**Introduction**

- Atmospheric parent polycyclic aromatic hydrocarbons (PAHs) react with atmospheric oxidants (e.g., OH•, NOx, O3) (Jaryasopit, et al., Environ. Sci. Technol., 2014).
- The reactions result in the formation of PAH-transformation products (PAH-TPs) such as nitrated-PAHs (NPAHs), oxygenated-PAHs (OPAHs), and hydroxylated-PAHs (OH-PAHs) (Yu, et al., Environ. Sci. Health C. Environ. Carcinog. Ecotoxicol. Rev., 2002).

**Research Question**

Can PAH-TPs that are most likely to form in the atmosphere be predicted from the structure of parent-PAHs?

**Approach**

- Laboratory Data
- Most reactive site on parent-PAHs
- Clar's Resonance Structure
- Computational Chemistry

- Do they match laboratory data?
- Can structure analysis predict PAH reactivity?

**Laboratory Data**

- 59 published works
- Gas and particle phase laboratory experiments
- 15 tested parent-PAHs (13 PAHs in the U.S. Environmental Protection Agency priority list of pollutants and 2 molecular weight 302 amu PAHs)
- Collected data are limited to exposure to three atmospheric oxidants: OH•, NOx, and O3
- PAH-TPs are limited to just primary NPAH, OPAH, and OH-PAH products—and not on further degradation products

**Computational Chemistry: ΔG_rxn**

- Parent-PAHs react with OH•, resulting in OH-PAH adducts
- The change in Gibbs free energy of the reaction (ΔG_rxn) resulting in the formation of OH-PAH adducts can predict the likelihood substitution site on a parent-PAH
- Computational chemistry calculates the most negative ΔG_rxn (i.e., the most favorable site for reaction)

**Computational Chemistry: Mulliken**

- The electron density of a parent-PAH can be determined based on partial charge calculation
- Carbon with the most negative partial charge is predicted to have the most electron density, indicating carbon that is most susceptible to be attacked by atmospheric oxidants
- Computational chemistry calculates carbon with the most electron density

**Computational Chemistry: ALIE**

- Average local ionization energy (ALIE) is a molecular surface parameter that determines the average energy required to remove an electron from a certain position on a molecule
- The reactivity can occur on atom or bond sites
- Lower ALIE = more reactive site

**Results**

- Most reactive atom sites
- Most reactive bond sites

**Conclusions**

- Structural analysis alone cannot predict the formation of atmospheric PAH-TPs
- ALIE is a robust computational model that predicts the formation of atmospheric PAH-TPs
- Computational approach can help predict a list of PAH-TPs that are previously unstudied