Parametric uncertainty analysis of GEOS-Chem simulations of benzo[a]pyrene

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Background

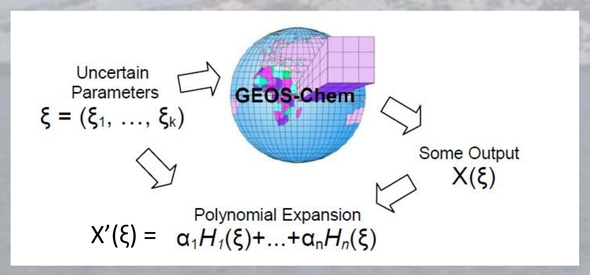
Persistent organic pollutants (POPs) are chemicals that can travel long distances in the atmosphere and deposit in remote areas such as the Arctic. The GEOS-Chem global chemical transport model has been used to assess Arctic transport for the specific case of polycyclic aromatic hydrocarbons (PAHs) including benzo[a]pyrene (BaP), toxic byproducts of incomplete combustion, which have been termed "emerging Arctic contaminants" because of increasing concentrations in Arctic marine organisms[1].

While GEOS-Chem deterministically calculates the concentration of benzo[a]pyrene across the globe[2], these chemistry calculations rely on highly uncertain chemical parameters. It is therefore very important to be able to quantify the uncertainty in predicted concentrations that arises from the uncertain parameters, and to be able to identify which parameters are contributing most to the uncertainty. With this in mind, this work looks to answer the following three questions:

1. ***What is the uncertainty in benzo[a]pyrene concentration resulting from highly uncertain chemical parameters in GEOS-Chem simulations?***
2. ***Which parameters contribute most to the uncertainty?***
3. ***Can measurements combined with a polynomial model response estimator constrain parameter uncertainty?***

Methodology

To estimate the uncertainty in GEOS-Chem simulations, a polynomial chaos expansion of the model output is calculated, which acts as an estimator of GEOS-Chem's response to changing chemical parameters. In this work, the polynomial expansion is carried out to 3rd order for 6 uncertain parameters, modeled here as being log-normally distributed. A single run of GEOS-Chem is conducted at a prescribed set of parameter values (a "collocation point") for each term in the polynomial in order to solve for the polynomial coefficients. The resulting polynomial expansion yields uncertainty distributions, relative importance of each uncertain parameter, and an estimator of GEOS-Chem's response to any set of values for the uncertain parameters.



Model Specifics:

- Run at 4° longitude by 5° latitude
- 1 year spin up
- 84 runs for coefficients, 70 validation runs
- Global BaP emissions from Zhang and Tao[3]

Results

1. Regions far from sources have relatively lower mean concentrations but also relatively higher uncertainty .

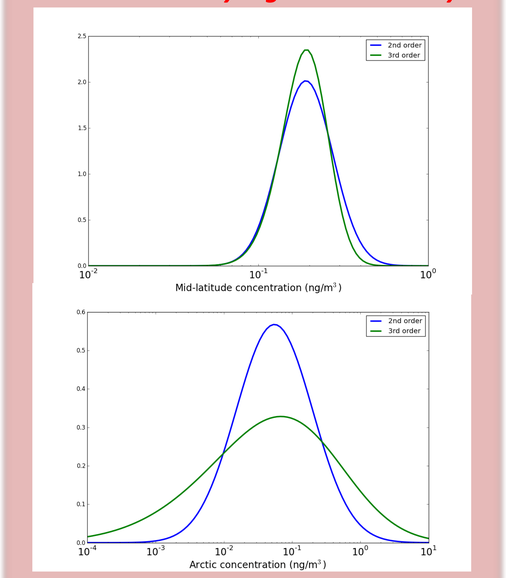


Figure 1. Annual average mid-latitude (**top**) and Arctic (**bottom**) parametric uncertainty distributions for benzo[a]pyrene.

Estimator evaluation: Polynomial estimator reproduces actual GEOS-Chem output successfully

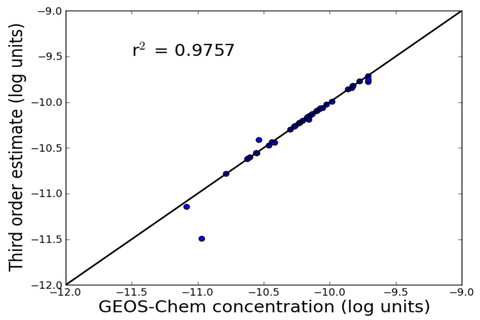
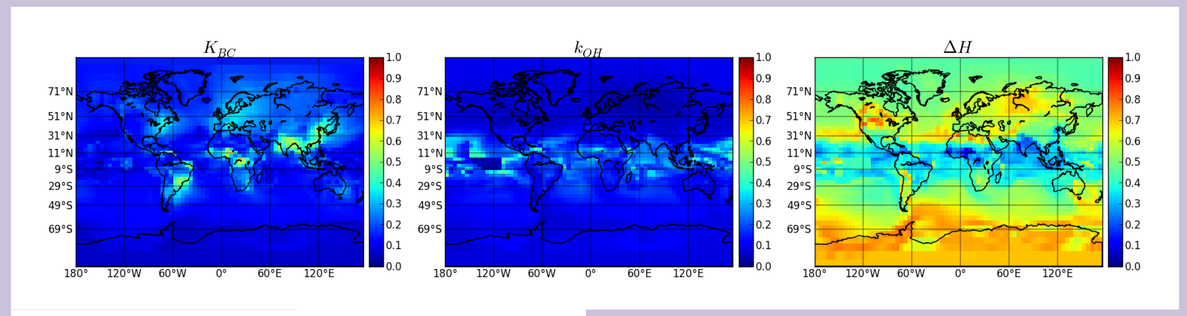


Figure 3. Arctic annual average estimated total concentrations of BaP in surface air by polynomial expansion versus full GEOS-Chem simulation at same parameter values.

2. Enthalpy of vaporization is the most important contributor to uncertainty globally especially in regions far from sources. Black carbon partition coefficient uncertainty dominates close to sources.



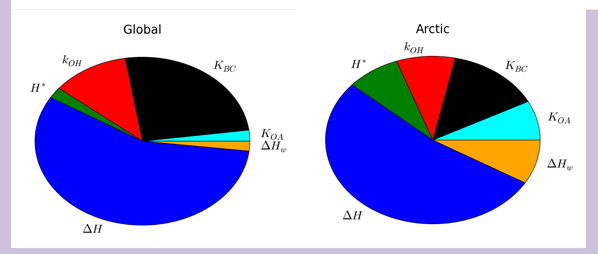
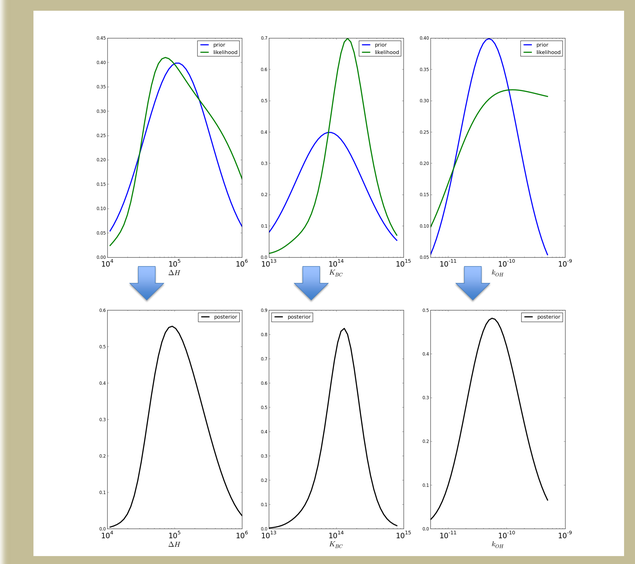


Figure 2. (**Top three panels**) Fraction of total uncertainty contributed by the most important uncertain parameters, spatially resolved. (**Bottom two panels**) Fractional uncertainty contribution of each parameter to the global and Arctic annual averages. ΔH is the most important parameter for uncertainty everywhere except in the tropics. K_{BC} plays a secondary role, except near the biomass burning regions that are the main sources of BC and BaP. In the Arctic, interaction of other parameters with ΔH increase their contribution to overall uncertainty.

3. Measurements of annual average benzo[a]pyrene concentrations can be used to constrain parameter uncertainties with a Bayesian inference approach.



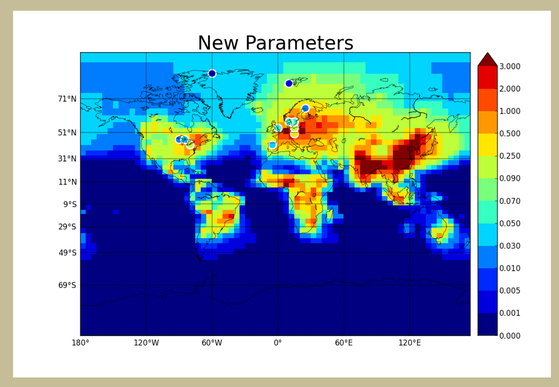


Figure 4. (**Left**) Bayesian inference of parameter uncertainties. Likelihoods are calculated from a weighted least-squares comparison with measurements. LS weights are a sum in quadrature of measurement uncertainties and emission-based uncertainty . (**Right**) Full GEOS-Chem run at most probable parameter values agrees better with measurements.

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[2]Friedman, C.; Selin, N.E.; 2012 . Long-range atmospheric transport of polycyclic aromatic hydrocarbons: a global 3-D model analysis including evaluation of Arctic sources. *Environ. Sci. Technol.*, 46:9501-9510.
[3]Zhang, Y.; Tao, S.; 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmospheric Environment*, 43:812-819

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