Assessing the Influence of Secondary Organic Aerosols on Long-Range Atmospheric PAH Transport

Carey L. Friedman and Noelle E. Selin
Center for Global Change Science (clf@mit.edu)
Engineering Systems Division and Department of Earth, Atmospheric, and Planetary Sciences (selin@mit.edu)
77 Massachusetts Ave., Cambridge, MA 02139 USA

MIT ATMOSPHERIC CHEMISTRY

Background

Polycyclic aromatic hydrocarbons (PAHs) are toxic semivolatile compounds that partition between gas and aerosol phases and undergo atmospheric long range transport (LRT). Physicochemical processes influencing PAH transport to remote regions (e.g., the Arctic) are still largely unknown. In particular, the influence of aerosols on PAH LRT and how to best model PAH gas-particle (G-P) partitioning are highly uncertain. **Here, we conduct simulations using the chemical transport model GEOS-Chem under different assumptions about (1) G-P partitioning and (2) physicochemical characteristics of aerosols, to test how these variables affect PAH LRT efficiency.**

G-P partitioning of PAHs has been described by a number of different schemes, each employing the assumption of instantaneous equilibrium partitioning (EqP). Only one (the Dachs and Eisenreich[1] scheme, or "D&E") considers adsorptive partitioning to black carbon (BC), and consistently performs best; hence, we use it in our model[2,3]. No partitioning scheme, however, captures observed PAH G-P distribution without fault: most underpredict PAH particulate fraction (f_p), and D&E can overpredict f_p.

Recently, a new hypothesis has been put forth based on laboratory work: PAHs are incorporated into SOA as it forms, which traps them and protects them from oxidation, ensuring their LRT in the particulate form[4].

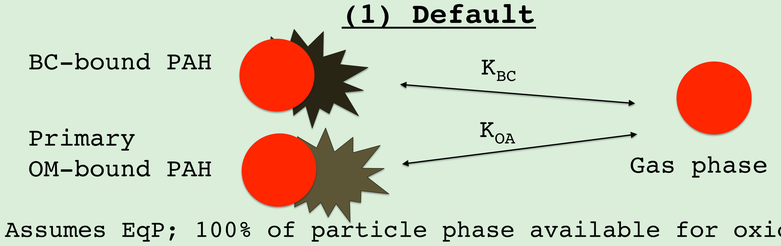
SOA has never explicitly been considered in a PAH modeling study before. We develop new configurations of the GEOS-Chem PAH model to test whether incorporating SOA and a G-P scheme that traps PAHs, rather than assumes instantaneous EqP, better represents PAH LRT compared to our default model.

Literature Cited:
1) Dachs & Eisenreich. 2000. Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.*, 34:3690-3697.
2) **Friedman & Selin. 2012. Long-range atmospheric transport of polycyclic aromatic hydrocarbons: A global 3D model analysis including evaluation of Arctic sources. *Environ. Sci. Technol.*, 46:9501-9510.**
3) **Friedman, Zhang, & Selin. 2013. Climate change and emissions impacts on atmospheric PAH transport to the Arctic. *Environ. Sci. Technol.*, In Press.**
4) Zelenyuk et al. 2012. Synergy Between Secondary Organic Aerosols and Long-Range Transport of Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol.*, 46:12459-12466.

Methodology

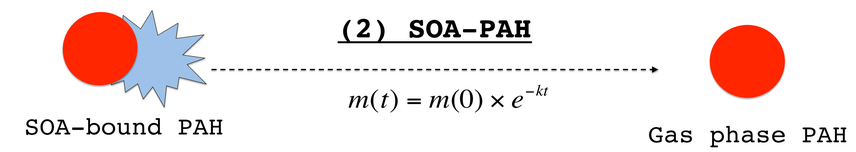
We test 3 configurations of the GEOS-Chem PAH model:

(1) Default



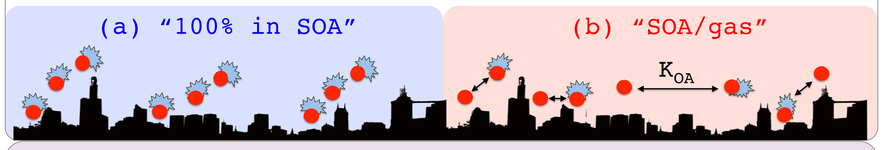
Assumes EqP; 100% of particle phase available for oxidation

(2) SOA-PAH

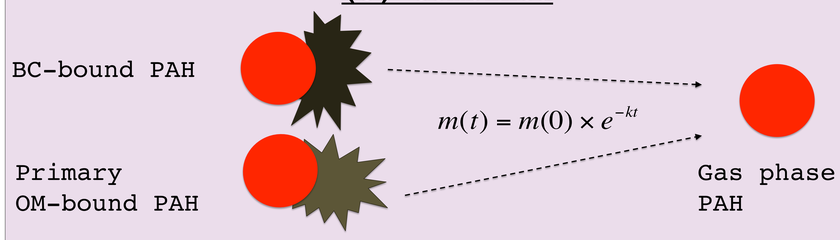


Assumes slow evaporation from SOA to gas phase; 10% of particle phase available for oxidation

Two PAH emissions scenarios:

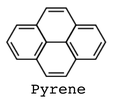


(3) Combined



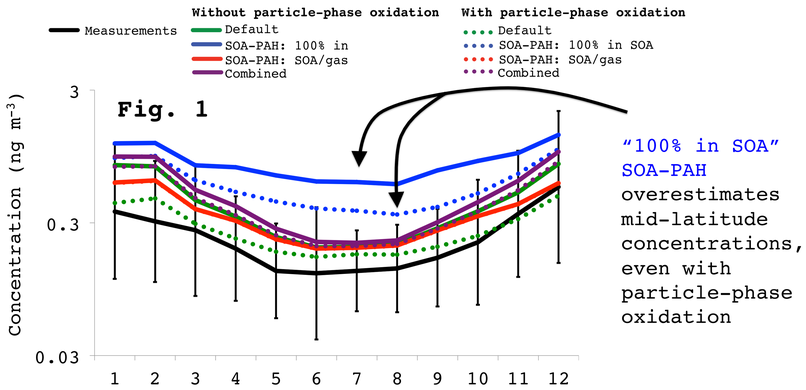
Assumes slow evaporation from primary carbonaceous aerosols to gas phase; 10% of particle phase available for oxidation

- In (2) and (3), evaporation is modeled with a rate (k) corresponding to 80% remaining on particles after 24 hours
- All simulations are conducted for the PAH pyrene because of its semivolatility
- Particle phase oxidation is by O_3 and NO_3
- For details on PAH model development, evaluation, and use, see Friedman & Selin[2] and Friedman, Zhang, and Selin[3]


Pyrene

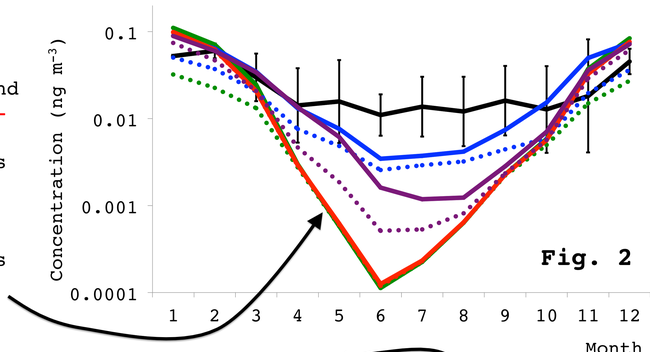
Results

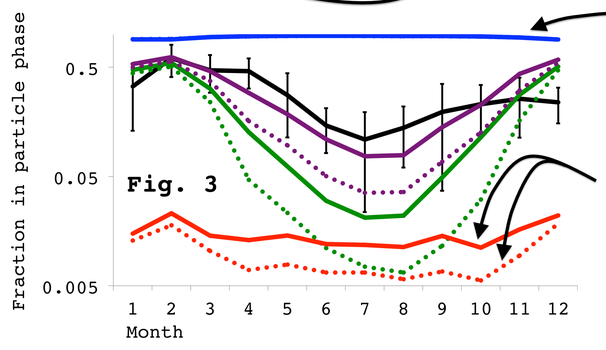
We evaluate each configuration's ability to replicate PAH LRT by assessing mean (2006-2008) northern hemisphere **mid-latitude (Fig. 1)** and **Arctic (Fig. 2)** total concentrations, and **mid-latitude f_p (Fig. 3)**. **Only the "Combined" configuration captures all three metrics simultaneously:**



"100% in SOA" SOA-PAH overestimates mid-latitude concentrations, even with particle-phase oxidation

The default and "SOA/gas" SOA-PAH configurations severely underestimate remote Arctic concentrations





SOA-PAH configurations either over- or underestimate f_p and do not capture seasonal variation

Take-home Message

- **Trapping PAHs in particles and protecting them from oxidation improves model-measurement agreement in remote areas compared to an instantaneous EqP scheme**
- **Observed f_p magnitude and seasonal cycle are not captured unless G-P partitioning is simulated with primary carbonaceous aerosols (especially BC) rather than SOA**