

Response to Reviewer 2

General comments

The manuscript discusses the uptake of polycyclic aromatic compounds by a specific passive air sampler for deployments lasting up to 1 year. Contrary to expectations, several compounds did not remain in the linear uptake phase; several PAHs either plateaued, or decreased after about 6 months deployment. The behaviour observed for PAHs was in contrast to results for other semi-volatile organic compounds. Three possible reasons were explored (i) impact of particle-bound PACs; (ii) degradation of PAC by ozone and (iii) equilibration of certain PACs.

None of these were concluded to be responsible for the observed observations.

Overall, the manuscript is well written, and includes good data, figures and tables.

We appreciate the positive feedback.

There is a lack of additional creativity beyond the 3 reasons investigated by the authors. Let's try a few:

1. What amount of XAD is oxidized, and thus losing sorption capacity during the year?
2. The curves depicted in Figure 1 might indicate competition for sorptive sites. And the PACs might simply be replaced by stronger sorbing compounds.

Re 1: There is little reason to expect that oxidation of the XAD should result in a loss of its sorption capacity for PACs, unless that oxidation would result in a massive loss of surface area. On the contrary, one might expect oxidation of XAD to lead to a functionalization of its surface, i.e., the introduction of oxygen-containing functional moieties such as carbonyl, hydroxy and carboxylic acid groups. A more polar surface could be expected to sorb PACs more strongly than the original polystyrene-divinylbenzene resin, because of the addition of possible polar interactions between sorbent and sorbate.

Re 1 and 2: A loss of sorption capacity and competitive sorption are simply alternative reasons for a "limited sorbent uptake capacity" and therefore can be subsumed under the second hypothesis we explore. Whatever the underlying reasons for an insufficiently large sorptive capacity, the extent of loss of a PAC from the sampler would be expected to be related to compound volatility, which is not observed. We have added the following sentence to the introduction of the second hypothesis:

"A variant of this hypothesis is that something is causing a decrease in the sorption capacity of the XAD-resin over time, i.e. the aging of the resin or competition by other sorbates."

Specific comments

L66 – very detailed list what is the difference between urban and regions with high traffic density?

Not all regions with high traffic density are in urban areas. Some highways with high traffic volume are in rural areas, if they connect major population centres.

L 149 – give better reason why ozone was chosen (NO_x or OH)

We are not sure why the reason we provide in the paragraph introducing the third hypothesis are not good enough. With regard to NO_x we write: "While nitrogen dioxide may also react with some PAHs, either no reactions were found (Grosjean et al., 1983; Pitts et al., 1980), or only negligible percentages of PAHs were observed to react with nitrogen dioxide (Tokiwawa et al., 1981)." With regard to OH we write: "Even though gaseous and sorbed PAHs can react with OH radicals (Brubaker and Hites, 1998; Atkinson and Arey, 2007; Esteve et al., 2004, 2006; Bedjanian et al., 2010), such reactions are less likely to occur within the dark environment of a XAD-PAS housing."

Formation of OH requires sunlight and the atmospheric lifetime of OH radicals is very short, on the order of a second or less. It is a dark within the XAD-PAS housing, and it is not very likely that many OH radicals would survive long enough to diffuse to the sorbent to react with the sorbed PACs. We have added the phrase: ", because of the short atmospheric lifetime of OH radicals" to make this clearer.

L193 – reference for chosen air boundary later?

It is a commonly used air boundary layer thickness in the model by Zhang and Wania (2012). We now refer to two papers have used this thickness during simulations " Zhang and Wania, 2012 Li et al., 2023b"

Figure 3 – This is supposed to simulate an equilibration experiment, right? Make that explicit in the caption

We modified the caption to Figure 3 as follows " Predicted uptake curves for a **volatile chemical reaching equilibrium between XAD and gas phase, i.e.**, with a $\log (K_{\text{XAD/air}} / (\text{L air g}^{-1} \text{XAD}))$ value of 2.69 at 20 °C, during calibration experiments starting in June and November, while assuming air concentration and temperature variability typical for Southern Ontario."

Figure 5 would benefit from some descriptive statistics – presumably all compounds but PACs, and PACs on their own

Figure 5 displays four relationships between the empirically determined sampling rates (SRs) and the estimated sorption constant to XAD-resin. Descriptive statistics for those relationships for the PCBs and other SVOCs have been provided in earlier publications (Li et al., 2023a, b). Descriptive statistics for the relationships for the PACs are provided in the text (equations 2 and 3).

We suggest that the relationship for PCBs be used to estimate sampling rates for PCBs (Li et al., 2023b) and that the relationship from Li et al., 2023a be used for estimating SRs for SVOCs other than PCBs and PACs. As such, we do not think it is advisable to provide another relationship that combines the SRs for all compounds other than the PACs.

Technical corrections

L145 – sandwich

We prefer to keep using the plural "sandwiches" as we used more than one PUF-XAD-PUF sandwich during our active air sampling.

L335 – Thus it should?

The original formulation is also grammatically correct.