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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Depletion of gaseous polycyclic aromatic hydrocarbons by a forestcanopy" *by* S.-D. Choi et al.

M. MacLeod (Referee)

macleod@chem.ethz.ch

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General Comments

This paper describes an elegant experiment designed to directly observe the depletion of PAHs in air by deposition to a deciduous forest canopy shortly after bud break in the spring. The study is well conceived and appears to have been carried out carefully and competently. The paper is well written and supported by well-executed figures. I believe the data generated from the study provide valuable empirical evidence of the spring-time depletion of gas-phase semi-volatile organic chemicals due to deposition to emerging forests canopies. I am not totally satisfied with the assumptions used by the authors to estimate dry gaseous deposition velocities to the canopy, and I believe these calculations require a bit more discussion to clearly convey their uncertainties.

However, I concur with the authors that this study represents the most direct empirical observation of this interesting phenomenon reported to date, and I believe the paper should be published, after attention to the points raised below.

Specific Comments

2361, Line 7-9: The factor of 5 reduction in SVOC concentrations in air due to the presence of a forest canopy that is often cited from Wania & McLachlan (2000) is a very misleading number since it was derived from a model parameterization that totally neglects the competing process of advection through the region. I have re-done the model calculations from Wania & McLachlan (2000) using a realistic residence time of air in the model region, and found a maximum reduction in regional-average air concentrations due to the forest canopy of a factor of 1.2 (MacLeod, *Stochastic Environmental Research and Risk Assessment*, 17, 256-259, 2003). I would therefore like to see the reference to the factor of 5 reduction removed, since I believe it doesn't provide an accurate picture of the magnitude of the influence of forests on concentrations of SVOCs in air that might be observed in the field.

2362, Line 16-17: The statement that PAH uptake in the forest canopy is expected to be largest in the spring should be supported by a statement of why the authors have this expectation.

2362, Line 17-18: Is it correct that the four samples at the different heights were collected simultaneously? This should be stated explicitly here.

2369, Line 8: "As expected, no strong gradients were observed". This statement is not quite true for Anthracene. From inspection of Figure 2, the gradients between A-B-C on April 24 & 25 are just as strong as those on May 12, 15, 21, and June 2.

2370, Line 13-22: It is frustrating that it isn't possible to make a flux estimate from the observed gradient between levels D and C, accepting the author's suggestion that the forest floor is acting as a source of PAHs. But, based on the discussion in this section

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I see that it would not be possible to make a flux estimate because of the lack of a diffusivity estimate under the canopy and the interference from uptake by the canopy between levels D and C. The authors may want to comment on the possibility of future studies that use measurements of the vertical gradient in concentrations below and inside the canopy to estimate uptake fluxes by emerging leaves.

2370, Line 23 - 2370, Line 10: The assumptions used in the scenarios to account for diurnal variability of the concentration gradient and estimate depositional fluxes are my biggest concern about the paper. First, I believe that Scenario III does not make sense as it is presented, and that is should be removed from the paper. If temperature-driven volatilization from the surface was the dominant source of PAHs to the atmosphere between Level B and A, one would indeed expect to see the strongest gradient in concentrations during the day, but the gradient would be in the opposite direction to the one that is observed. I.e., the concentration at B would be greater than at A. This is the situation below the canopy (between D and C), but as noted above it isn't possible to make flux calculations based on these data.

Scenario I is, in my opinion the one that provides the most quantitative information about the fluxes. Because we expect an inverse correlation between K_{Heat} and DC/Dz that isn't accounted for in this Scenario, and because K_{Heat} goes to near zero at night, it seems reasonable to expect that Scenario I will provide an overestimation of the flux. But, this expectation could be wrong because of an additional complicating factor that isn't discussed in the paper: During the day when there is higher turbulent mixing and higher windspeeds, the effective boundary layer thickness at the surface of the leaves will be thinner, and the dry gaseous deposition velocity to the canopy will be higher. This could lead to higher than expected gradients during the day. Considering all of the uncertainties in this calculation, I expect that Scenario I provides no more than an order of magnitude estimate of the flux to the forest canopy. The authors should provide some guidance of the expected uncertainty associated with their calculations. (This would be in addition to the variability that is already communicated by the range

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of values for each scenario in Table 2).

Despite the high uncertainties, Scenario II is valuable and should be retained in the paper for illustrative purposes, however the assumption that the concentration gradient is 50% lower during the day compared to at night is totally arbitrary, and I think this Scenario should be presented with additional caveats. Given all of the uncertainties associated with these calculations, I think the authors might want to re-think their presentation of three significant figures in some cases in Table 2.

One interesting thought that occurred to me: The lack of a vertical gradient in concentrations for the particle-associated PAHs implies that vertical mixing is fast compared to dry particle deposition to the canopy. In contrast, vertical mixing must be slow compared to dry gaseous deposition to the canopy. According the Horstmann & McLachlan and Su et al., the dry gaseous deposition velocity in deciduous forests is between a factor of 4.7 (H&M) and 27 (Su et al) faster than dry particle deposition, and these papers provide some estimates of how fast these processes are in absolute terms. Have the authors undertaken any back-of-the-envelope mass balance calculations to determine whether their assumed vertical diffusivities used in this paper correspond to a rate of vertical mixing that would swamp out the effect of particle deposition, but still allow observable depletion due to gaseous deposition? Such calculations might be a useful addition to the paper since they could clarify whether the results reported here are consistent with the findings in H&M and Su et al.

Figure 2: The three measurements of 100% particle association for Anthracene at the 16.7 m level jump out of the figure as unusual. Is there any explanation for these data?

Technical Corrections

2361, Line 15: "Simultaneous *measurement* of air concentrations ... has been applied to *estimate*"

2373, Line 19: Suggest you replace "measuring" with "estimating".

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Figure S8: There is a typo in the units on the vertical axis (should be pg m^{-3} m^{-1}).

Figure S9: I'd like to see zero indicated on all the vertical axes in this figure.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 2359, 2008.

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