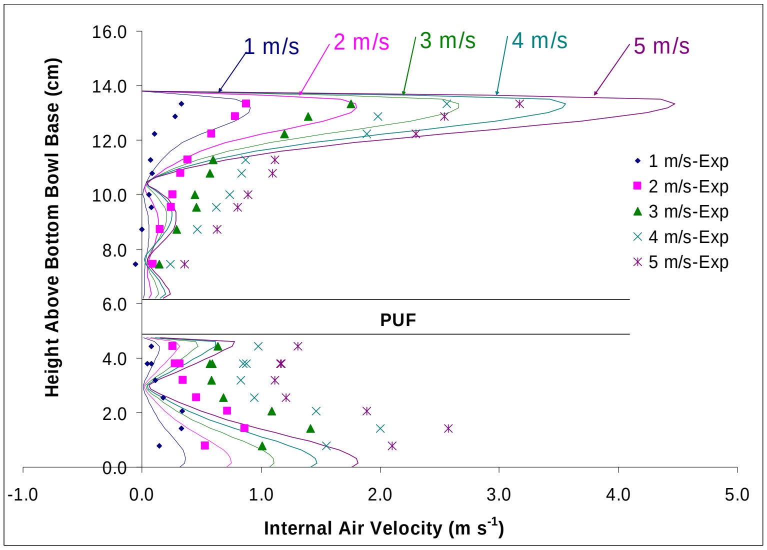

Figure 3. Comparison of experimental and the FLUENT velocity magnitude results inside the sampler.

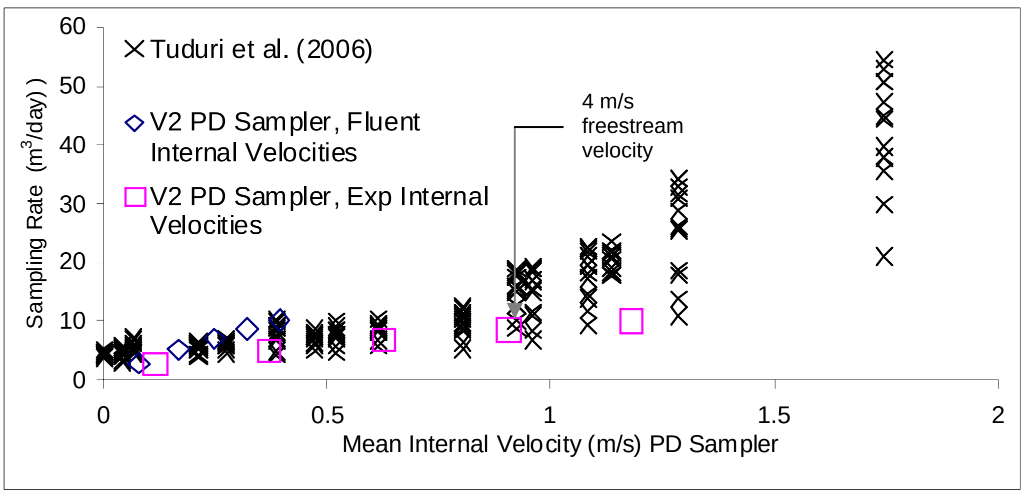

Figure Error! No text of specified style in document.**: Experimental and simulated sampling rates in relation to internal wind velocities**

Predicted sampling rates agree well with those measured by Tuduri et al, (2006)(Figure 4). Both experimental and modeling results suggest the sampling rate increases linearly with wind speed. Mercury uptake experiments performed in the wind tunnel agree well with CFD simulations (Figure 5). CFD simulations with two different grid sizes gave comparable results, suggesting grid-independent results. In addition both simulations and experiments suggest that the uptake rates by both the top and bottom of the PUF are approximately equal.

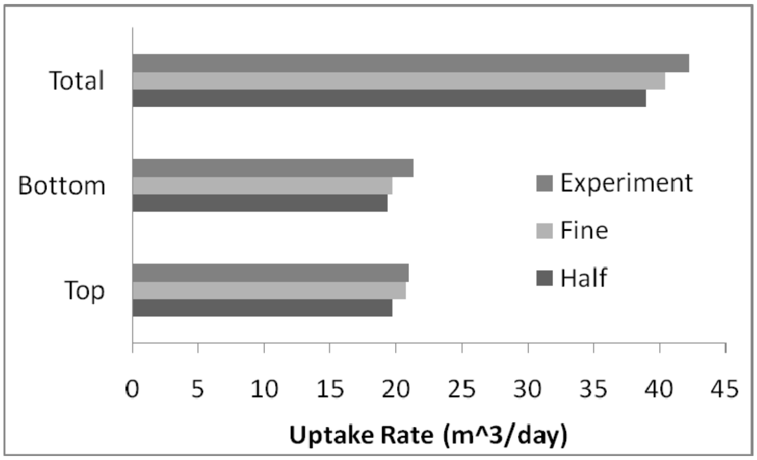

Figure 5: Uptake rates from 3D simulations with a freestream velocity of 3 m/s.

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