Measured and modeled PAN at N. mid-latitude mountain sites: Insights into hemispheric ozone transport?

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1. Introduction

Multi-model studies supporting the Task Force on Hemispheric Transport of Air Pollution (TF HTAP) show a wide range (often more than a factor of 2) in individual model estimates for hemispheric transport of O_3 and precursors [e.g., *TF HTAP, 2007, 2010; Sanderson et al., 2008; Shindell et al., 2008; Casper Anenberg et al., 2009; Fiore et al., 2009; Jonson et al.,2009; Reidmiller et al., 2009; Wu et al., 2009; Lin et al., 2010*]. Comparisons with ozonesondes and surface observations are complicated by the large O_3 background.

Evaluation with free tropospheric PAN and NOy measurements may be useful:

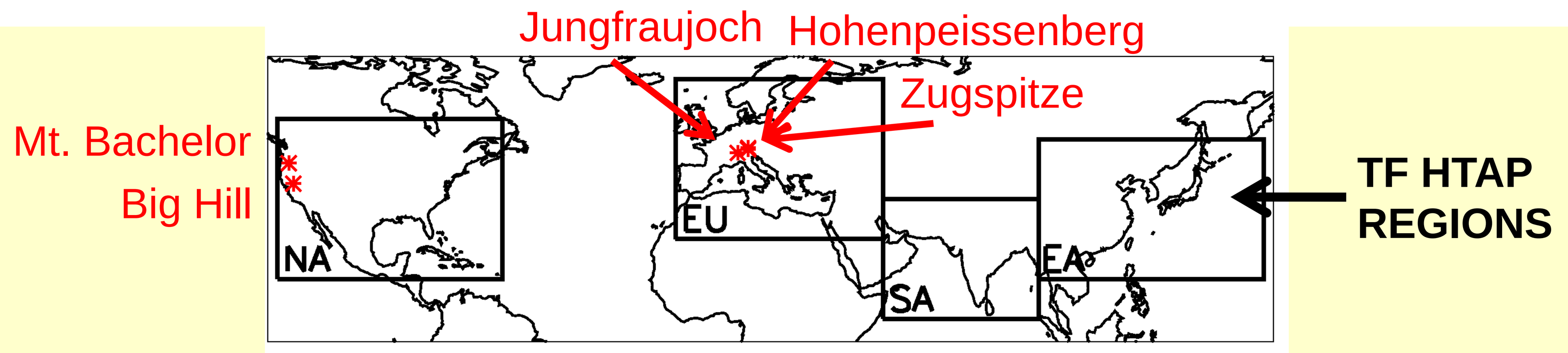
- PAN decomposition enhances O_3 far from source regions, as observed in Asian plumes [*e.g., Moxim et al., 1996; Heald et al., 2003; Hudman et al., 2004; Zhang et al., 2008; Fischer et al., 2010*]
- PAN formation differs across models [*e.g., von Kuhlmann et al., 2004; Emmerson and Evans, 2009*]
- The signal of anthropogenic emission perturbations should be larger for PAN than for O_3 [*Jaffe et al., 2007*]

2. HTAP simulations and mountain sites

BASE SIMULATION (21 models): horizontal resolution of 5°x5° or finer; 2001 meteorology; CH_4 =1760 ppb; each group's best estimate for 2001 anthropogenic & natural emissions

SENSITIVITY SIMULATIONS (13-18 models): -20% regional anthrop. **NO_x, CO, NMVOC** emissions, individually + **all three O_3 precursors (NOx+CO+NMVOC)** =16 simulations

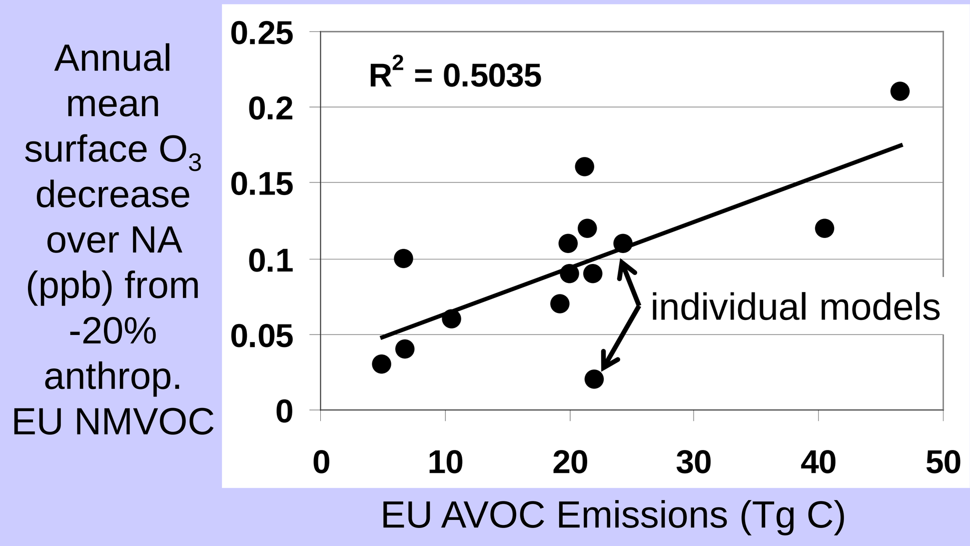
MONTHLY MEAN 3D model distributions of PAN, O_3, NO_2, HNO_3 archived for analysis.



Models are sampled at the mountain sites shown in red.

3. How (and why) do models vary in estimates of intercontinental influence?

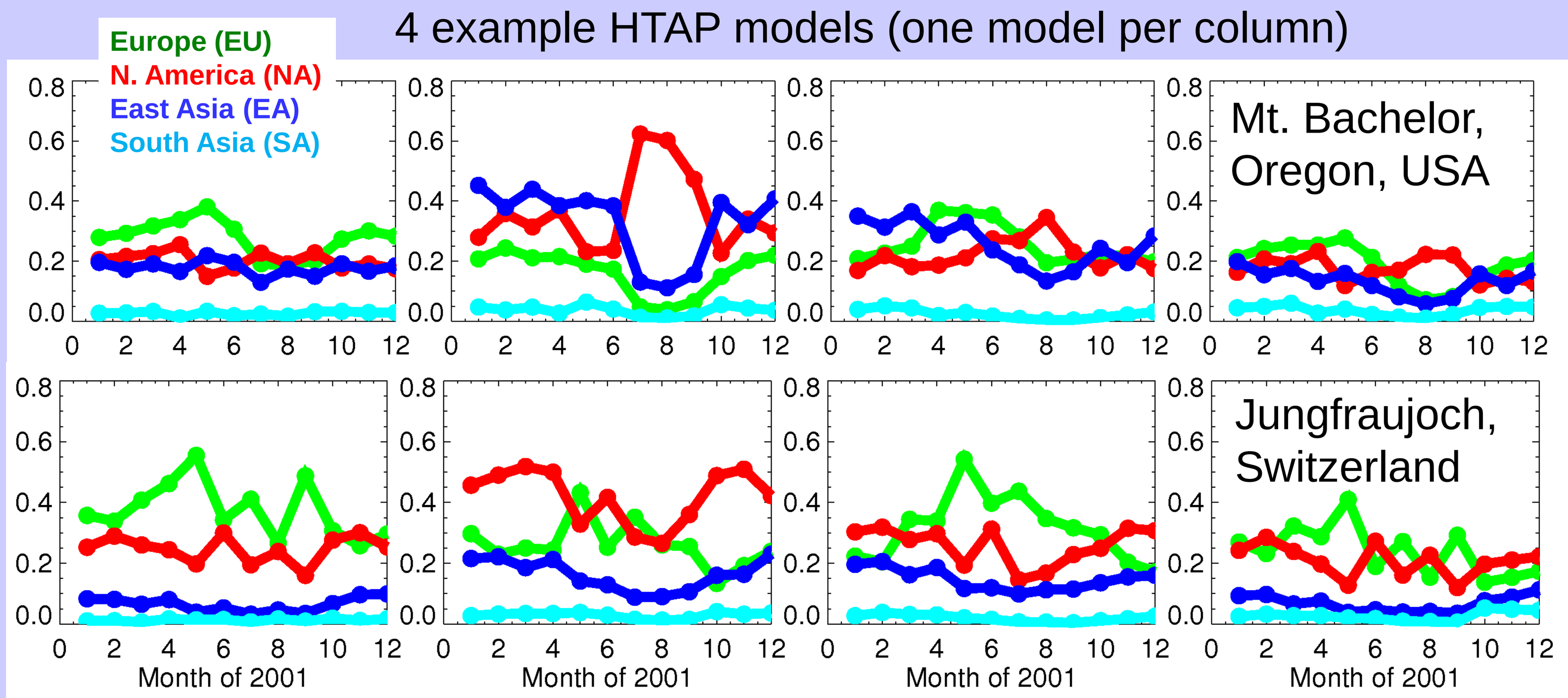
We previously showed that individual model estimates of the NA O_3 response to EU anthropogenic NMVOC (AVOC) emissions correlates strongly with the EU AVOC inventories used in the models (see figure below from *Fiore et al.*, 2009). In contrast, we do not find a similar relationship for exported O_3 with regional anthropogenic NO_x emissions since they are similar across the models (<10% standard deviation). We extend this analysis to explore model variability in intercontinental influence on PAN (figures to the right).

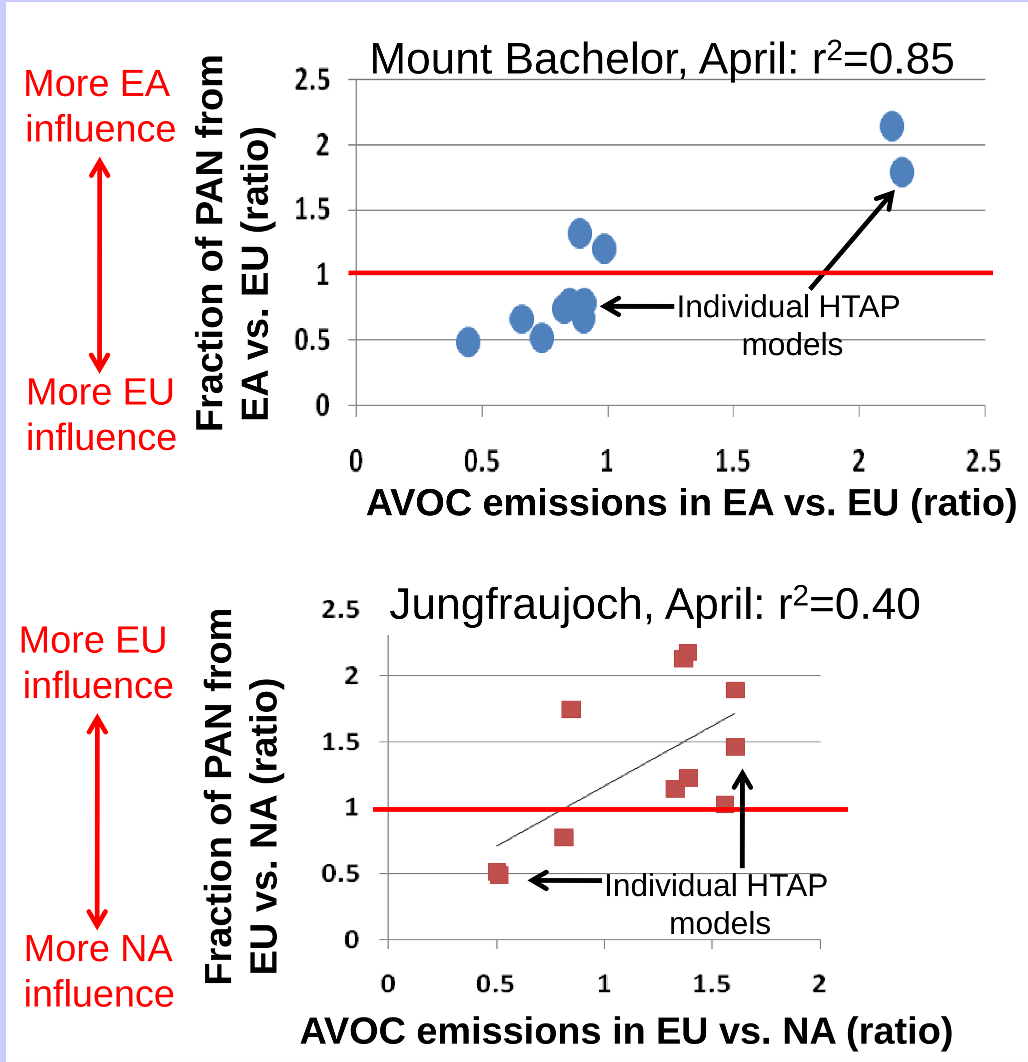


Relative importance of source region influence on PAN in the models varies:
- **seasonally; "domestic" influence typically strongest in summer**
- **with the ratio of regional anthropogenic NMVOC (AVOC) emissions in April**
- **with other processes (meteorology, other emissions) not considered here**

Model fraction of PAN at mountain sites from regional anthrop. emissions

4 example HTAP models (one model per column)

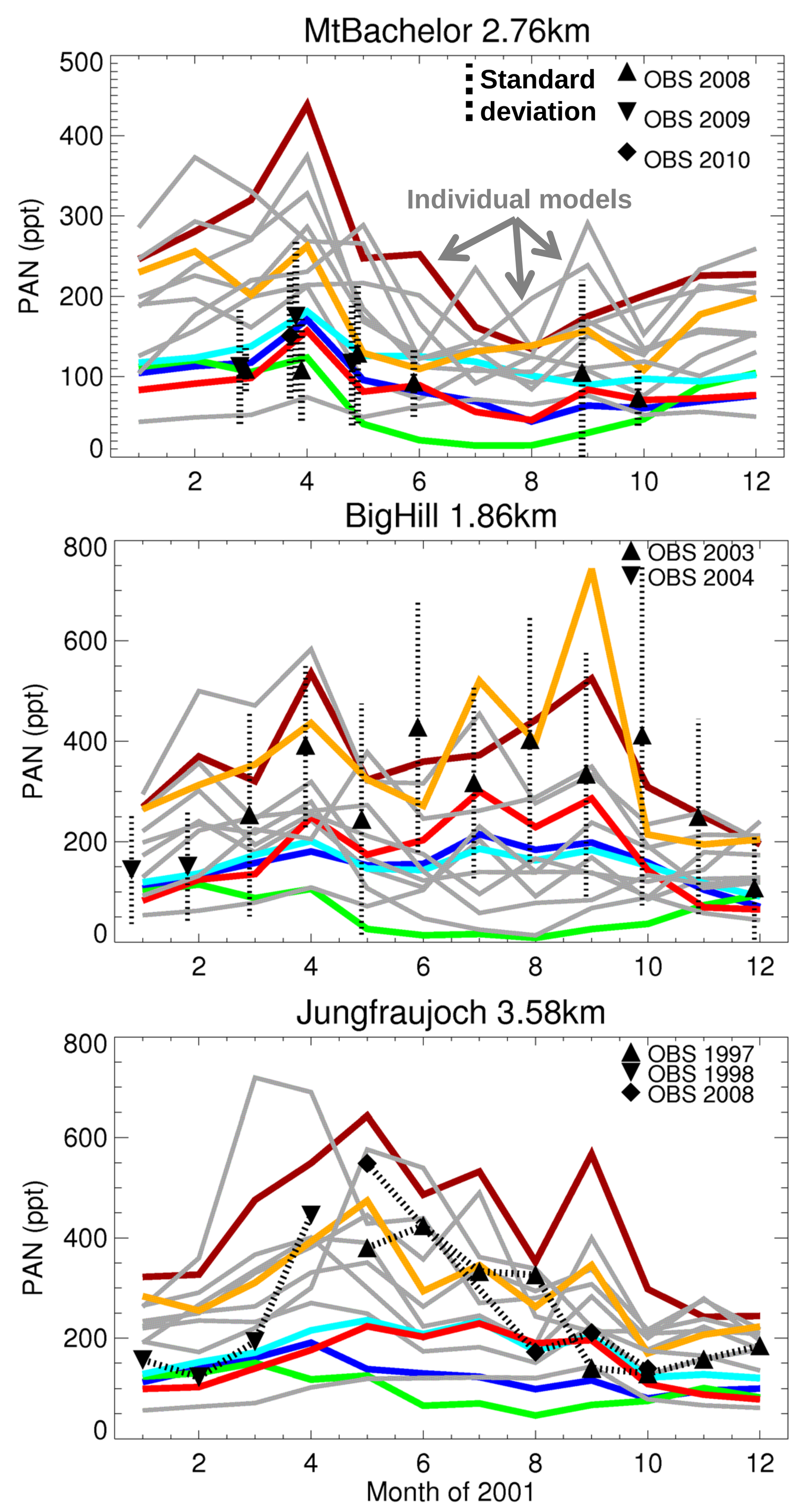




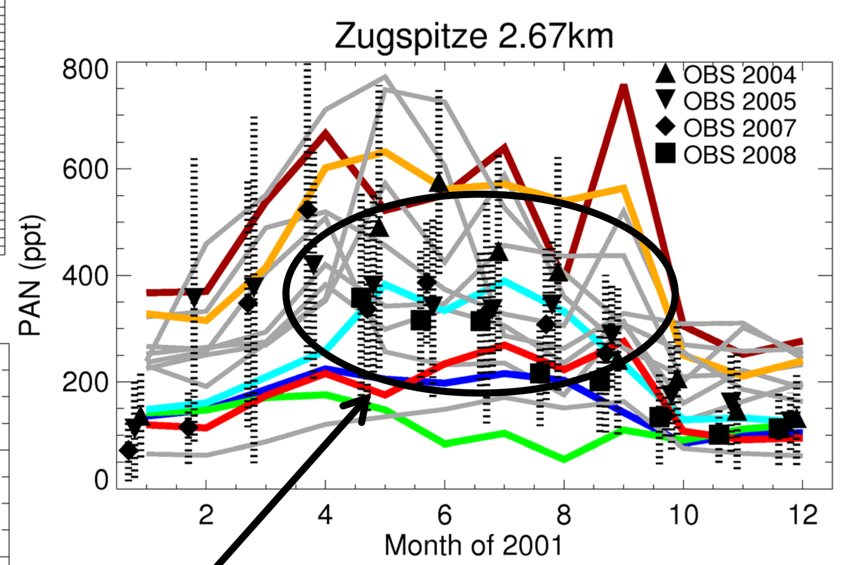
4. Measured vs. Modeled PAN at mountain sites

Year-to-year and seasonal changes in sources and meteorology contribute to variability in measured PAN abundances. Differences in model representations of these processes, and their ability to resolve transport to the mountain site, leads to a large spread in simulated PAN at the mountain sites.

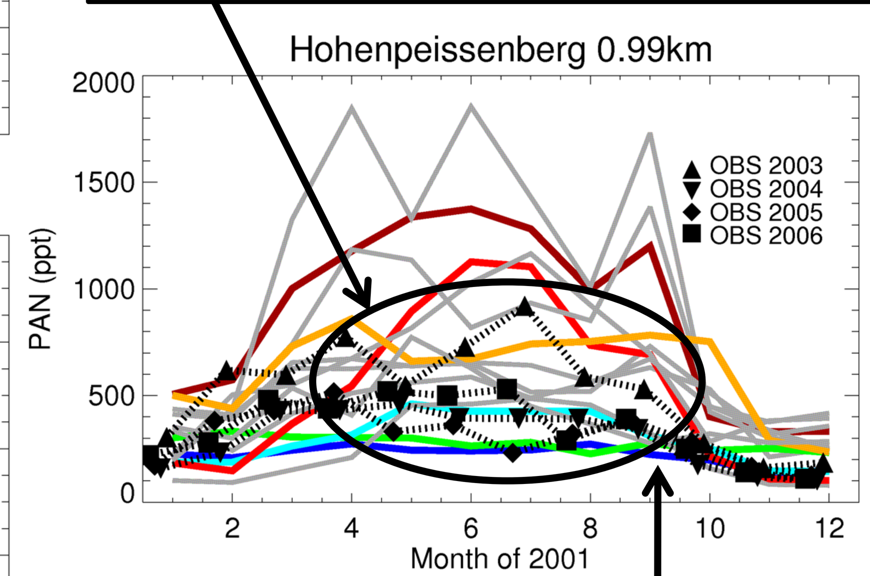
Lack of 2001 obs. (year of model data) precludes definitive conclusions.



We highlight 6 models in color to show that some models are high at all sites, and some are low; their ability to match observations varies by site.

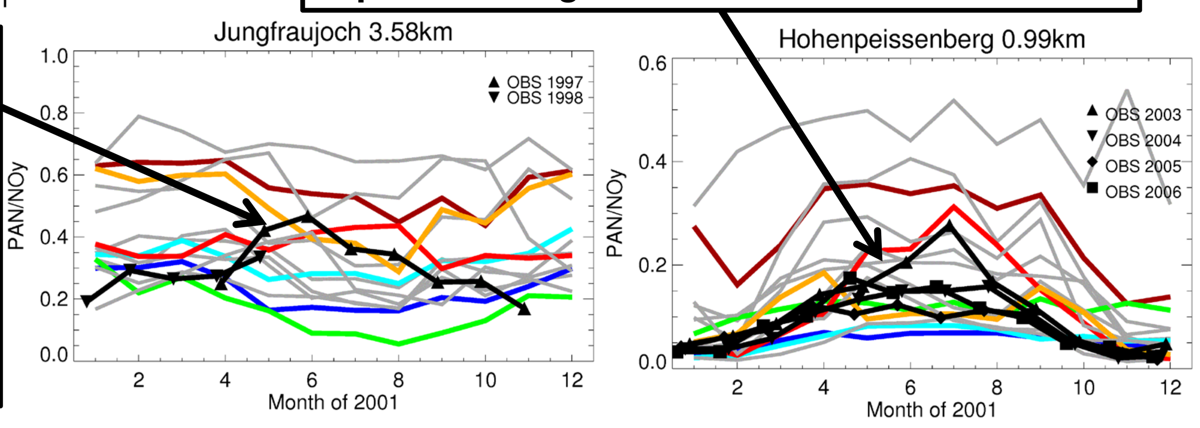


Large interannual variability in observations



Higher observed PAN values and low PAN/NO_y ratios suggests a stronger regional pollution signal at this lower altitude site

Warmer months with higher PAN/NO_y ratios suggest presence of more polluted air masses. Models are unlikely to resolve local upslope flows, which may account for discrepancies.



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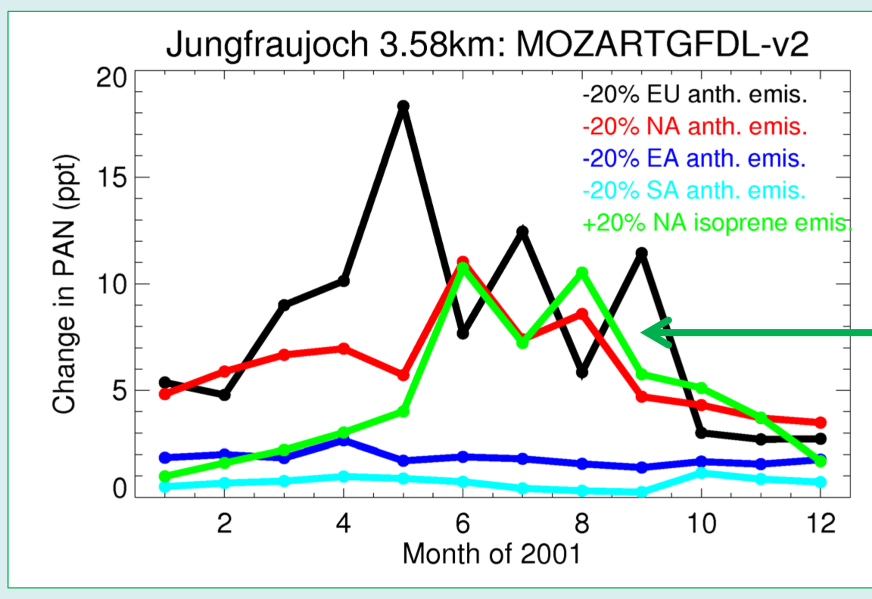
5. Impacts on PAN from isoprene and lightning

In addition to anthropogenic sources considered in the HTAP study, isoprene [*e.g., von Kuhlmann et al,. 2004; Pfister et al., 2008*] and lightning NO_x [*e.g., Labrador et al., 2005*] influence PAN, and they contribute to model differences in tropospheric O_3 [*e.g., Stevenson et al., 2006; Wild et al., 2007, Wu et al., 2007*].



With the MOZART-2 model [*Horowitz et al*., 2003], we place the PAN response to the anthropogenic emission perturbations in the HTAP study in the context of interannual variations of isoprene emissions over NA (+/- 20-30%) [*Palmer et al*., 2006].

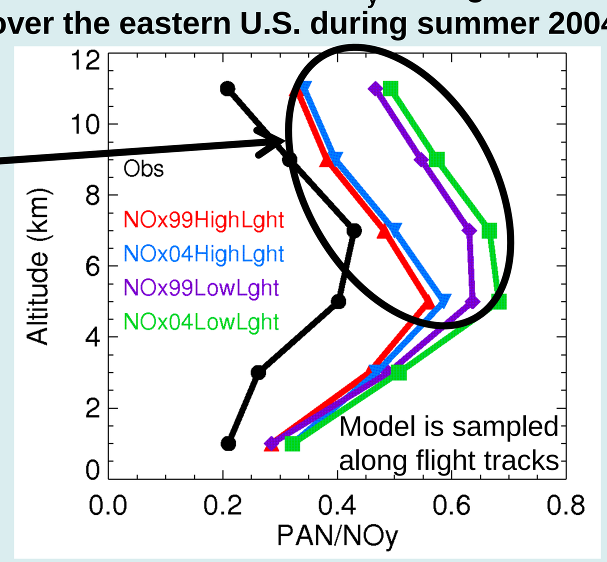
The influence of NA isoprene on PAN at Jungfraujoch is equivalent to that from EU and NA anthrop. emissions in summer

With the MOZART-4 model [*Emmons et al*., 2010], we examine the sensitivity of PAN to changes in anthropogenic NO_x (23% decrease over the USA from 1999 to 2004), and to uncertainties in lightning NO_x which are quite large [*Fang et al*., 2010]. For this simulation the northern mid-latitude lightning source over continents is increased by a factor of 10 (a similar absolute perturbation over NA as from anthropogenic NO_x). The model vertical profile adjusts to increase upper tropospheric NO_x [*Fang et al*., 2010], which is closer to observations over North America [*Pickering et al*., 2006; *Ott et al*., 2010].

Cross-model differences in lightning NO_x may contribute not only to variations in total PAN, but also to hemispheric O_3 transport (by influencing PAN and the downwind O_3 production efficiency [*Fang et al*., 2010]).

PAN/NO_y in the free troposphere is much more sensitive to changes in lightning NO_x (LowLght vs. HighLght) than to changes of similar magnitude in anthropogenic NO_x (NOx99 vs. NOx04)

Ratio of mean PAN and NO_y during INTEX-NA over the eastern U.S. during summer 2004



6. Summary: Consistent multi-year measurements of free tropospheric PAN and NO_Y are sparse. Given the large spread in model simulated PAN and source attribution, observations at mountain sites are expected to provide important information on the intercontinental transport of reactive nitrogen.

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