Quantifying parametric uncertainties in the world of global atmospheric PAH modeling

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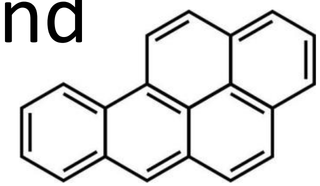
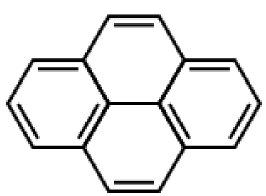
MIT ATMOSPHERIC CHEMISTRY

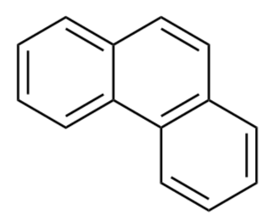
Polycyclic Aromatic Hydrocarbons (PAHs)

- Atmospheric pollutants that have been identified as carcinogenic, mutagenic and teratogenic (esp. benzo[a]pyrene)



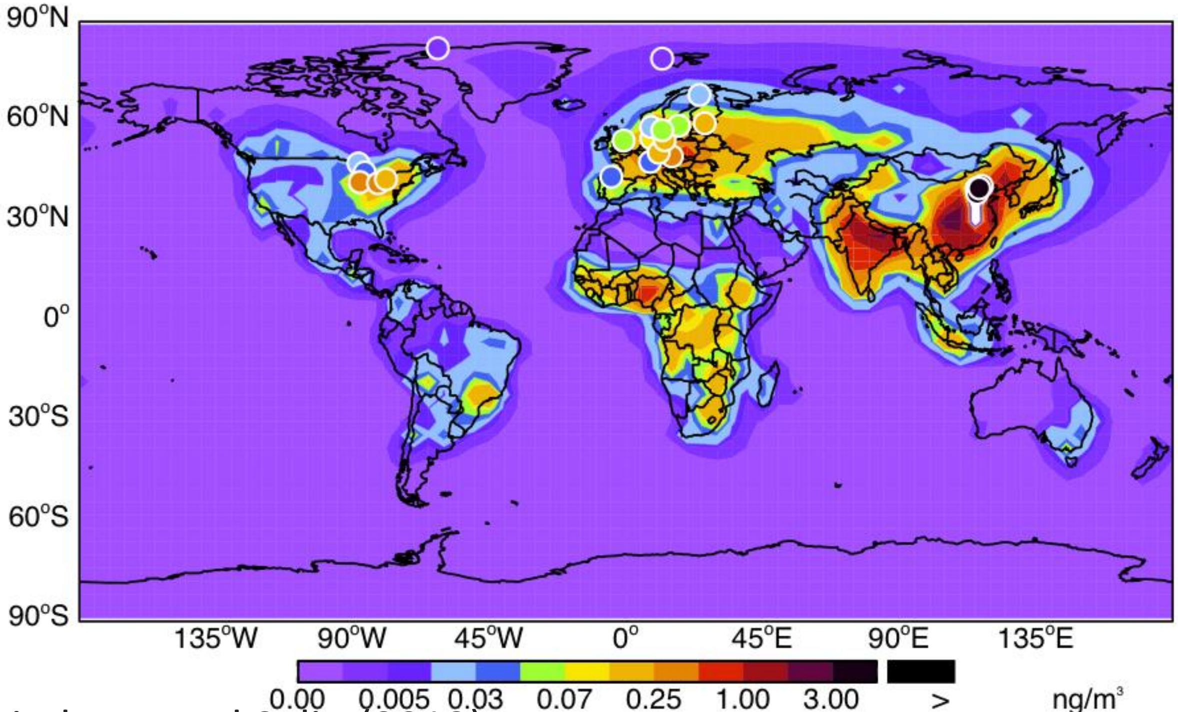
- Present in both gas and particle phases
- Observed at remote locations (long-range transport)
- Highly uncertain chemical property values





Long-range transport of PAHs

- Interested in the long-range transport potential of PAHs
- PAHs are measured at mid-latitudes and at a couple of Arctic sites, but otherwise we rely on model simulated concentrations
- How big are the uncertainties associated with our simulated results?

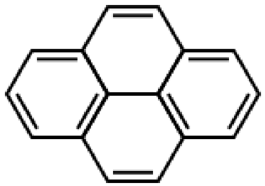


Friedman and Selin (2012)

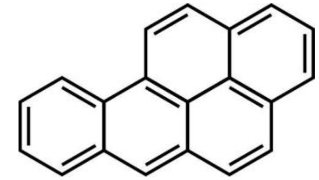
GEOS-Chem BAP annual average total concentrations (gas + part. phase)

Dots: Measurement sites

- Low spatial coverage
- No Southern Hemisphere measurements
- Few remote/Arctic locations



Outline

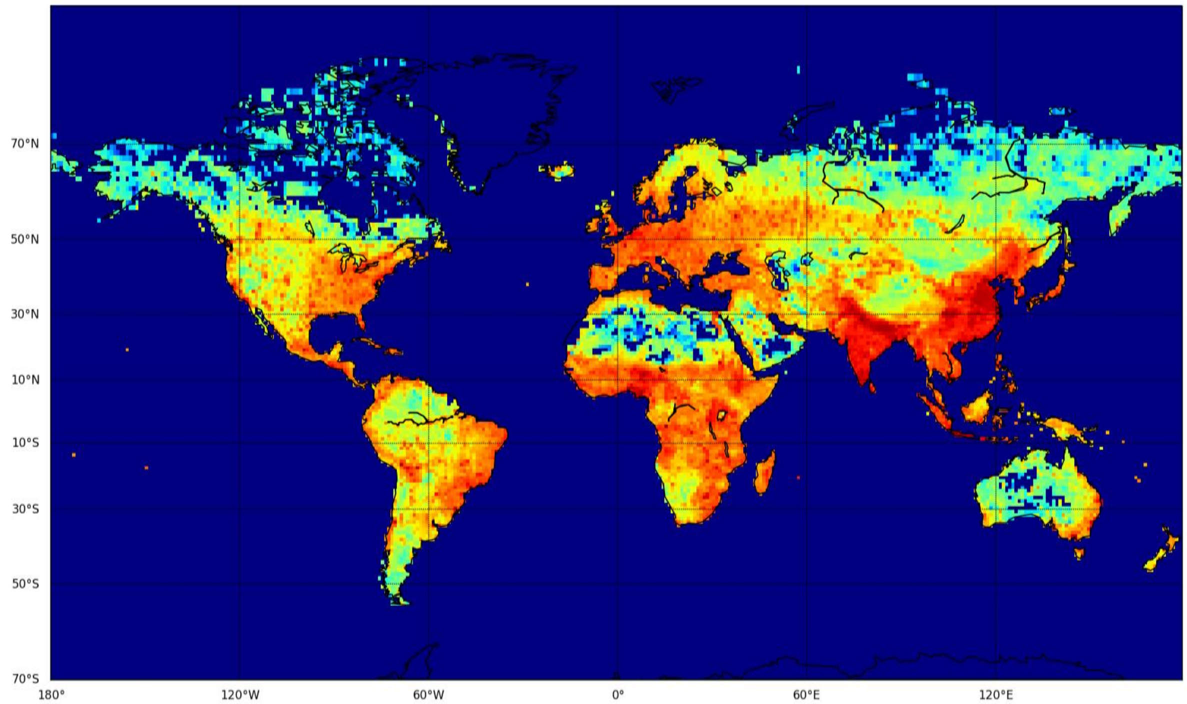


1. An introduction to PAHs and the model representation of their atmospheric chemistry
2. Uncertainty in the model parameters that govern PAH chemistry
3. Polynomial chaos: a way to cheaply propagate parameter uncertainties to model outputs
4. Simulated parametric concentration uncertainty and its leading contributors
5. Using measurements and PC to constrain parameter uncertainty

Sources of PAHs

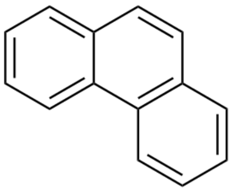
- Sources: **Burning**
  - Fossil fuels, coal
  - Biomass (wood, grass, animal dung)
  - Wildfires
  - Waste incineration
  - Secondary metal production

Phenanthrene yearly emissions map (log scale)

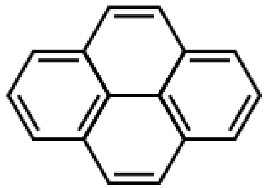


Zhang and Tao (2009)

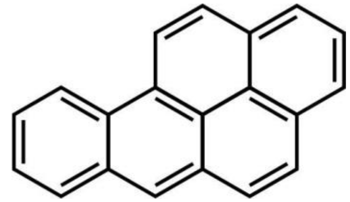
GEOS-Chem simulation of PAH chemistry



Phenanthrene
(PHE)

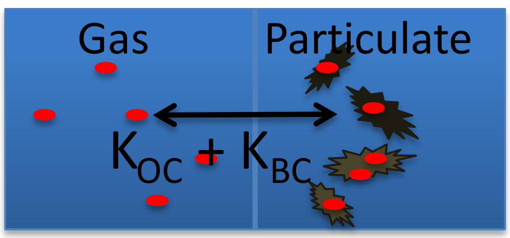


Pyrene
(PYR)

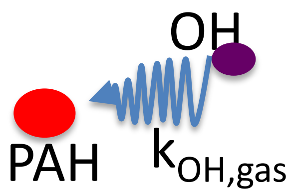


Benzo[a]pyrene
(BaP)

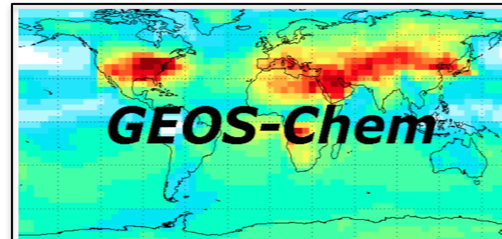
100% gas ⟷ 100% particulate



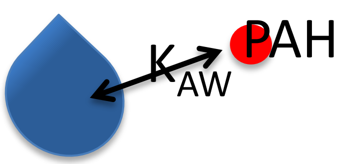
Gas-particle partitioning



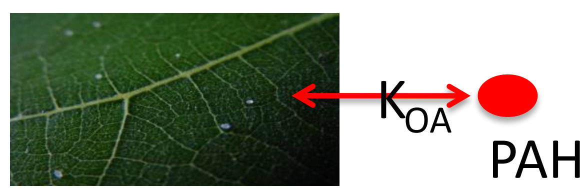
Oxidation



4°×5°
47 vertical levels
Emissions from Zhang & Tao
(*Atmos. Environ.* 2009)
Monthly OC/BC from 2008
Simulation: 2005-2009

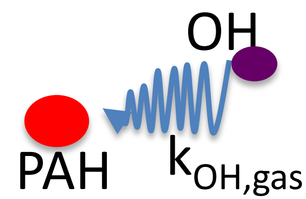


Wet deposition

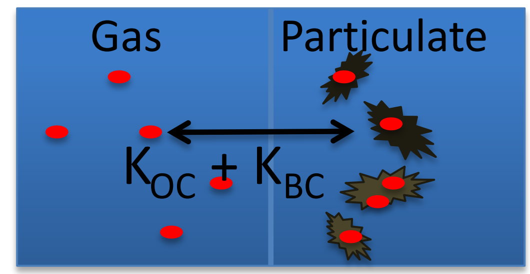


Dry deposition

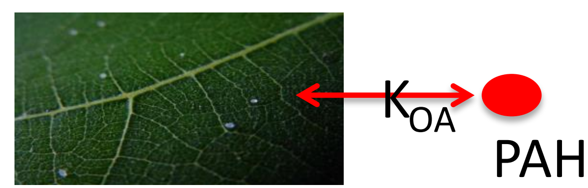
Model Physicochemical parameters



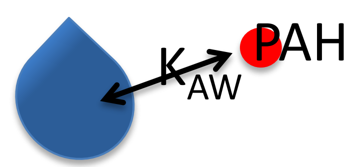
- **k_{OH}** – oxidation rate coefficient
  - Gas-phase lifetimes
  - Measured or estimated via ionization potential



- **K_{BC}** – partitioning to black carbon particles
  - Particulate fraction
  - $K_{BC\text{-}W}$ is measured and combined with K_{AW}
- **ΔH_{vap}** – enthalpy of vaporization
  - Temperature dependence of particle partitioning
  - Measured or inferred from enthalpy of sublimation, fusion
- **K_{OA}** – partitioning to organic carbon
  - Dry deposition, particulate fraction
  - Measured experimentally

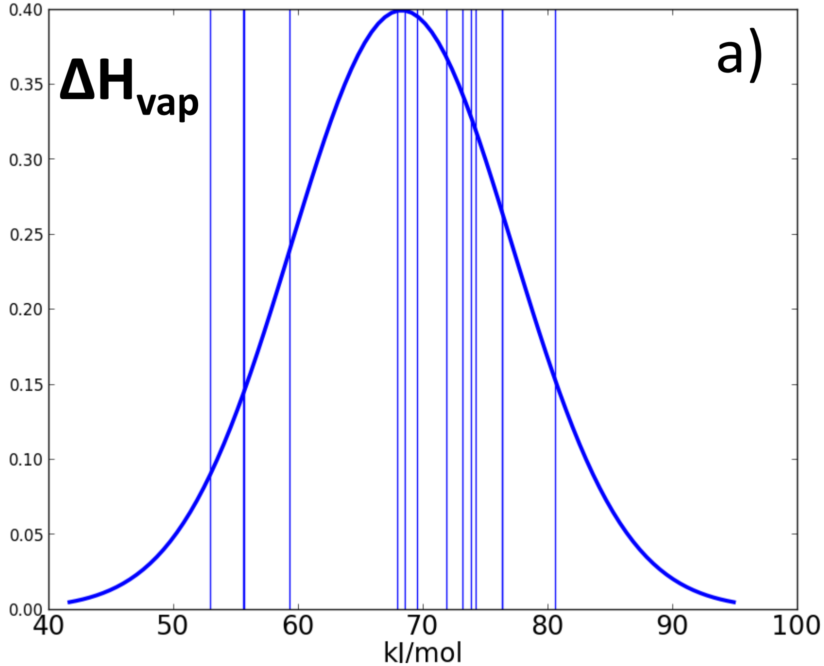


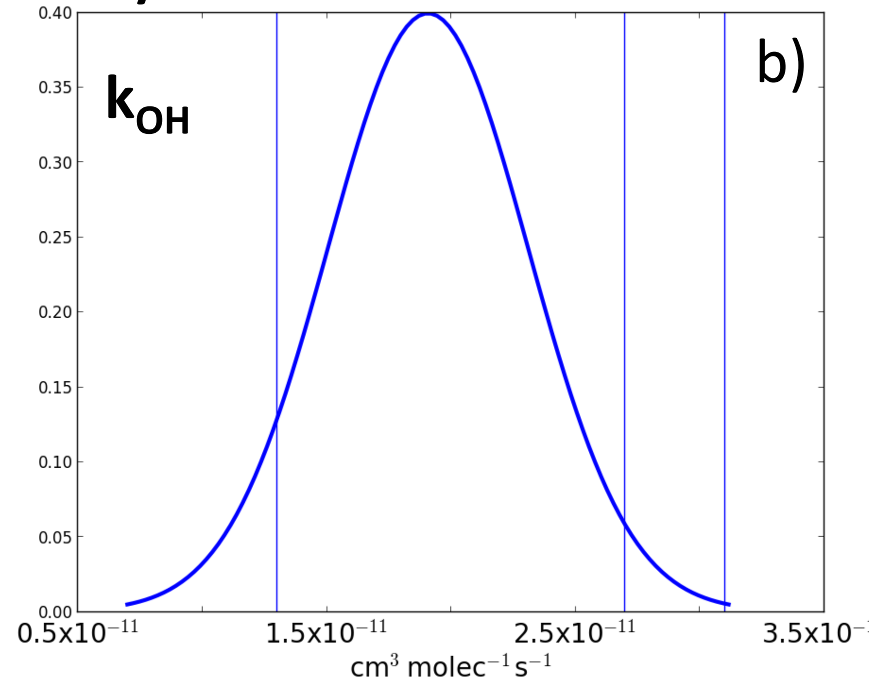
- **K_{AW}** – partitioning to water
  - Wet deposition
  - Measured experimentally

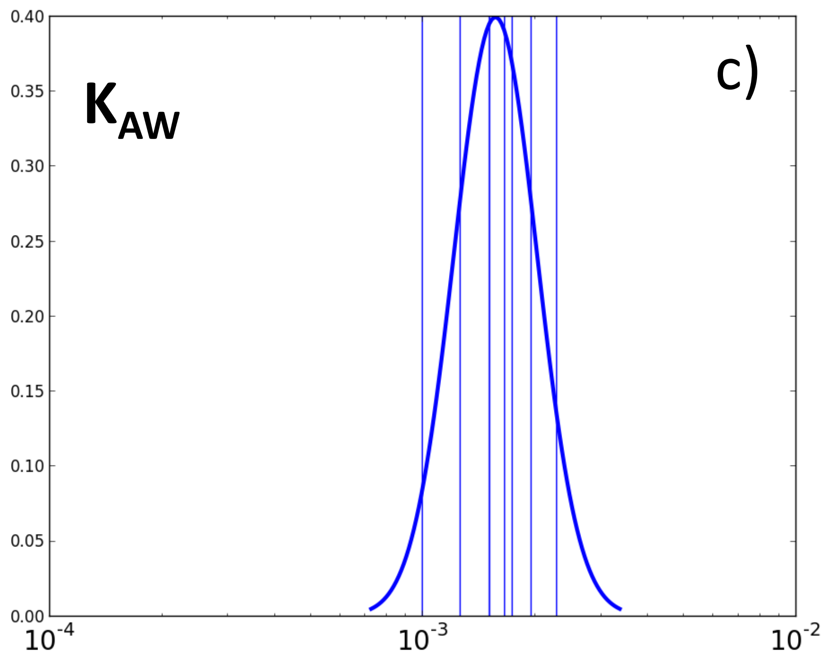


- **ΔH_{sol}** – enthalpy of solvation
  - Temperature dependence of water partitioning
  - Measured experimentally

Parameter uncertainty distributions







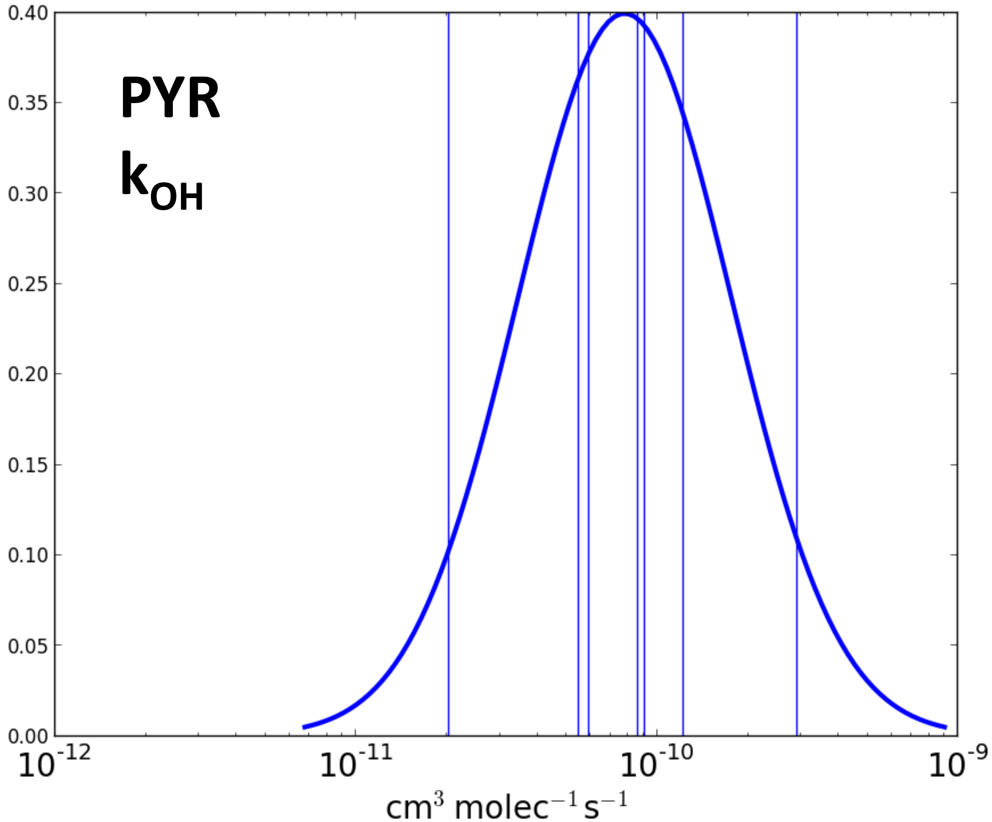
Three ways uncertainty distributions are generated:

a) Mean and variance of the set of literature values
b) Mean and variance from combining literature values and their uncertainties
c) Mean and variance of the set of literature log values

References:

Shiu and Ma (2000), Brubaker and Hites (1998), Atkinson (1989), Kwok et al. (1994)

A note on large-PAH k_{OH} uncertainty



- **k_{OH}** shows the largest uncertainty for PYR and BaP, coming from estimation using ionization potential:

$$\ln(k_{OH}) = -4.345 - 2.494[\mathrm{IP}]$$

- where k_{OH} and IP have units of $cm^3\ s^{-1}$ and eV, respectively
- Uncertainty in ionization potential of BaP and PYR leads to large k_{OH} uncertainty

References:

Biermann et al. (1985)

Kazakov et al. (1999)

Emissions Inventory Uncertainty

- 2004 Emissions from Zhang and Tao (2009)
- Country-level emissions:

Sector's activity

Country's Emissions

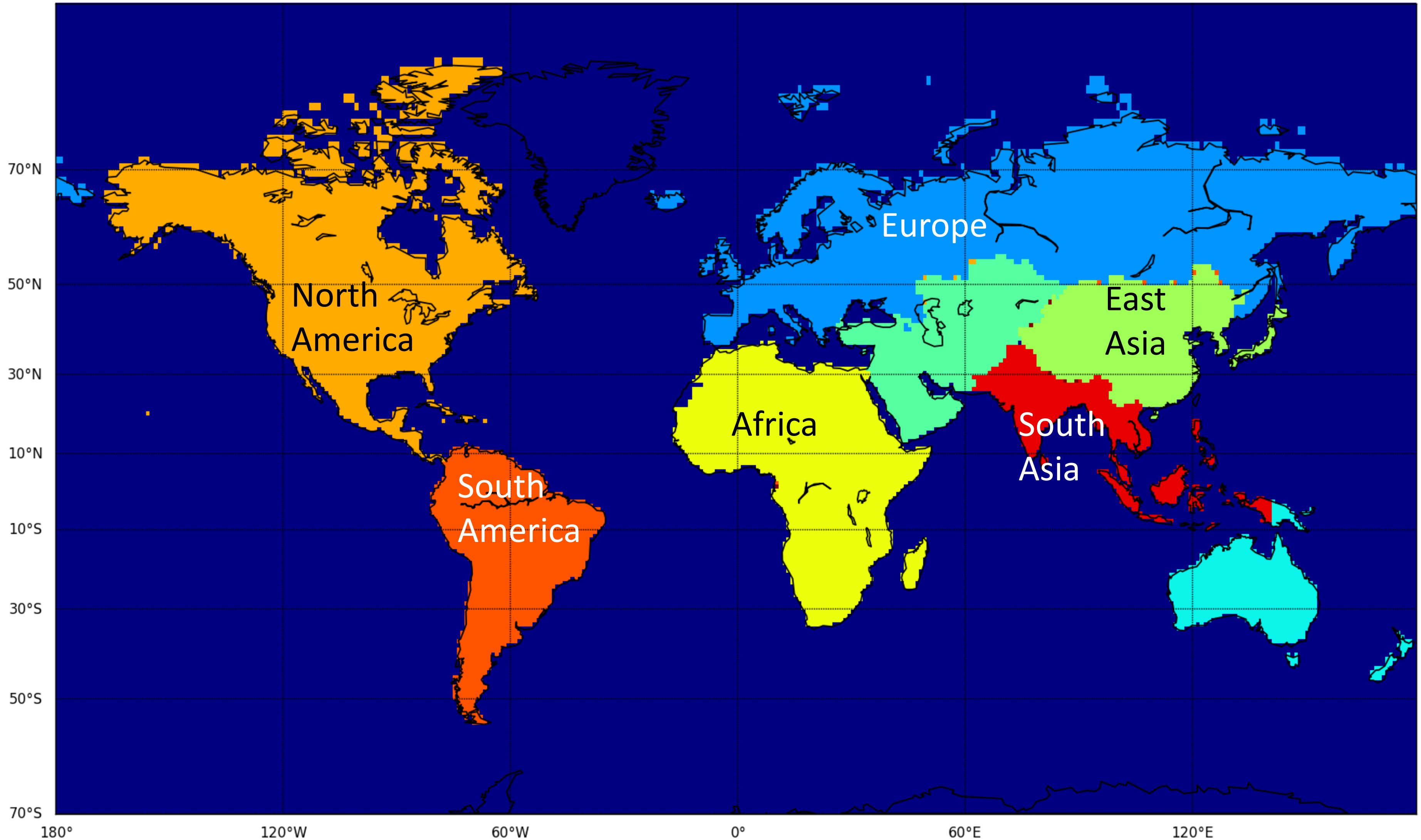
$$E_C = \sum_i (A_C{}^i e_F{}^i)$$

Sum over all sectors

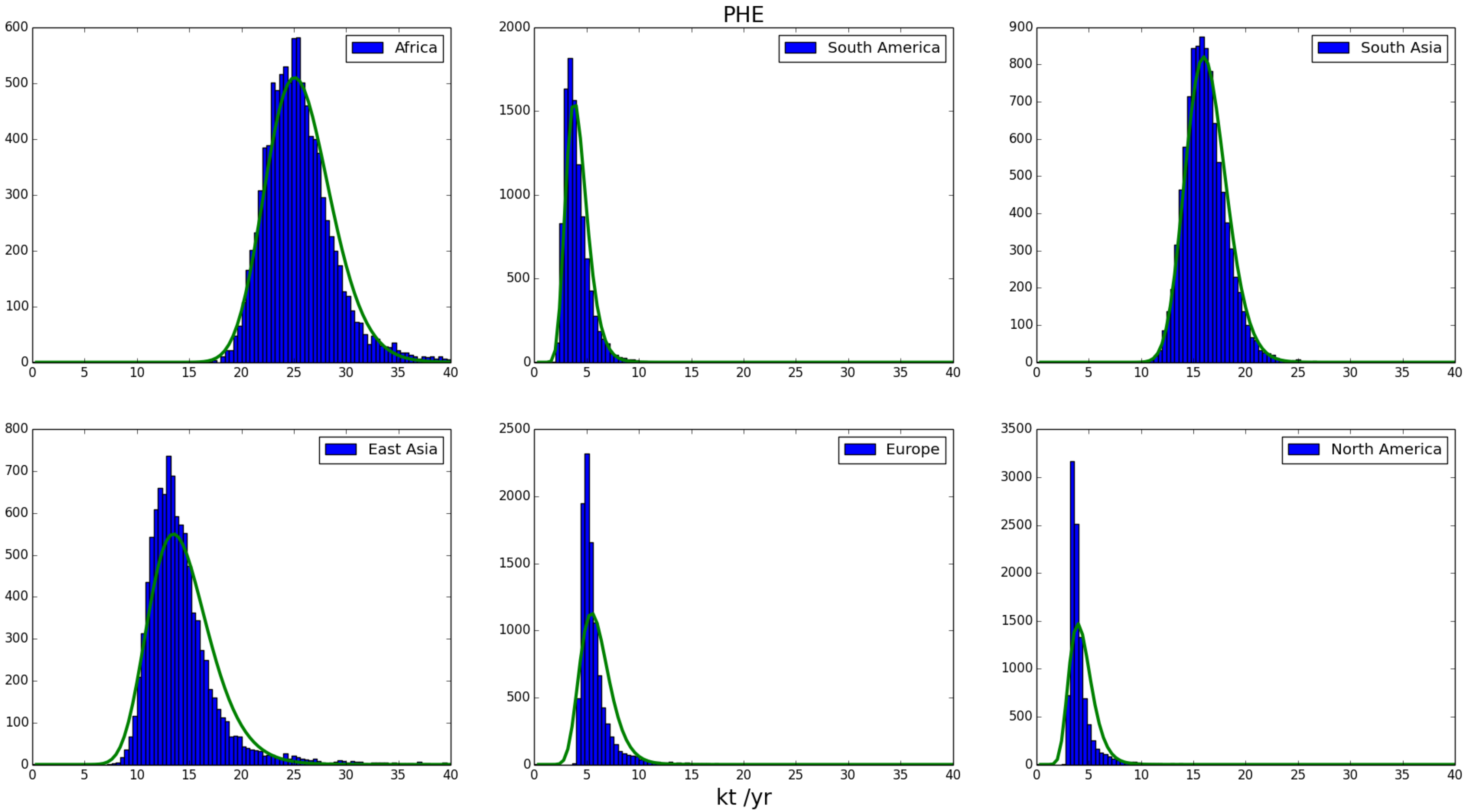
Emissions factor

- Consolidate into regional emissions: sum over countries in region
- Spatial distribution is preserved

Emissions Regions



Regional emissions uncertainty distributions by Monte Carlo



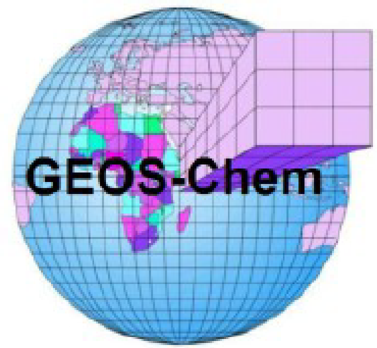
Uncertainty Quantification by Response Surface Modeling

- Ideally, would use Monte Carlo methods to get detailed output uncertainty distributions from prior parameter uncertainties – prohibitively expensive for GEOS-Chem (1000s of hrs)
- The goal is to **propagate PDFs**
- **Response surface modeling**: simplify the complicated model using an **inexpensive estimator of the model** output
- Result: Detailed uncertainty distributions at low cost

Polynomial chaos estimator of model output

Uncertain Parameters

$\xi = (\xi_1, \ldots, \xi_k)$



Some Output

$X(\xi)$

Polynomial Expansion

$\alpha_1 H_1(\xi) + \ldots + \alpha_n H_n(\xi)$

- *H* are Hermite polynomials
- Each *H* in the expansion varies in Order

- PCM: Solve for α by generating model output at specific ξ
- Number of model runs required: n
- n grows quickly with k and order of expansion

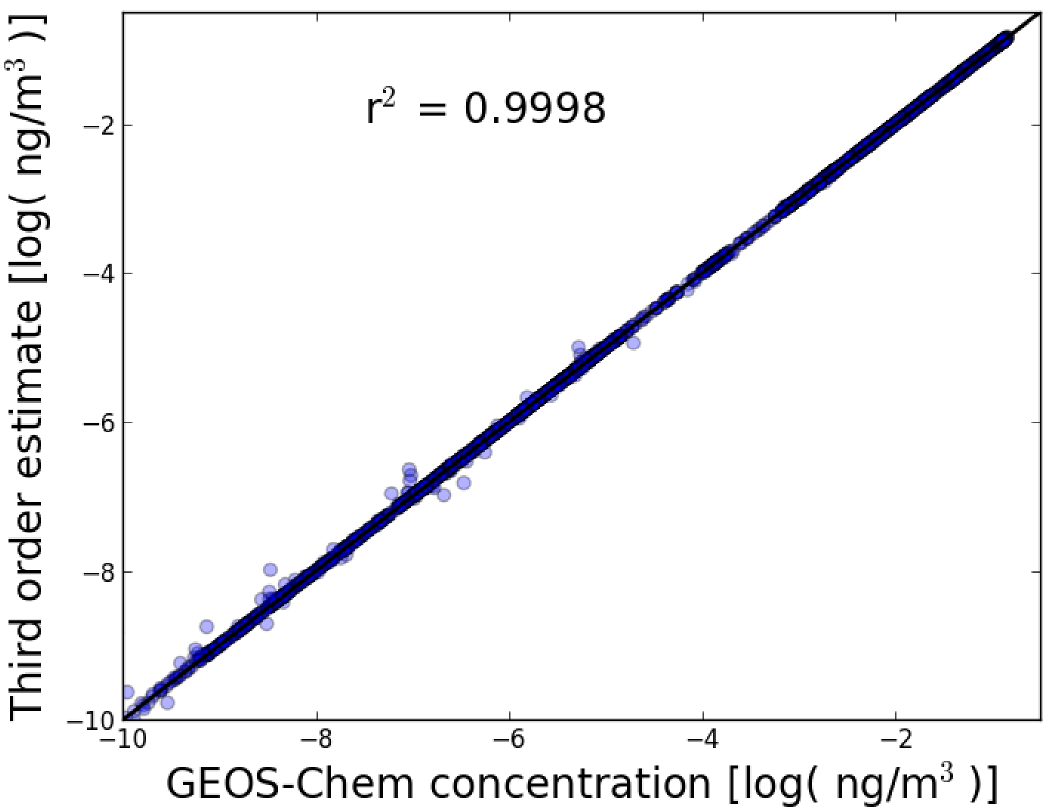
Estimator of output

$\varkappa(\xi) = \alpha_1 H_1(\xi) + \ldots + \alpha_n H_n(\xi)$

Estimates model output at parameter values ξ without running the model

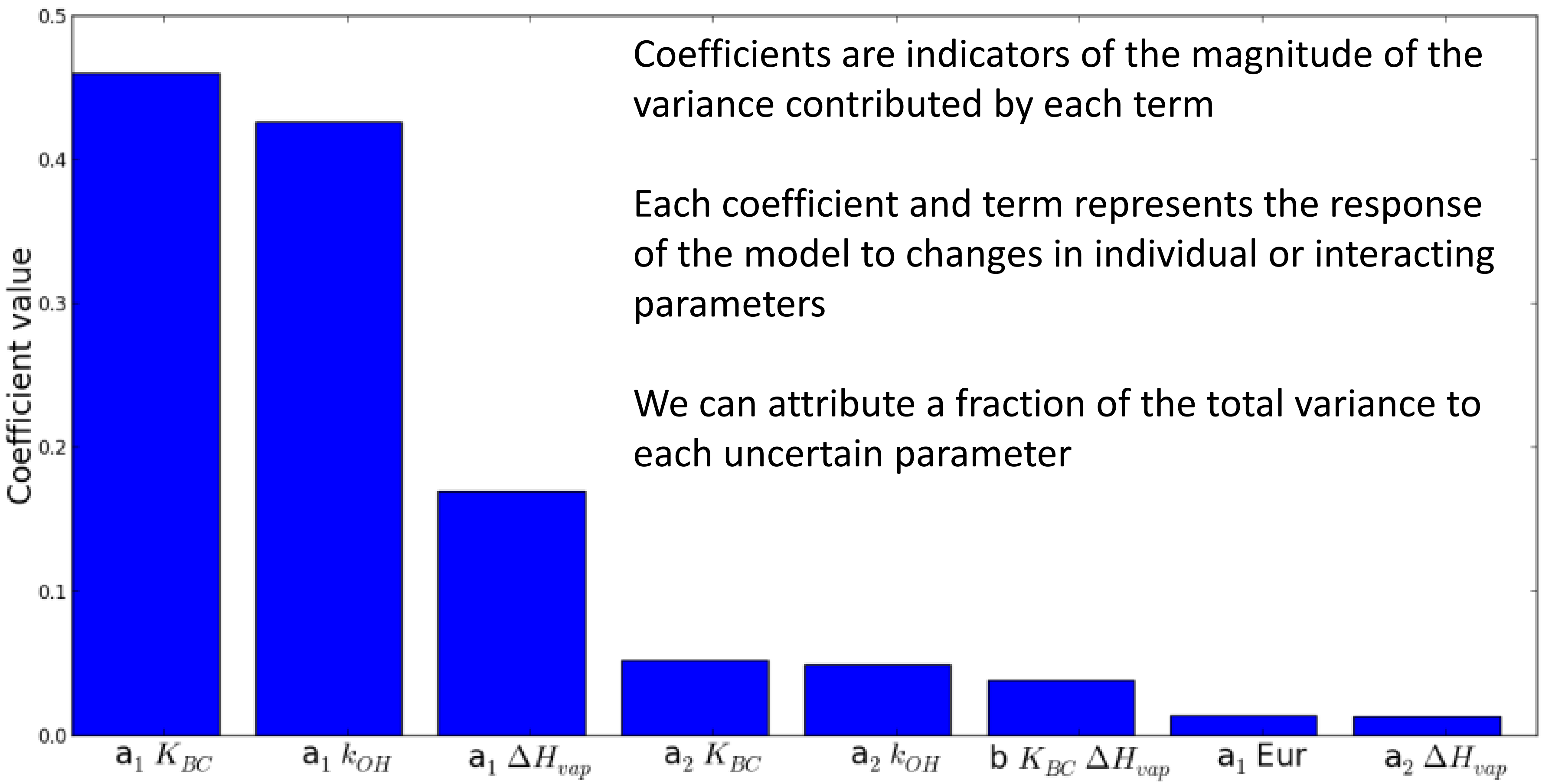
How well does the PCE estimate GEOS-Chem PAH concentrations?

Example: BaP total concentration



- Each point represents a grid-box from a real GEOS-Chem BaP simulation at a set of parameter values compared to the PC estimate for that same grid-box and set of parameter values.
- 50 test runs were performed sets of parameter values independent from the training set.
- PYR and PHE estimators perform similarly to BaP estimator

Spectrum of expansion coefficients



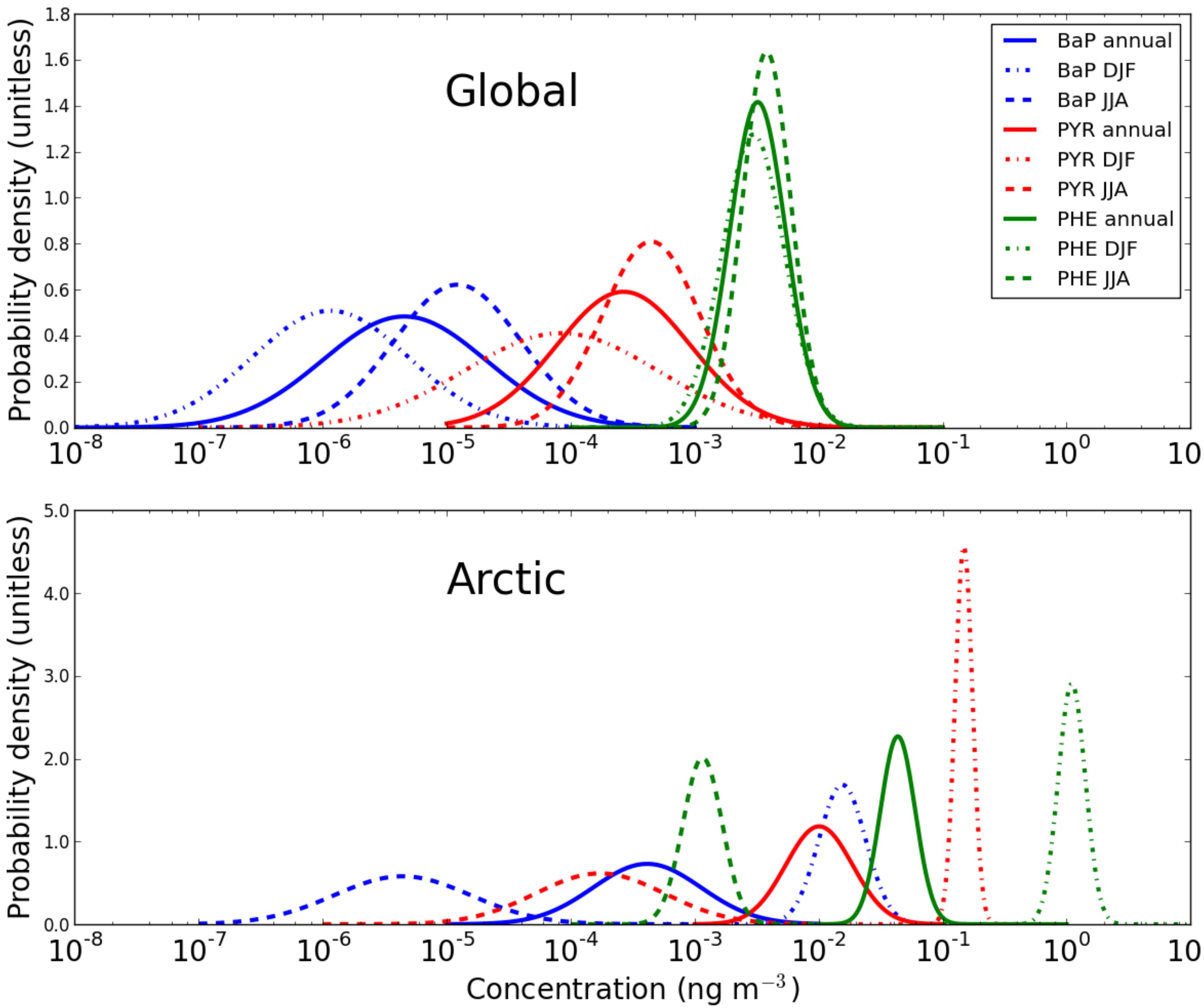
Coefficients are indicators of the magnitude of the variance contributed by each term

Each coefficient and term represents the response of the model to changes in individual or interacting parameters

We can attribute a fraction of the total variance to each uncertain parameter

Coefficients

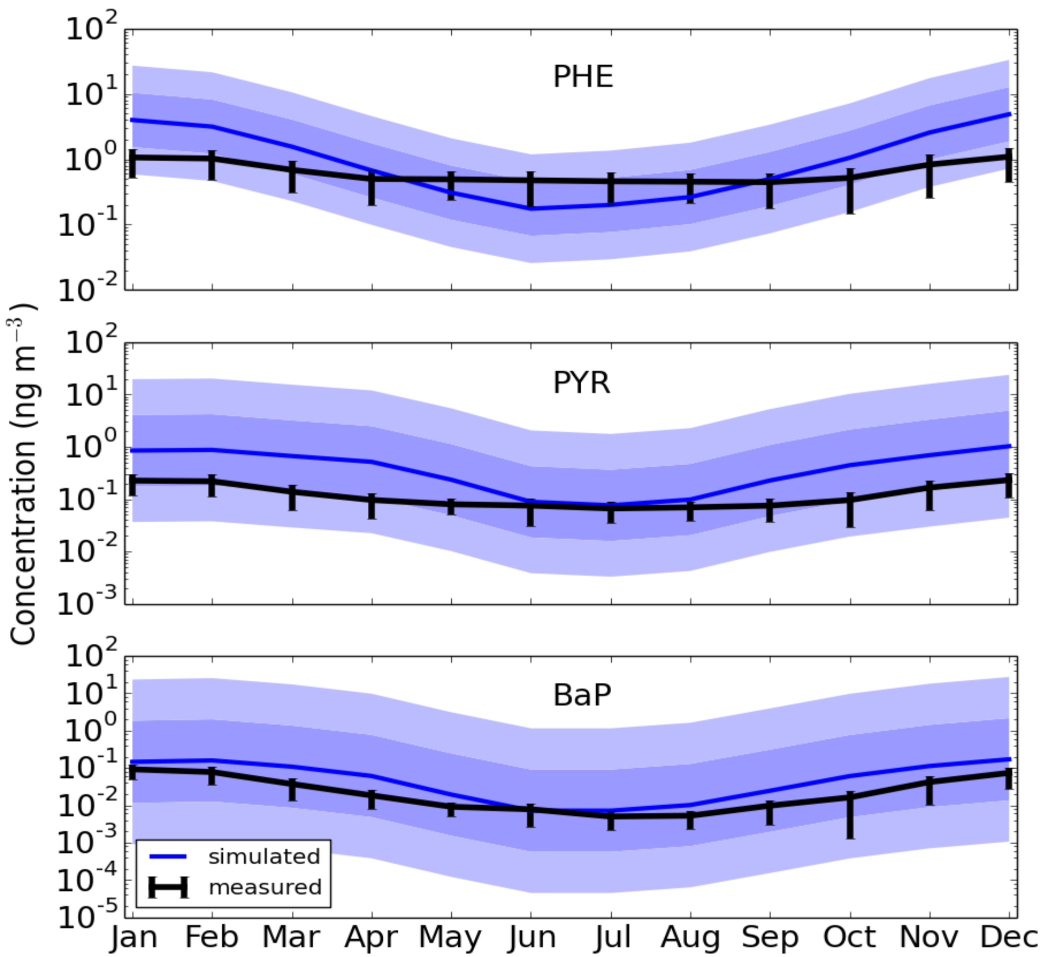
Global and Arctic average uncertainty distributions



How much does each parameter contribute to concentration uncertainty?

	k_{OH}	K_{BC-W}	ΔH_{vap}	E_{Eur}	E_{NA}
PHE – Annual, Global	99%	0%	0%	1%	0%
PHE – Annual, Arctic	68%	0%	0%	31%	1%
PYR – Annual, Global	98%	0%	0%	1%	0%
PYR – Annual, Arctic	96%	0%	0%	4%	0%
BaP – Annual, Global	43%	50%	7%	0%	0%
BaP – Annual, Arctic	27%	62%	9%	2%	0%

How do simulated concentrations and uncertainties compare with measurements?



3-year average monthly concentrations at 9 non-urban mid-latitude sites and 2 Arctic sites.

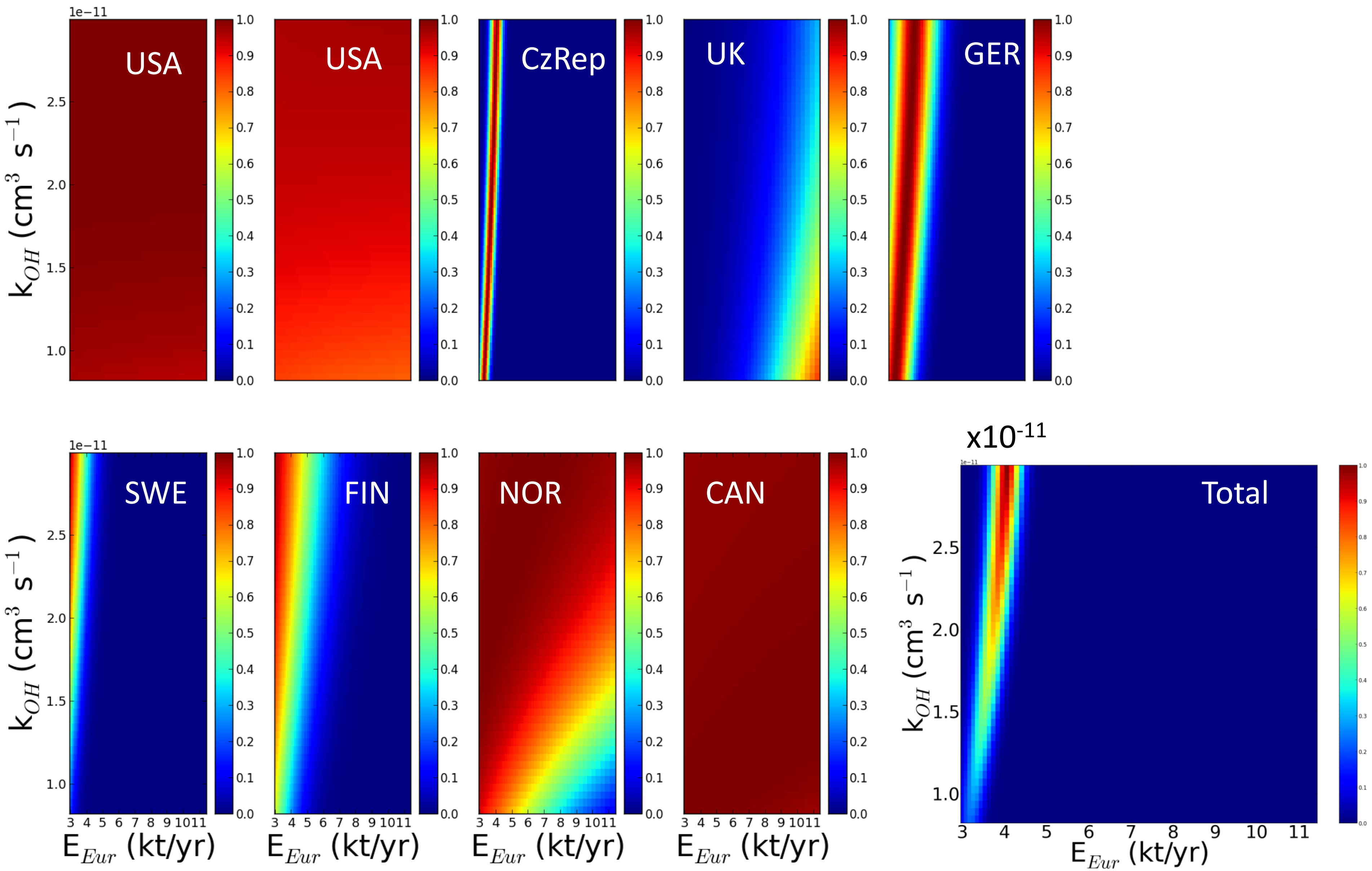
Very large model uncertainty bounds !

Simulated PAH concentrations show a stronger seasonal cycle than measured.

Using measurements to constrain uncertain parameters

- We want to know how annual measurements of our PAHs at a collection of non-urban mid-latitude and Arctic sites can help to constrain our uncertainties
- From Bayes: $P(\xi, Y) \propto P(\xi)\, P(Y, \xi)$
- $P(\xi, Y)$ is the posterior distribution of probability of parameter values ξ given measurements Y
- $P(\xi)$ is the set of prior uncertainty distributions for the parameters
- $P(Y, \xi)$ is the likelihood of measurements Y given parameter values ξ.
- We can calculate the likelihood $P(Y, \xi)$ using a least-squares cost function: $K(\xi)^2 = \sum_{i=1}^{N} \left(\frac{Y_i - \chi_i(\xi)}{\sigma_i}\right)^2$ where we can sum over the measurement sites i.
- The likelihood will then be given by $P(Y|\xi) \propto \; e^{-K(\xi)^2}$

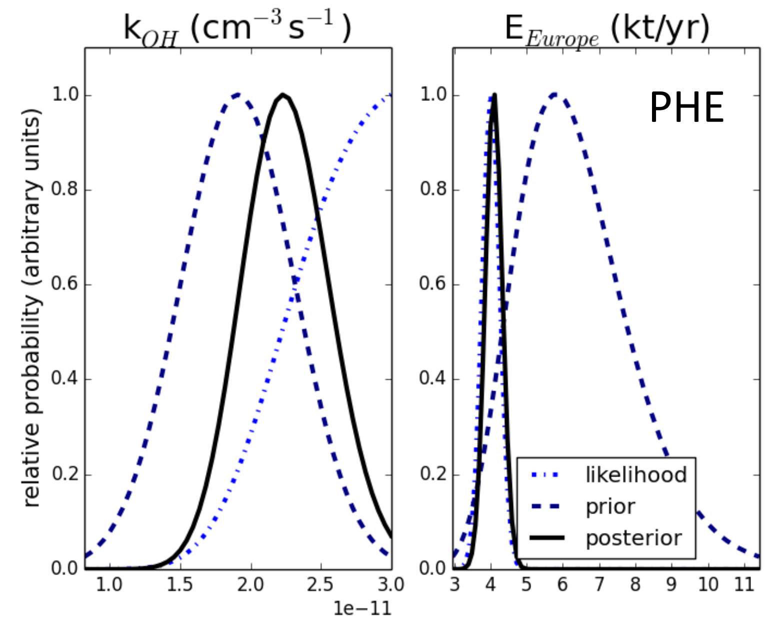
Example: PHE site-by-site and total parameter constraint

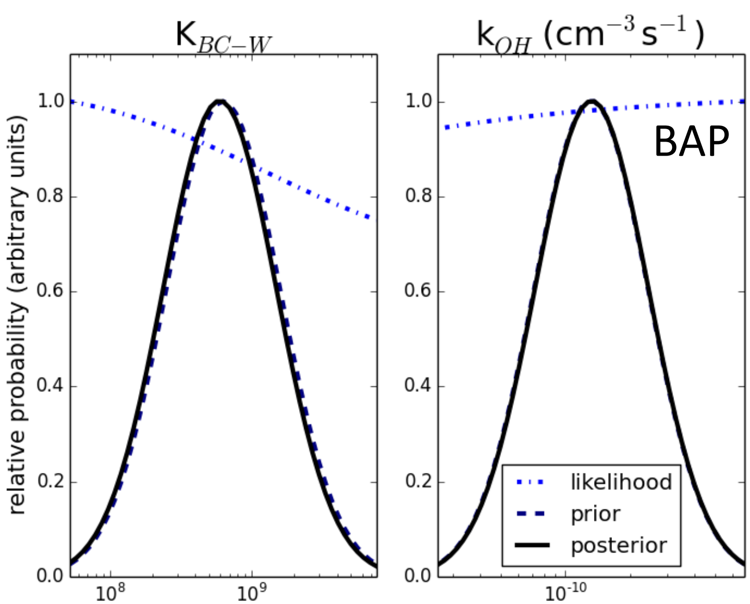


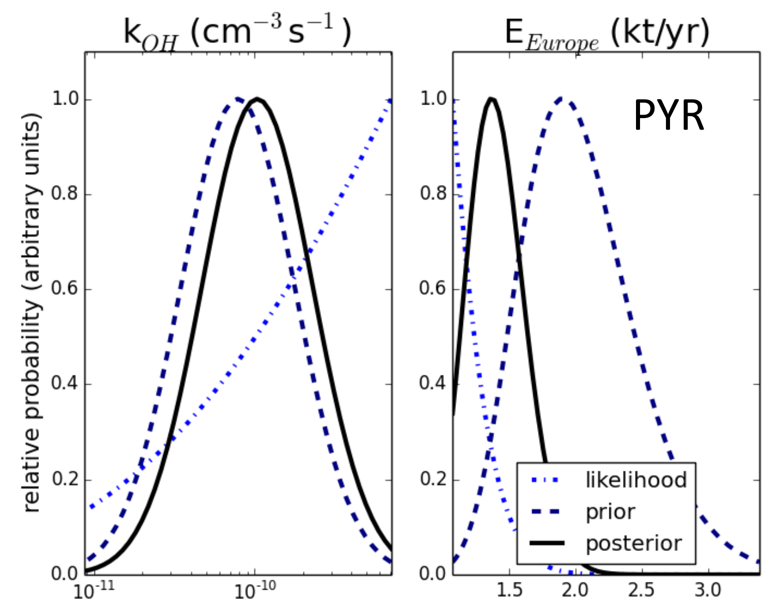
Posterior distributions of parameter uncertainties

$$P(\xi, Y) \propto P(\xi)\, P(Y, \xi)$$

Posterior **Prior** **Likelihood**







Where would measurement sites be to best constrain parameters?

- To best constrain the k_{OH} of each of the PAHs, sites would be located far from sources: over open oceans and Antarctica
- A site on Antarctica would also be ideal for constraint of BaP's $K_{BC\text{-}W}$ and ΔH_{vap}, but would have to be more sensitive to very low concentrations than current sites are

Some uncertainties not addressed

- Meteorology (Rainout, washout, advection, etc.)
- Unresolved processes (oxidation by NO_x, O_3, etc.)
- Changing emissions through time, space
- Numerical things (e.g. grid box size, time resolution of prescribed concentrations)
- And many more…

Conclusions

- As the size of the PAH increases, so too does the uncertainty in its simulated concentrations.
- PYR and PHE uncertainty is governed by uncertainty in k_{OH}, while BaP uncertainty is due to k_{OH}, and $K_{BC\text{-}W}$.
- Currently available measurement sites modestly constrain the k_{OH} of PHE, but are too close to sources to further constrain PAH physicochemical parameters
- (Better) experimental determinations of PAH reaction rates are the best bet for reducing model uncertainty.