Aerosol impacts on photolysis frequencies in the Denver metropolitan area

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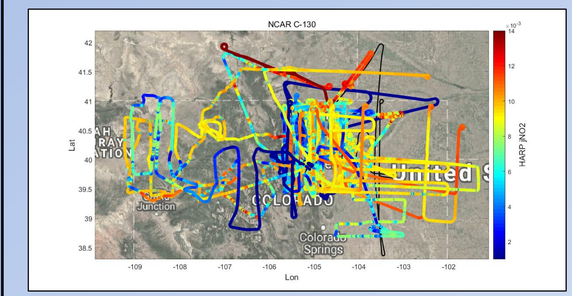
Abstract

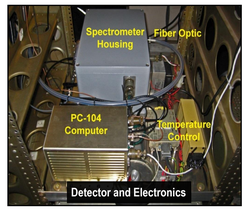
Spectrally resolved up and down-welling actinic flux was measured from the NCAR C-130 aircraft by the HIAPER Airborne Radiation Package (HARP-AF). Photolysis frequencies were then retrieved for ~40 species. Surface measurements of jNO_2 were made at the BAO Tower in Erie, CO. We examined the effects of aerosol extinction, particularly in boundary layer aerosols that can significantly reduce surface photochemistry rates

In addition, a new technique for detecting UV absorbing aerosols (e.g. BrC, BC) shows promise for real-time flight detection of smoke. Although fires were notably absent during the FRAPPE time period, some smoke plumes were detected by satellite and in the airborne actinic flux measurements. HARP spectral UV measurements provide the opportunity to determine absorption trends in the UV-B where few other measurements exist. Future is work is required to determine if quantitative spectral absorption retrievals are possible.



Actinic flux detectors

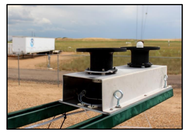
HIAPER Airborne Radiation Package – Actinic Flux HARP-AF



- Charged-coupled device monochromator
- Spectrally resolved: 280-680 nm
- 2π steradian quartz hemispherical optics
- Fiber optics : doped-OH fused silica for UV transmission
- Secondary scanning system (SAFS) deployed to characterize HARP-AF UV

jNO_2 Filter Radiometers BAO Tower

- Metcon, GmbH
- 2π steradian quartz hemispheric optics
- Downwelling only
- Total from estimated upwelling



Photolysis Frequencies

$j[O_3 \rightarrow O_2+O(^1D)]$
$j[NO_2 \rightarrow NO+O(^3P)]$
$j[H_2O_2 \rightarrow 2OH]$
$j[HNO_2 \rightarrow OH+NO]$
$j[HNO_3 \rightarrow OH+NO_2]$
$j[CH_2O \rightarrow H+HCO]$
$j[CH_2O \rightarrow H_2+CO]$
$j[CH_3CHO \rightarrow CH_3+HCO]$
$j[C_2H_5CHO \rightarrow C_2H_5+HCO]$
$j[CHOCHO \rightarrow H_2+2CO]$
$j[CHOCHO \rightarrow CH_2O+CO]$
$j[CHOCHO \rightarrow HCO+HCO]$
$j[CH3COCHO \rightarrow CH3CO+HCO]$
$j[CH_3COCH_3 \rightarrow CH_3CO+CH_3]$
$j[CH_3OOH \rightarrow CH_3O+OH]$
$j[CH_3ONO_2 \rightarrow CH_3O+NO_2]$
$j[CH_3COCH_2CH_3 \rightarrow CH_3CO+CH2CH_3]$
$j[CH_3CH_2CH_2CHO \rightarrow C_3H_7+HCO]$
$j[CH_3CH_2CH_2CHO \rightarrow C_2H_4+CH_2CHOH]$
$j[HO_2NO_2 \rightarrow HO_2+NO_2]$
$j[HO_2NO_2 \rightarrow OH+NO_3]$
$j[CH_3CH_2ONO_2 \rightarrow CH_3CH_2O+NO_2]$
$j[Br_2 \rightarrow Br+Br]$
$j[BrO \rightarrow Br+O]$
$j[Br_2O \rightarrow products]$
$j[BrCl \rightarrow Br+Cl]$
$j[HOBr \rightarrow HO+Br]$
$j[BrONO_2 \rightarrow Br+NO_3]$
$j[BrONO_2 \rightarrow BrO+NO_2]$
$j[Cl_2 \rightarrow Cl+Cl]$
$j[ClO \rightarrow Cl+O(^3P)]$
$j[ClONO_2 \rightarrow Cl+NO_3]$
$j[ClONO_2 \rightarrow ClO+NO_2]$
$j[BrNO \rightarrow Br+NO]$
$j[BrONO \rightarrow BrO+NO]$
$j[BrONO \rightarrow Br+NO_2]$
$j[BrNO_2 \rightarrow Br+NO_2]$
$j[CHBr_3 \rightarrow Products]$
$j[ClNO_2 \rightarrow Cl+NO_2]$
$j[ClONO \rightarrow Cl+NO_2]$
$j[N_2O_5 \rightarrow NO_3+NO_2]$
$j[CH_3CO(OONO_2) \rightarrow CH_3CO(OO)+NO_2]$
$j[CH_3CO(OONO_2) \rightarrow CH_3CO(O)+NO_3]$
$j[CH_2=C(CH_3)CHO \rightarrow Products]$
$j[CH_3COCH=CH_2 \rightarrow Products]$

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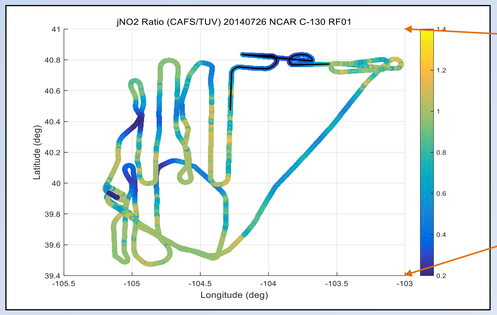
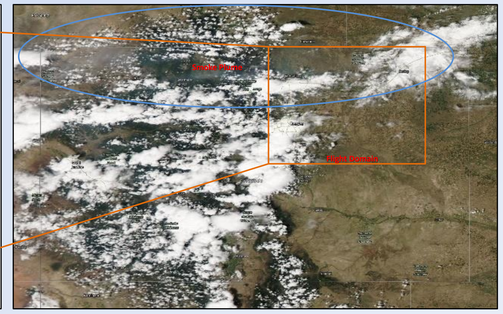
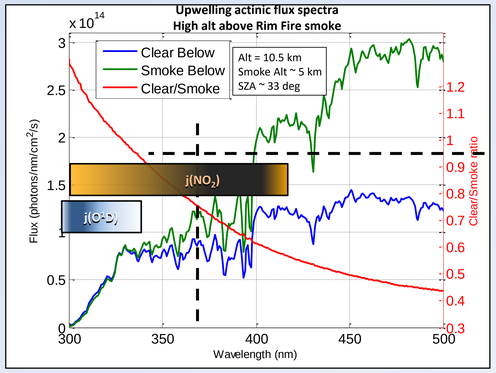
Real-time smoke detector (Ok,… enhanced UV-extinction detector)

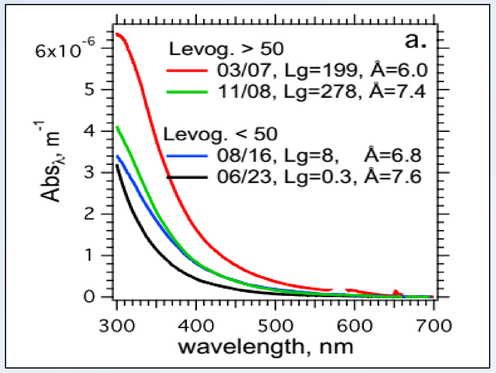




jNO_2 ratio to cloud-free TUV along the C-130 flight track. Dark/light colors indicate reduction/enhancements primarily due to clouds. The strongest smoke encounter is shown as a black line in NE Colorado.

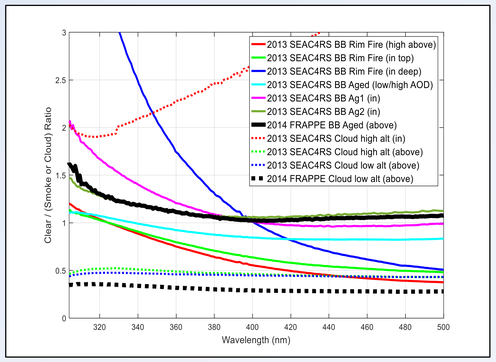
MODIS reflectance (true color). An aged smoke plume (Utah) overlaps the flight domain and was detected below the aircraft by spectral analysis, but not by in situ biomass burning chemical signatures.

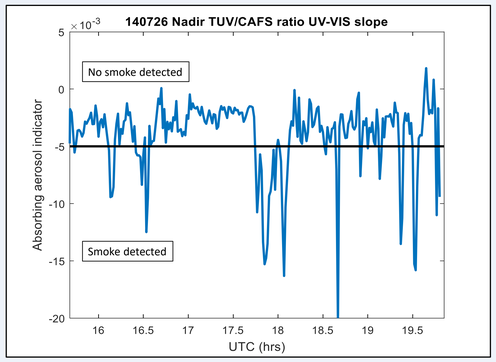




Spectral upwelling actinic flux over adjacent clear and smoke filled regions near a fire plume. The flux ratio indicates enhanced UV absorption by organic aerosols in the plume.

Absorption spectra from filters for biomass burning (levoglucosan >50 ng m−3) and non-biomass burning (levoglucosan <50 ng m−3) periods (*Hecobian et al., ACP, 2010, doi:10.5194/acp-10-5965-2010*).





Ratio of clear/smoke or clear/cloud under varying conditions indicating consistency in the brown carbon enhanced UV absorption in BB and clouds dominated by scattering.

Smoke detection along the flight track. Qualitative measure of relative UV extinction by comparison of measured actinic flux to cloud-free TUV fluxes. Below the black line suggests smoke detection.

Future work

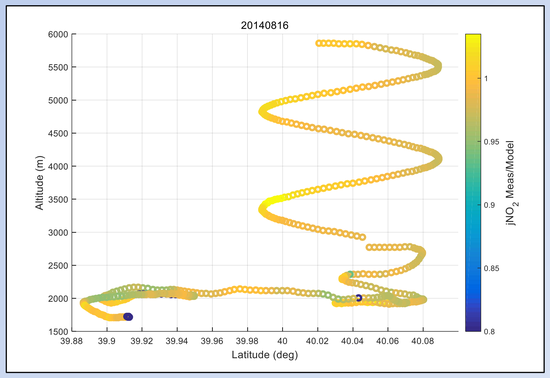
Real-time analysis questions

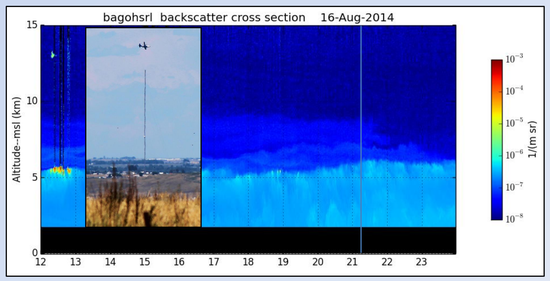
- How robust is the false positives/negatives)?
- What improvements can improve sensitivity and detection?
- Do nadir and zenith and nadir instruments provide vertical information about layers (above, within or below aircraft)?
- What other detectable impacts (scattering, cloud types, albedo, altitude, chemical absorbers, etc)?

Spectral analysis questions

- How does aerosol size-distribution affect spectral UV extinction (via scattering)?
- Can spectral analysis retrieve UV spectral absorption?
- Can spectral analysis distinguish BrC from BC?
- Can the retrievals be applied to RTMs to determine flux and photolysis profiles?
- Can the results be applied to regional chemistry models to assess photochemical impacts?

BAO Tower profile





The C-130 spiraled over the BAO tower allowing comparison between airborne and surface jNO_2. Weak aerosol in the boundary layer (see UW HSRL above) resulted in mild photolysis reduction below about 3500 masl. The *in situ* surface AOD = 0.120 at 340 nm (derived from AERONET, 0.8 at 550 nm) and input to TUV to produce a profile shape similar to the measurements.