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RETROSPECTIVE

Forty-five Years of Foam: A Retrospective on Air Sampling with Polyurethane Foam

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Polyurethane foam (PUF) is used worldwide for active and passive sampling of semivolatile organic compounds (SVOCs) in air. Cheap, easy to handle, and efficient for collecting a wide range of compounds with moderate to low vapor pressures account for PUF's popularity. In 1973, Terry Bidleman was a postdoc in the laboratory of Dr. Charles Olney ("Charlie") at the University of Rhode Island. Terry is frequently credited with discovering PUF for air sampling, but that's not quite how things happened. He thought it wouldn't work.

Terry and Charlie were looking for a method to trap SVOCs from large volumes of air over the ocean. Previous studies employed nets coated with oil and hung in the trade winds (Risebrough et al. 1968; Seba and Prospero 1971), but these nets collected mainly the particle-bound compounds and missed the gas-phase contribution. Early on, Terry tried sending an airstream containing PCB vapors through multiple glass fiber filters (GFFs), but this failed due to extensive breakthrough. Charlie had read about PUF being used to collect PCBs from water (Gesser et al. 1971) and suggested we try this for air. Terry's response was: "I don't think so, the air will pass through the foam too quickly and the chemicals will never stick". Undaunted, Charlie removed some PUF from a discarded packing case and cleaned it up by Soxhlet extraction. He put two PUF traps (front and back) in a glass tube, poured a PCB mixture into a Petri dish, suspended the PUF cartridge above and drew air through it overnight. Analysis showed lots of PCBs on the first PUF and little on the second. No breakthrough—but a big breakthrough for the project! "There ya go", Charlie said.

Go they did, testing collection efficiencies and eventually employing a GFF–PUF cartridge to sample air over the ocean. The study culminated with papers in the *Bulletin* (Bidleman and Olney 1974a), *Science* (Bidleman and Olney 1974b) and book chapters (Bidleman et al. 1976; Rice et al. 1977). For the first time, they showed that PCBs and pesticides in background air were in the gas phase, with only minor fractions on particles. The key point of this story is about Charlie, a wise and generous mentor. He could have taken his early discovery of PUF sampling and run with it. Instead, he turned over the idea to his struggling postdoc, stood back and let him take the credit.

By the late 1970s–early 1980s, other groups were using PUF, and breakthrough of the more volatile SVOCs was recognized as a limitation. Sorbents such as Amberlite XAD® or other resins and PUF-resin "sandwich" cartridges were investigated to improve collection efficiency, since the resins have higher specific surface areas than PUF (reviewed by Melymuk et al. 2014). Terry joined the University of South Carolina where his group continued to investigate collection of SVOCs on PUF and other sorbent beds. In those days the air sampling community didn't agree on a short name for PUF. "PU-foam" and "PPF" (porous polyurethane foam) were used, but PUF ("Puff") stuck, maybe because of a Magic Dragon in the popular song. An active sampling method based on PUF or PUF-resin cartridges became standard for many SVOCs in ambient air (U.S. EPA, 1999). Chromatographic behavior and breakthrough investigations in active sampling have continued into the recent decades (Bidleman and Tysklind 2018; Melymuk et al. 2014, 2016; Xiao et al. 2009).

Another major breakthrough for sampling SVOCs was the development of PUF-based passive air sampling. The pioneering work in this field was done by Drs. Tom Harner

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and Mahiba Shoeib of Environment and Climate Change Canada, who first characterized PUF as a passive, rather than an active, sampler for SVOCs (Shoeib and Harner 2002). Their work led to the first passive air sampling rates for PCBs and PCNs and set the stage to produce quantitative measurements of SVOCs in air by passive sampling. As passive sampling of SVOCs was under development, many different sampling matrices were explored: synthetic matrices such as XAD resins, semipermeable membrane devices, solid-phase microextraction, and polymer-coated glass; and natural materials such as soil, tree bark, pine needles and other vegetation. From all these matrices, PUF has sprung forward as the most common, primarily due to its ease of use and applicability for a wide range of SVOCs. The use of PUF in passive sampling has grown enormously in the past decade—a Web of Science search for "PUF" and "passive air" comes up with over 200 publications, with more than half of them in this decade. In addition to outdoor applications, PUF passive sampling has made the quantification of SVOCs in indoor air easier, as the small sampler footprint and silent operation are ideal for non-disruptive use indoors.

PUFs have also been adapted by impregnating them with finely ground XAD-4 resin (Shoeib et al. 2008) These "SIPs"—sorbent-impregnated PUF—have a higher sorptive capacity than PUF disks alone and allow quantitative collection of more volatile compounds such as perfluorinated compounds and siloxanes (Shoeib et al. 2008; Wang et al. 2018).

The issue of how "quantitative" the results are of the PUF passive sampling remains contentious–passive uptake rates has been the subject of numerous theoretical (Bartkow et al. 2005) and practical assessments using field calibration with active samplers (Chaemfa et al. 2008) or depuration compounds (Moeckel et al. 2009). The PUF/air partition coefficient of SVOCs is a critical parameter in deriving sampling rates (Okeme et al. 2017). Recent calibration strategies model sampling volumes based on meteorology and compound properties (e.g., Herkert et al. 2016). While uncertainties remain, as with any sampling technique, the attention to calibration for a wide set of compounds has greatly improved the applicability of PUF for passive sampling.

PUF-based sampling has been a game-changer in understanding the global distribution of SVOCs. Thanks to PUF passive sampling we can now measure SVOCs in regions that were previously inaccessible to active sampling techniques, either due to the remoteness or because of the cost of active samplers. PUF-based sampling networks are now found around the world, most notably the GAPS–Global Atmospheric Passive Sampling—network, a truly global network with 50 sites on seven continents, as well as regional active and passive networks in North America, Europe, Africa, Asia and Australia. The Stockholm Convention on Persistent Organic Pollutants relies on PUF-based active and passive sampling as a key part of the Global Monitoring Plan for effectiveness evaluation of the Convention.

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