Conference(s) debrief: QUACCS & ACCOMC

Keiran Rowell - Group Meeting - 18th Jan 2019

Australian Government
Bureau of Meteorology

Atmospheric Composition and Chemistry Observations and Modelling Conference
incorporating the
Cape Grim Annual Science Meeting 2018

Tuesday 4 December – Thursday 6 December 2018

CSIRO

Cremer D., *WIREs Comput Mol Sci* **2011**, *1*, 509-530.

QUACCS - Write your own MP2 - Simon McKenzie

Workshop less about MP2 than its implementation

In brief:

First level of theory to include e^--e^- correlation.

Perturb with virtual orbitals from HF solution.

$$H = H_o + \lambda V$$

$$E = E^{(o)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \ldots$$

$$E_{\mathrm{MP}}^{(2)} = \sum_{ij}^{\mathrm{occ}} \sum_{ab}^{\mathrm{vir}} \frac{<ia|jb>[2<ia|jb> - <ib|ja>]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

The importance of loops

Since you are calculation electron repulsion integrals (ERI), many permutation loops.

► Naive implementations scale as $O(N^8)$!

```
// Perform the naive AO to MO integral transformation

for(unsigned i=0; i < n_occ; i++ )
for(unsigned a=0; a < n_vir; a++ )
for(unsigned j=0; j < n_occ; j++ )
for(unsigned b=0; b < n_vir; b++ )
for(unsigned mu=0; mu < n_ao; mu++ )
for(unsigned nu=0; nu < n_ao; nu++ )
for(unsigned lam=0; lam < n_ao; lam++ )
for(unsigned sig=0; sig < n_ao; sig++ ) {
t_mo_int[i][a][j][b] += mat_mo_coeff(i,mu)*mat_mo_coeff(n_occ+a,nu)*mat_mo_coeff(j,lam)*mat_mo_coeff(n_occ+b,sig)*t_ao_int[mu][nu][lam][sig];
}
```

► Conventional implementations scale as $O(N^5)$ *or better*

- Preference looping over occupied (i,j) rather than virtual (a,b) orbitals – *many more virt. orb.s*

- Piecewise MO -> AO transformation - ERI pre-screening - $4e^- \rightarrow 3e^-$ & $2e^-$ integrals w/ aux. basis

1 Kettle A., Kuhn U., von Hobe M., Kesselmeier J., Andreae M., *J. Geophysical Research*, **2002**, *107*, 4658
2 Protoschill-Krebs G. Kesselmeier J., *Plant Biology*, **1992**, *105*, 206-212
3 Brasseur G., Jacob D., *Modelling of Atmospheric Chemistry*, **2017**, Cambridge University Press, Cambridge.

ACCOMC - Testing estimates of terrestrial productivity using carbonyl sulfide - Peter Rayner

- ▶ S=C=O (COS) most abundant sulfurous compound (0.5 ppb) in the atmosphere[1]

  Sources: CS_2 oxidation, oceanic vents, soils, biomass burning

- ▶ Loss mechanism is from vegetation,[2] CO_2-fixing enzymes making a mistake!

- ▶ ∴ COS direct tracer of plant fixing rates — Gross Primary Productivity (GPP)

- ▶ Inversion modelling is where you work backwards from atmospheric observations

  Budget modelling: sum known sources & sinks

  Inversion modelling: statistically estimate the variables driving an observation[3]

Uncertainties in GPP

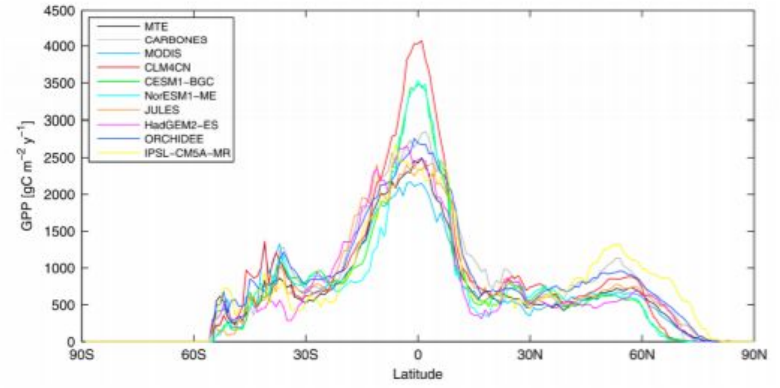


figure taken from Anav et al. 2015.

- global estimates of GPP vary by 40%
- Even larger variations regionally;
- trends, variability and sensitivity equally uncertain.

Sinks ∝ [COS]

F_{canopy} = λ x GPP x [COS]

λ = COS vs. CO_2 pref.

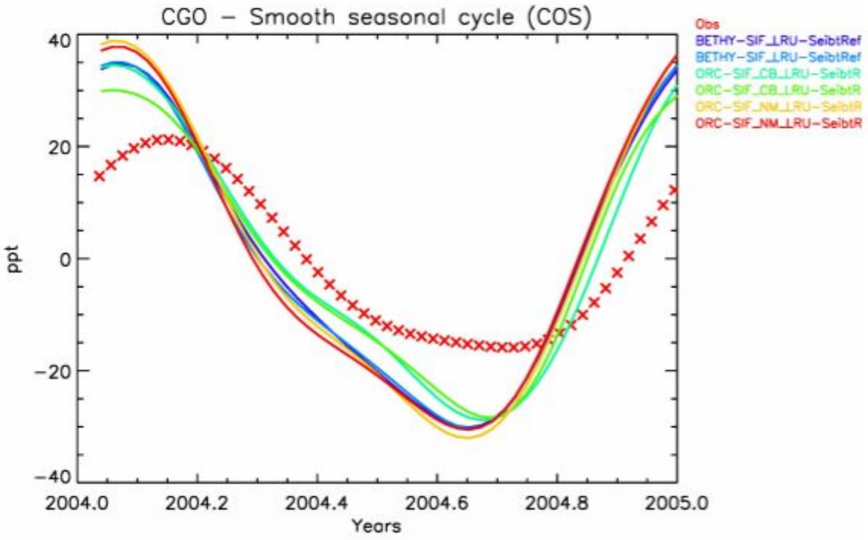
λ highly uncertain!

From known budget:

-Insert flux into transport models.

-Vary estimates of GPP & λ

Comparison at Cape Grim



1 Denning S., *et al.*, *Farquhar Photosynthesis Model*, http://biocycle.atmos.colostate.edu/shiny/photosynthesis/, (Acessed 18th Jan 2019)

Future Work & Conclusions

Future Work:

► Global & local inversion models attempt to constrain good estimates for λ

► Implement improved transport parameters & a photosynthesis model[1]

Conclusions:

► Seasonal variance in [COS] offers a window to constrain GPP estimates

► Many confounding factors, but they don't seem to affect seasonal variations

► No clear best estimate, location dependent

► Inversion modelling can quantify confidence. Need leaf uptake parameters.v

Thank you!