Development of a Flow-Through Passive Air Sampler for Semi-Volatile Organic Compounds

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Introduction

The quantification of trace amounts of semi-volatile organic compounds (SOCs) in the atmosphere is required for many applications, for example in efforts to assess the regional and global transport of airborne contaminants and their delivery to receptors such as the aquatic food webs in the Great Lakes or the Arctic Ocean. Conventional air sampling techniques used for SOCs rely on a pump to pass large volumes of air through or over a sampling medium, which traps the compounds of interest either in the gas phase or sorbed to atmospheric particles. Sampling media include foams, such as polyurethane foam (PUF) plugs, resins, such as polystyrene-divinylbenzene, and glass fibre filters. The need for a pump, makes such active sampling approaches generally quite expensive, labour intensive and limited in applicability to locations where power is readily available. It is thus difficult to sample in remote locations (such as the Arctic and in mountain regions) or developing countries, and to sample simultaneously at a large number of locations, i.e. they are generally not practical for establishing the spatial variability of SOC air concentrations.

Responding to a growing need for inexpensive and simple monitoring of SOCs in the atmosphere, several so-called passive air sampling techniques have been developed in recent years. A passive air sampler is a device that collects chemicals from the atmosphere without the help of pump. Passive air samplers are promising to address the need for spatially resolved atmospheric concentrations of SOCs, because of (1) their capability of time-integrated sampling over extended time period, (2) their independence from power supplies and regular maintenance, and (3) their relatively low production and operating cost. The capability of passive air samplers to provide information on the large scale variability of atmospheric SOC concentrations has been shown through the results of continental sampling networks in both North America[1] and Europe[2]. Passive air samplers have also been used to establish urban-rural gradients of SOC concentrations in South Ontario[3].

Various passive air sampling designs and sampling media have been explored in recent years. Common sampling media include semi-permeable membrane devices (SPMD)[4,5], polyurethane foam discs[2,5], polymer-coated fibres[6], organic-rich soil[5], polymer-coated glass[7,8] and XAD-resin[1,9]. Most of these approaches employ some kind of structure to shelter the sampling medium from sunlight, precipitation, and large particles subject to gravitational settling. Examples of such structures are Stevenson's screen boxes, cyclindrical steel cans[1], and hemispherical steel bowls[2,5]. The fact that these shelters eliminate, or at least reduce, the influence of wind speed on the rate of SOC uptake in the sampling medium is seen as an advantage, because it allows for the interpretation of the sampled amounts in terms of volumetric air concentrations if the sampling rate and deployment period is known. Various sampler designs therefore have been characterised in terms of their uptake kinetics[9]. These studies revealed that in many cases, the uptake is controlled by molecular diffusion to the sampling medium[9].

Molecular diffusion is a slow process and, as a result, sampling rates of existing PAS designs are quite small, typically on the order of a few m^3 of air per day[1,5]. Because very low concentrations of SOCs in the remote atmosphere often necessitate large air sampling volumes in the order of 500 m^3 and higher, the low sampling rates of existing passive air sampling designs imply the need for long deployment periods on the order of several months to more than a year. Variations in air concentrations on the time scale of months or shorter can thus not be resolved, but are often of considerable interest. The challenge is to significantly increase the sampling rate of passive air samplers, while maintaining their ability to provide quantitative information. Here we report on an ongoing project that

seeks to address that challenge.

Methods

We are pursuing the strategy to greatly increase the sampling rate of a passive air sampler by forcing the ambient wind to blow through the sampling medium. The sampler consists of a horizontally oriented, aerodynamically shaped, stainless steel flow tube mounted on a post with ball bearings, that allow it to turn into the wind with the help of vanes (Figure 1). The sampling medium is placed into a stainless steel cyclinder of approximately 20 cm length and an inner diameter of 10 cm. That cylinder is mounted inside the flow tube assembly with the help of a thread. At the same time, it serves as a sturdy storage and shipping container, that can be sealed air-tight by screw caps that use the same thread.

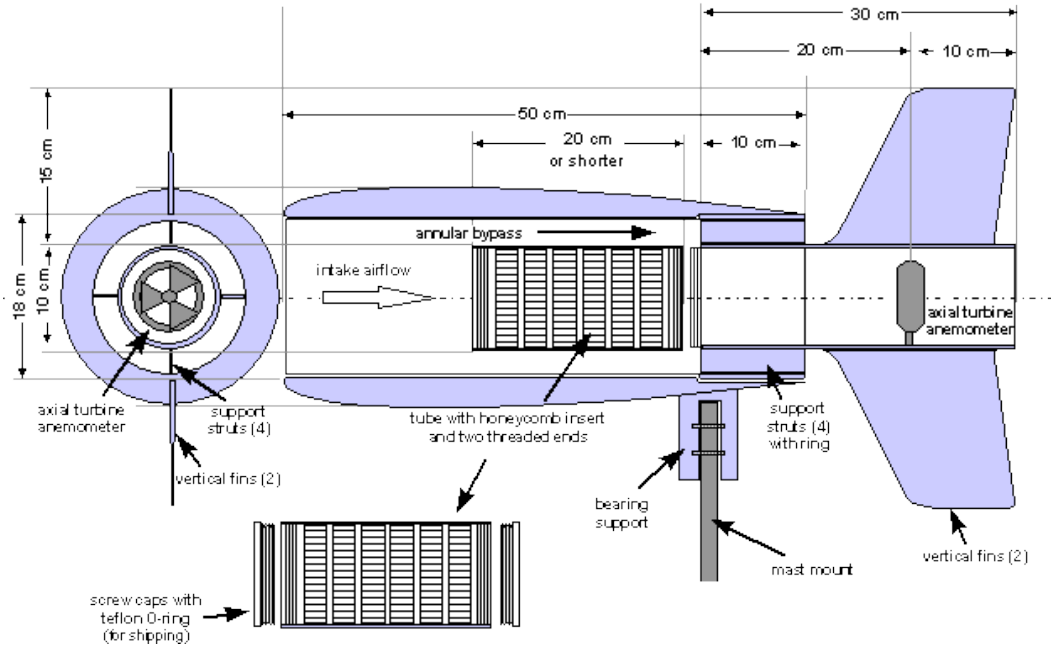

Figure 1: Design of the flow-through passive air sampler with EVA coated honeycomb as sampling medium.

By taking advantage of the wind blowing through the sampler, significantly higher sampling rates can be achieved. In contrast to previous sampler designs, however, the sampling rate is no longer a constant but becomes dependent on the wind speed. This means that it is necessary to record the sampled air volume, if the amount of SOC quantified in the sampling medium is to be (1) converted into volumetric air concentrations or (2) compared between locations differing in wind speed. In the prototype sampler, the sampled air volume is recorded with the help of a battery-operated turbine-counter mounted at the exit of the flow tube (Figure 1), which has been pre-calibrated with a hot wire anemometer. The wind speed dependence of the sampling rate further implies that sampling is biased towards time periods with higher wind speeds, i.e. contaminant uptake in the sampling medium is minimal during windstill time periods, but rapid during windy days. The sampler design includes an annular bypass (Figure 1), which stabilizes the wind speed through the flow tube and reduces the uptake rate during periods of very high wind speeds and thus limits the extent of sampling bias. Such bias is not a problem if wind speed and SOC air concentrations are independent of each other, which often can be assumed to be the case.

To allow air to pass through the flow tube and to collect the SOC quantitatively from that air stream requires a sampling medium that ideally combines a low flow resistance with a high uptake efficiency. Two types of sampling media were explored:

- aluminum honeycomb discs of 1/8" cell size and 1" thickness, coated with a thin film of ethylene vinyl acetate (EVA). EVA has previously been used in passive air samplers[5,6].

- polyurethane foam (PUF) discs of 1" thickness and different densities (P-10, P-20, P-30 and P-50, corresponding

to pore sizes of 10, 20, 30 and 50 pore per inch, respectively). PUF is regularly used as sampling medium for SOCs in both active and passive air samplers.

Honeycomb inserts were coated with EVA by a method described previously[8]. In order to improve the uptake efficiency, honeycomb inserts were separated by half-inch spacer rings to maximize the turbulence. A large box fan was used to generate an indoor air flow field. The mass (thickness) of the EVA coating and the number of inserts was varied. The flow resistance was determined by comparing the wind speed within the sampling tube and through the annular bypass under different wind scenarios. The angles between the wind direction and alignment of the honeycomb were also adjusted to increase wind resistance. Honeycomb samples were extracted with 400 ml methanol for 1 hour twice. PUF discs were extracted by Soxhlet using acetone and petroleum ether (1:1) overnight. All the samples underwent clean-up and were exchanged into iso-octane, then further reduced to 1 ml by nitrogen stream before instrumental analysis. PCB concentrations were determined using an Agilent 6890 GC equipped with splitless injector and an ECD or MS detector. Mirex was used as internal standard to correct for volume differences. The extent of breakthrough was quantified as the percentage of the total chemical amount trapped in the last disc. The effect of sampling time and wind speeds on sampling efficiency was conducted for different sampling media.

Results and Discussion

Preliminary results from the flow resistance experiments showed that the EVA-coated honeycomb display much lower air flow resistance than the PUF discs and that the resistance of the PUF discs depends on its porosity. The wind speed through 5 honeycomb units in series was only three time lower than the one through the annular bypass, whereas 5 low density PUF (P10) discs in series decreased the wind speed by about an order of magnitude. Nevertheless, low density PUF-discs (P-10) had a wind resistance sufficiently low to allow for sampling.

PCB concentrations in multiple, serially arranged EVA-coated honey-comb discs were found to be rather uniform. Additional experiments with thicker EVA films and different physical arrangement of the honeycomb inserts did not improve the sampling efficiency. This suggests that the contact time within the honeycomb units is too short (less than 0.1 s) to prevent substantial break-though. Despite its superiority in terms of flow resistance, the honeycomb inserts was thus judged not suitable for quantitative measurements of SOC air concentrations.

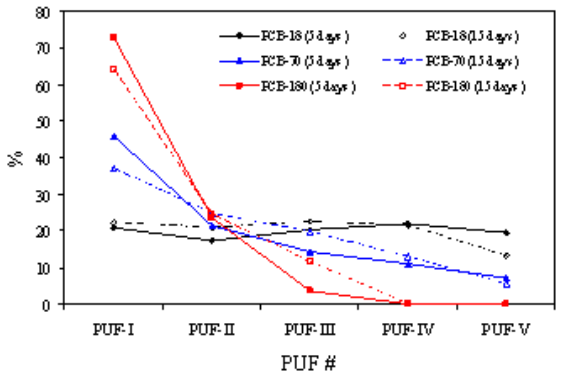

Figure 2. Percentage profile of selected PCB congeners through the five serially arranged PUF discs.

Figure 2 shows the percentage profile for three selected PCB congeners in two PUF assemblies (five serially arranged PUF discs), that had been exposed to laboratory air for 5 and 15 days, respectively. With artificially created constant wind speeds of 0.31 m/s this corresponded to sampling volumes of 1000 and 3000 m^3, respectively. The concentrations of the PCBs decrease from the first to the fifth PUF disc. The extent of the decrease is different for different congeners. Relatively volatile congeners, such as PCB-18, experience considerable break-through, whereas less volatile PCBs, such as PCB-70 and PCB-180, are efficiently stripped from the air stream by the first 4 PUF discs. The extent of the concentration decrease appears to be independent of the length of the sampling period, which suggests that wind speed through the sampling medium (i.e. contact time, rather than the capacity of the PUF discs) is the main factor determining sampling efficiency. This opens the possibility to achieve a desired sampling efficiency by simply adjusting the flow resistance of the PUF assembly. This in turn can be achieved by varying thickness, number and porosity of the PUF discs.

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