Photodegradation of performance reference compounds in semipermeable membrane devices (SPMDs) deployed in air

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Introduction

Recent research shows that photodegradation of polyaromatic hydrocarbons (PAHs) accumulating in passive air samplers occurs when the samplers are exposed to direct sunlight and when they are deployed in a chamber designed to reduce the effect of direct light on the sampler [1, 2]. Thus, further work is required to investigate whether passive sampler deployment chambers currently in use, are adequately protecting the samplers from sunlight. Semipermeable membrane devices (SPMDs) were deployed at the same site in commonly used passive sampler deployment chambers. In order to detect differences in SPMD performance, the release rates of performance reference compounds (PRCs) was examined.

Materials and Methods

A total of 24 standard SPMDs were loaded with two deuterated PAHs (D_{10}-anthracene (D_{10}-Ant): 1000 ng mL^{-1} and D_{10}-pyrene (D_{10}-Pyr): 100 ng mL^{-1}) as PRCs. The samplers were deployed at an EPA monitoring station in South Brisbane, Queensland, Australia, from the 24th of November until the 23rd of December 2003. South Brisbane is an inner city site adjacent to the M1 motorway and bordered on all sides by major transit lanes.

SPMDs were deployed in four different chambers at this site including a galvanized iron louvered box chamber, with and without a louvered base plate, bowl chambers, and a cage chamber. The box chamber (40 cm by 40 cm by 40 cm) with an open bottom was previously used by Bartkow et al. [2] and is very similar to the Stevenson Screens used to deploy SPMDs in previous studies (e.g. Ockenden et al.[3]). The closed box chamber was the same type of chamber except a louvered plate was fitted to the bottom of the box. The bowl chamber has been used to deploy SPMDs and PUF samplers in a range of recent studies (e.g. Harner et al.[4]), while the cage chamber is used to deploy SPMDs in the water.

Light levels inside the chambers were measured using a light meter (LI-COR, LI-1400 Data Logger and cosine-adjusted field of view sensor). Readings were taken between 1pm and 4pm on a clear sunny day and measured the photosynthetic active radiation only. Therefore these results can be used to show the relative differences in expsoure to light between chambers but not as an indication of total exposure to photodegrative solar radiation. Tests with the light meter revealed that levels inside the chambers generally doubled if the chambers were deployed above concrete, compared to being deployed over grass. All chambers were therefore deployed above the same surface (grass).

The preparation of SPMDs for analysis was similar to Bartkow et al. [2] however a different adsorption chromatography step was used as follows: 9 mm i.d. columns comprised of 1 g Alumina B – Super 1 (furnaced and stored at 180 ^{o}C), 2 g silica (precleaned and stored at 140 ^{o}C), and 1 cm of Na_2SO_4 (furnaced at 450 ^{o}C). The samples were eluted with 25 mL of *n*-hexane:DCM (1:1, v:v). Deuterated benzo[*e*]pyrene was added to each sample prior to analysis as a recovery standard. In all cases (including field blanks), each sample was comprised of two SPMDs. For details regarding the analysis procedure and determination of detection limits, refer to [2, 5].

Results and Discussion

Rate constants for the loss of each PRC (k_e) were calculated using time zero concentrations from field blanks (C_{PRC-0}):

$$k_e = \left(\ln \frac{C_{PRC-0}}{C_{PRC}} \right) / t$$

where C_{PRC} represents the mean concentration of each PRC in the SPMDs at time t. For a more complete development of passive air sampling theory refer to Bartkow et al. [6].

Reproducibility was determined using coefficients of variation (CV; expressed as a percentage). The CVs for both PRCs (where detectable amounts remained in the samples after deployment) ranged between 20 - 29%.

The k_es for both D_{10}-Ant and D_{10}-Pyr were several factors higher in SPMDs deployed in the cage chamber and open box chamber relative to SPMDs deployed in the closed box chamber and bowl chamber (Table 1). In the case of SPMDs deployed in the cage chamber, no D_{10}-Ant remained to quantify elimination rate constants. Not surprisingly, light levels measured in the chambers show that SPMDs were exposed to the most light in the cage chamber (228 µM s^{-1} m^{-2}) and open box chamber (71 µM s^{-1} m^{-2}), whereas light levels in the closed box chamber (11 µM s^{-1} m^{-2}) and bowl chamber (9 µM s^{-1} m^{-2}) were similar. Therefore, it is likely that photodegradation resulted in the elevated values of PRC k_es in SPMDs from the cage and open box chambers.

Table 1. Elimination rate constants for PRCs in SPMDs from different chambers.

Chamber	Elimination rate constant (day $^{-1}$)	
	D_{10}-Ant	D_{10}-Pyr
Cage	-	0.190
Open box	0.240	0.190
Closed box	0.060	0.057
Bowl	0.037	0.009

However, the more open design of these two chambers can also expose SPMDs to higher wind speeds. If samplers are exposed to higher wind speeds then the air-side boundary layer can be reduced. If chemical exchange is air-side limited, and this appears to be the case with PAHs [7], then a reduction in the effective thickness of the air-side boundary layer results in higher k_es.

One way to distinguish between the effects of wind and photodegradation is to examine the differences between k_es for D_{10}Ant and D_{10}Pyr. According to theory for air-side limited chemical exchange, PRC k_es will decrease with increasing sampler to air partition coefficient (K_{SV}) [6]. This observation relates to the following equation:

$$k_e = \frac{D_a A}{\delta K_{SV} V_S}$$

where D_a is the diffusion coefficient in the air boundary layer, A is the surface area of the SPMD, d is the effective thickness of the air boundary layer, K_{SV} is the SPMD-air partition coefficient and V_S is the volume of the SPMD. Evidence suggests that K_{SV} is related to K_{OA} for compounds which are predominately in the vapour phase (unpublished data, USGS, Columbia, MO, USA).The respective log K_{OA}s for natural Ant and Pyr are 7.70 and 8.70 [8]. Assuming these values can be applied to the deuterated analogs of these compounds, the k_es should be significantly different from each other. This should be the case regardless of wind speed (unless the wind speed is high enough to reduce the air boundary layer to the extent that air-side resistance is no longer the rate-limiting step in chemical exchange). In this study, wind speeds were not excessively high and the chambers were designed to minimize wind effects. Therefore, under the deployment conditions used in this study, k_es for D_{10}-Ant and D_{10}-Pyr should be

significantly different. If k_es are not significantly different among treatments, then another mechanism must be influencing the loss of PRCs, such as photodegradation (Bartkow et al. [2])

A comparison of the elimination rate constants for D_{10}Ant and D_{10}Pyr shows that they were relatively similar in all deployment chambers except the bowl chamber (Table 1). These results suggest that photodegradation of PRCs was occurring in SPMDs deployed in both the open and closed box chambers and also the cage chamber, whereas the bowl chamber provided adequate protection from sunlight. In view of the light levels measured inside the chambers, this argument seems reasonable for SPMDs deployed in the open box and cage chambers. However, light levels in the closed box chamber were similar to levels measured in the bowl chamber, yet the SPMDs in the closed box chamber appear to be significantly effected by photolysis.

One possible explanation for this difference could be due to the way in which the SPMDs are oriented inside these chambers. SPMDs inside the box chamber are oriented in a more 'open' manner, where the entire surface area of the SPMD is potentially exposed to reflected light entering through the louvers. The SPMDs deployed inside the bowl chamber are wrapped around a 'spider' device where the outer-most surface of the sampler is exposed to the reflected light entering through the side of the bowls however much of the SPMD is potentially shielded by the outside portion of the sampler. Although further work is required to confirm that sampler orientation is important, these findings have interesting ramifications for passive sampler deployments because using different passive samplers such as PUF disks [9] or polyethylene sheets [5] in the same chamber may result in different levels of exposure to reflected light. For example, the surface of a PUF disk or polyethylene sheet may not be as well shielded as the SPMDs, inside the bowl chamber.

Conclusion

The results of this study show that photodegradation of PAHs can occur in SPMDs that are not adequately protected from reflected sunlight. Currently, the bowl chamber appears to provide the most protection from photodegradation. However, it is possible that photodegradation of compounds is still occurring inside the bowl chamber. To account for this factor, a photosensitive, high K_{OA} deuterated-PAH could be used as a PRC. Importantly such a PRC could also be useful to account for differences in exposure to reflected light (i.e., albedo) which may result from samplers being deployed over different surfaces at different sampling sites. This could be particularly important for broad-scale monitoring programs where samplers are deployed over a range of sampling sites (e.g. concrete, grass, snow). Further work is required to quantify the influence of these particular factors on sampler performance.

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