

Dust modeling with GEOS-Chem: evidence for acidic uptake on dust surfaces during INTEX-B

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Mineral Dust Module in GEOS-Chem

- Dust mobilization (Fairlie et al., 2006)
- Transport (TPCORE/FvDAS) (Lin and Rood, 1996)
- Dry deposition – gravitational settling, turbulent transfer, impaction, interception, $V_d = V_d(D, r, sfc)$ (Zhang et al. 2001)
- Wet deposition – scavenging in convective updrafts; rainout and washout from large-scale precipitation and convective anvils (Liu et al., 2001).
- Size bins: 0.1-1.0, 1.0-1.8, 1.8-3.0, 3.0-6.0 μm radius (following Ginoux et al., 2001)

Mobilization

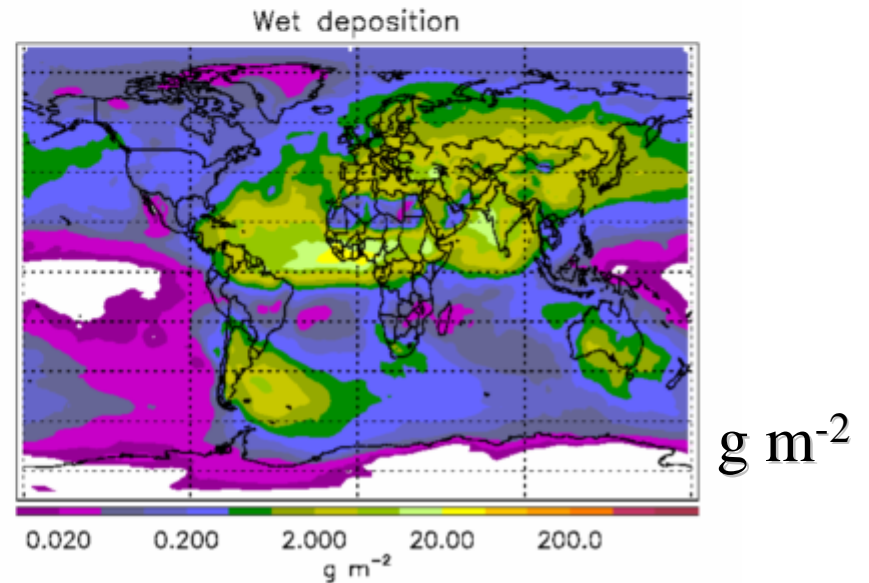
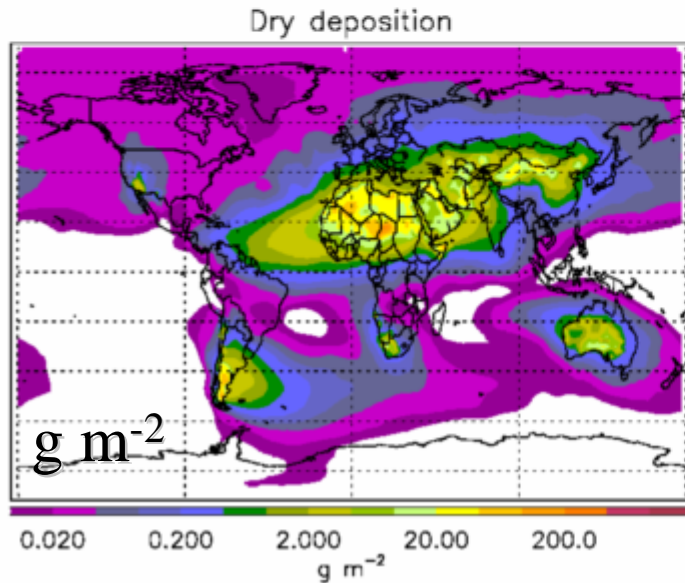
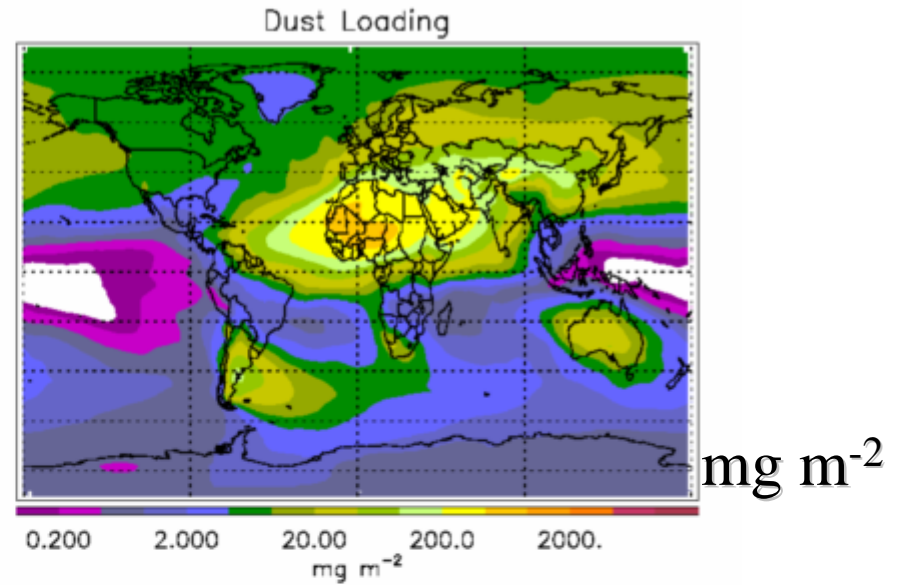
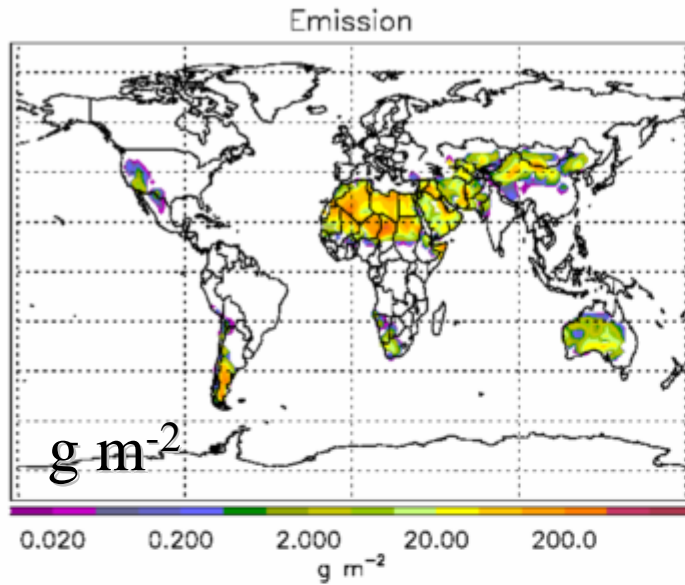
Vertical dust flux, F_d , proportional to the horizontal saltation flux, Q_s : $F_d \sim S Q_s$

- $Q_s \sim U_{10}^2 (U_{10} - U_t^*)$ (GOCART)
- $Q_s \sim U^{*3} (1 - U_t^*/U^*) (1 + U_t^*/U^*)^2$ (DEAD)

U_t^* – threshold friction velocity (particle size, density; air density, viscosity). U_t^* modulated by surface moisture.

S – source function (defines potential dust source regions, and comprises surface factors, e.g. vegetation, snow cover, and an efficiency factor e.g. topographic anomaly)

Emission, average load, wet and dry depositions for 2001

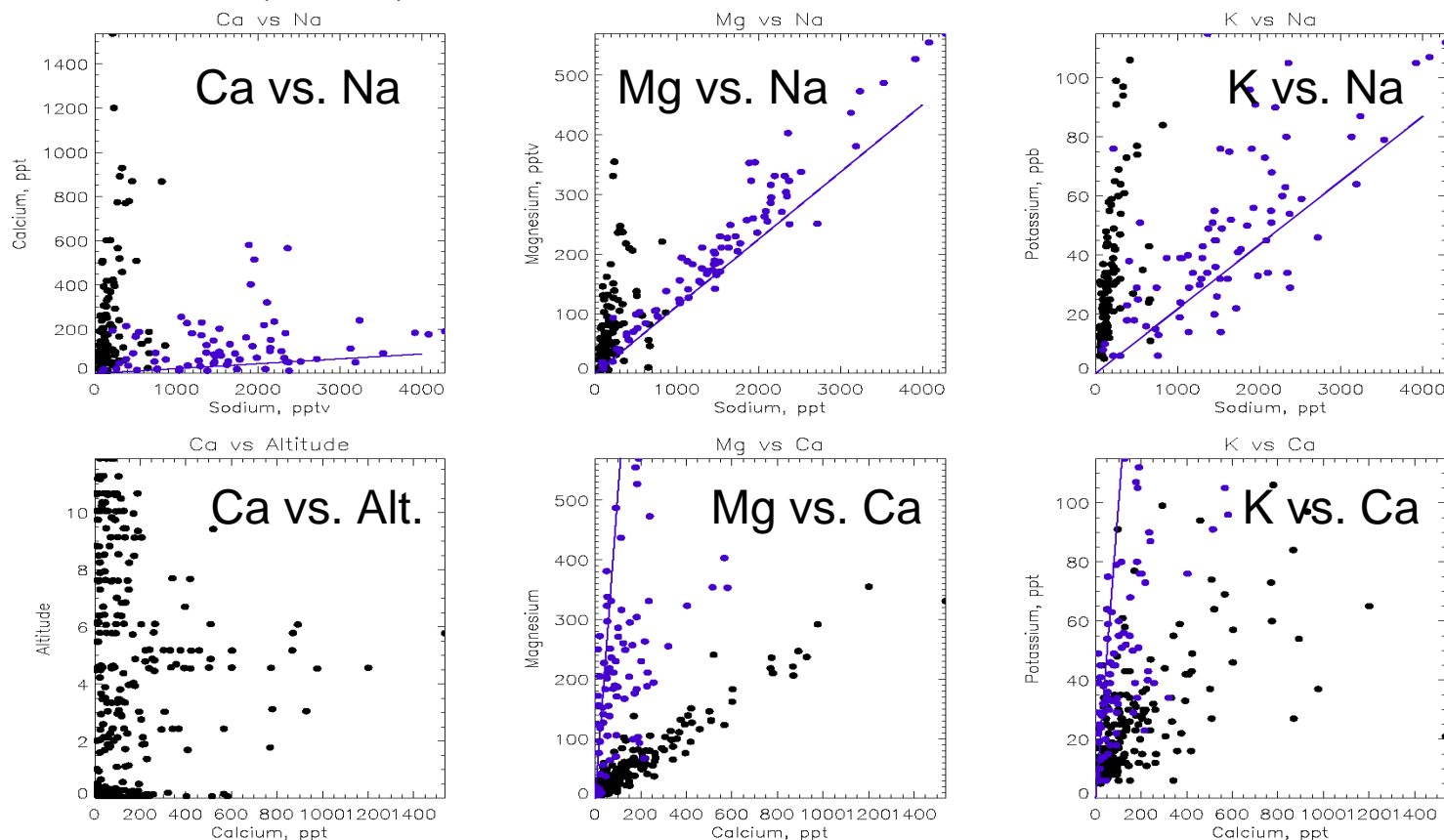


Observed and simulated mineral dust during INTEX-B: transpacific transport and evidence of acidic uptake on dust surfaces

- We use measurements of aerosol ion composition made from the SAGA instrument (Dibb et al., UNH) on board the DC8 aircraft during the 2006 INTEX-B airborne campaign to identify mineral dust signatures.
- Use Na^+ and Ca^{2+} to distinguish sea salt and mineral components of the aerosol distribution, respectively. Positive correlations of non-sea-salt sulfate and nitrate with calcium indicate that the dusty air stream is associated with polluted air masses.
- Look for evidence for interaction of dust with acidic components:

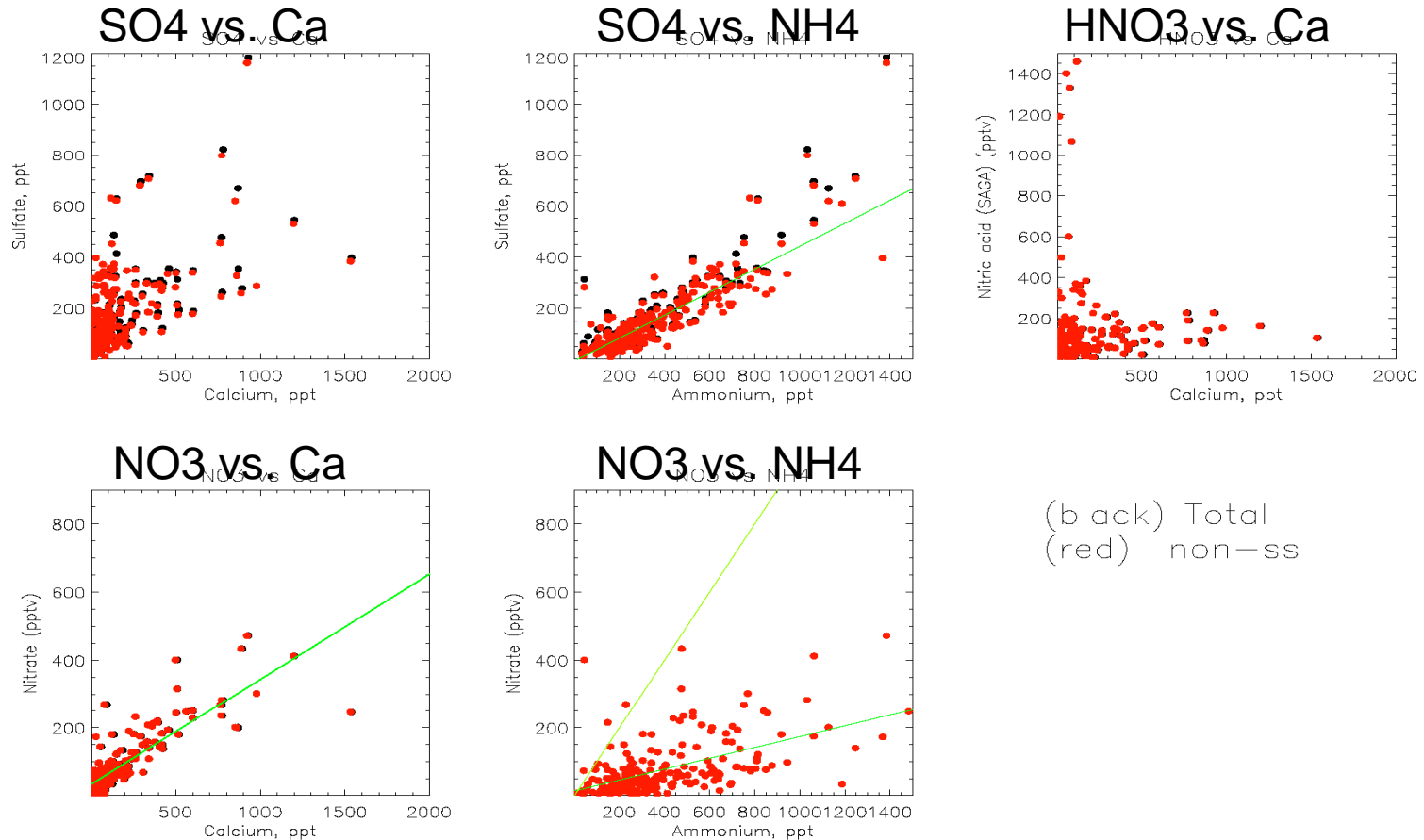
Coating of dust with sulfate or nitrate (i) shifts sulfate or nitrate towards larger sizes, (ii) favors uptake of water on dust surfaces, promoting dust particles as cloud condensation nuclei, (iii) promotes further uptake of SO_2 and of N_2O_5 , (iv) impacts NO_x/HNO_3 partitioning, and (v) affects atmospheric lifetimes for both aerosol and gas components.

INTEX-B (SAGA): 20060417 – 20060515, Pacific



Scatter plots of Ca^{2+} , Mg^{2+} , and K^+ vs. Na^+ ; Mg^{2+} and K^+ vs. Ca^{2+} , from the SAGA bulk aerosol measurements for the Pacific deployment of INTEX-B. Blue symbols indicate observations made below 1 km altitude, showing distinct sea salt signatures (blue lines). Above 1 km, observations show different but equally distinct signatures: $\text{Ca}/\text{Na} \sim 2.5$; $\text{K}/\text{Na} \sim 1/4$; $\text{Mg}/\text{Ca} \sim 3/10$. For Mg^{2+} and Ca^{2+} , $r^2 = 90\%$ above 1 km with a slope of approximately 0.3. This population with Ca^{2+} reaching in excess of 1200 ppt is characteristic of mineral dust.

INTEX-B (SAGA): 20060417 – 20060515, Pacific



Scatter plots of SO₄⁼, NO₃⁻, and HNO₃ vs. Ca(2+); SO₄⁼ and NO₃⁻ vs. NH₄⁺ from SAGA bulk aerosol data for the Pacific deployment of INTEX-B. [data limited to z > 1 km]

- SO₄⁼ is positively correlated with Ca(2+) => the dust is often associated with pollution.
- For SO₄⁼ vs. NH₄⁺, $r^2 = 71\%$, slope = 0.44, => SO₄ primarily in the form of (NH₄)₂SO₄.
- NO₃⁻ vs. NH₄⁺ shows little evidence for (NH₄)NO₃. NO₃⁻ positively correlated with Ca(2+) ($r^2 = 70\%$, slope = 1/3), while HNO₃ shows an inverse relationship with Ca(2+).
- Taken together, this suggests that much of the nitrate is in coarse mode, i.e. on the dust.
- The slope of NO₃⁻ vs Ca(2+) is well below 2, leaving excess Ca(2+).

GEOS-Chem 3-d model results:

Results shown from a full chemistry and a separate dust-only simulation for the INTEX-B period conducted at a horizontal resolution of 2 deg. by 2.5 deg.

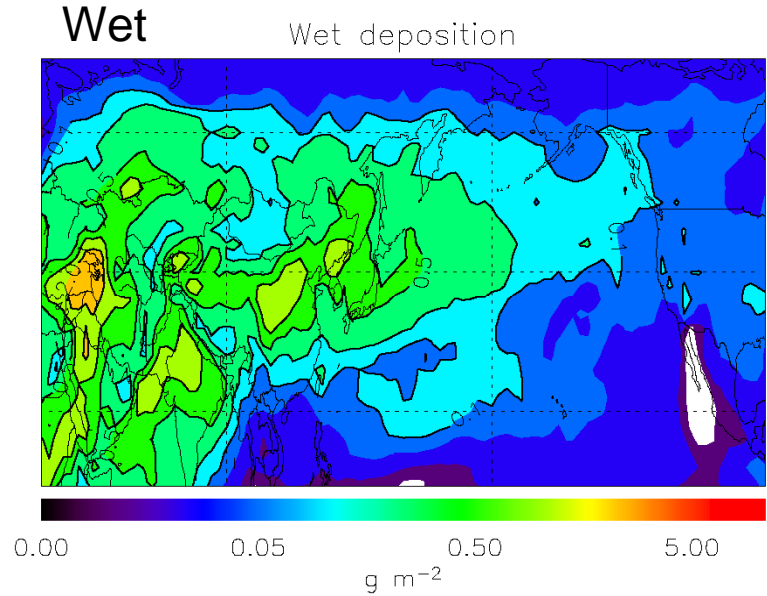
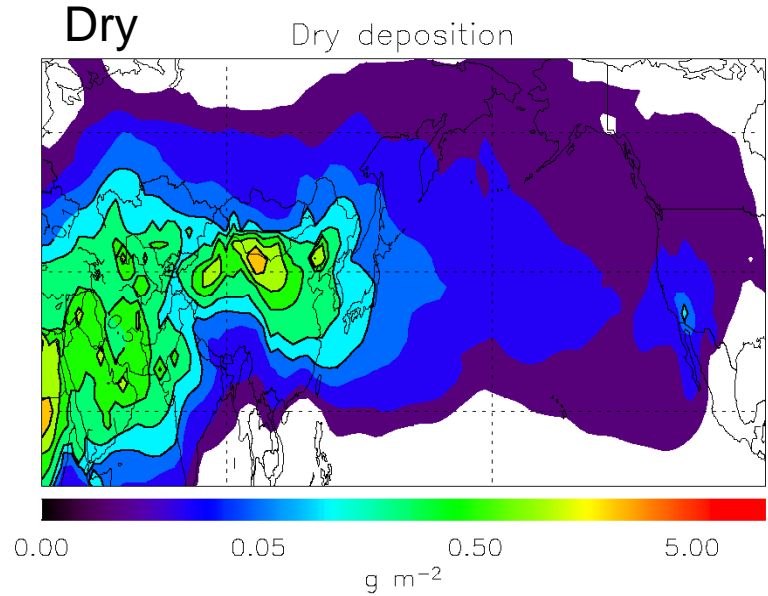
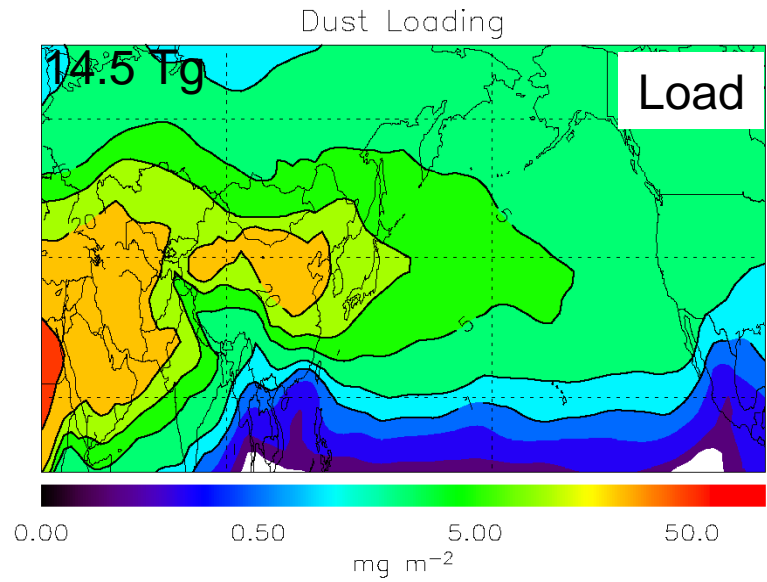
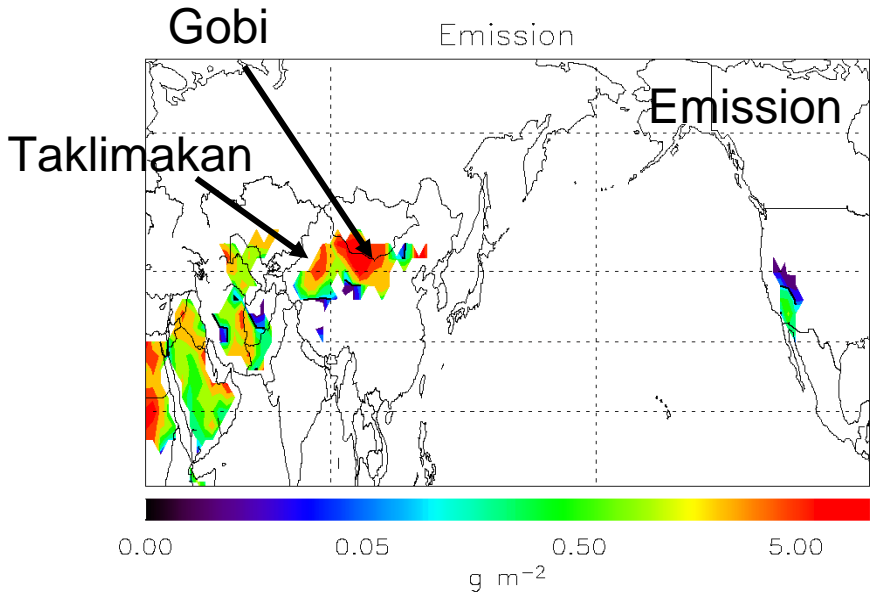
The model is driven by GEOS-4 assimilated meteorological fields.

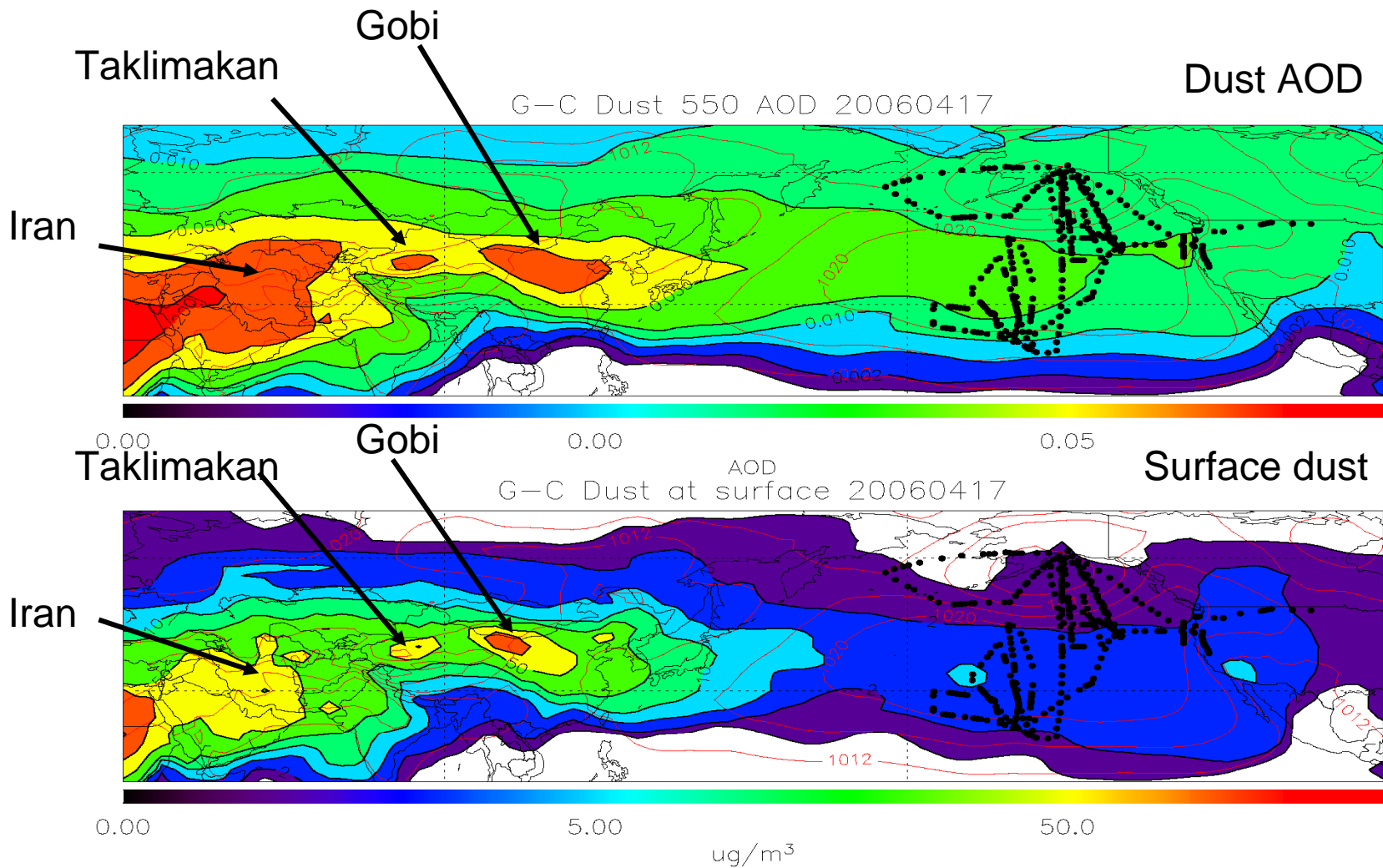
The simulation represents OC, EC, SO₄-NO₃-NH₄, sea salt, and dust aerosols. The latest version (v7.03.06) includes updated treatment of aerosols: (i) thermodynamical equilibrium is now computed using ISORROPIA (Nenes et al.); (ii) coarse mode SO₄ and NO₃ on sea salt aerosols (SO₄s, NITs) (Alexander et al.); (iii) hygroscopic growth of aerosols is now accounted for in dry deposition; the emission, transport, wet and dry deposition of mineral dust (Fairlie et al.). Full chemistry results are provided courtesy of Lin Zhang, Rokjin Park, Bob Yantosca.

To compare modeled dust with SAGA data, we computed Ca(2+) from the dust component, following Song and Carmichael (2001) in assuming Ca(2+) comprises 6.8% of (Asian) dust by mass.

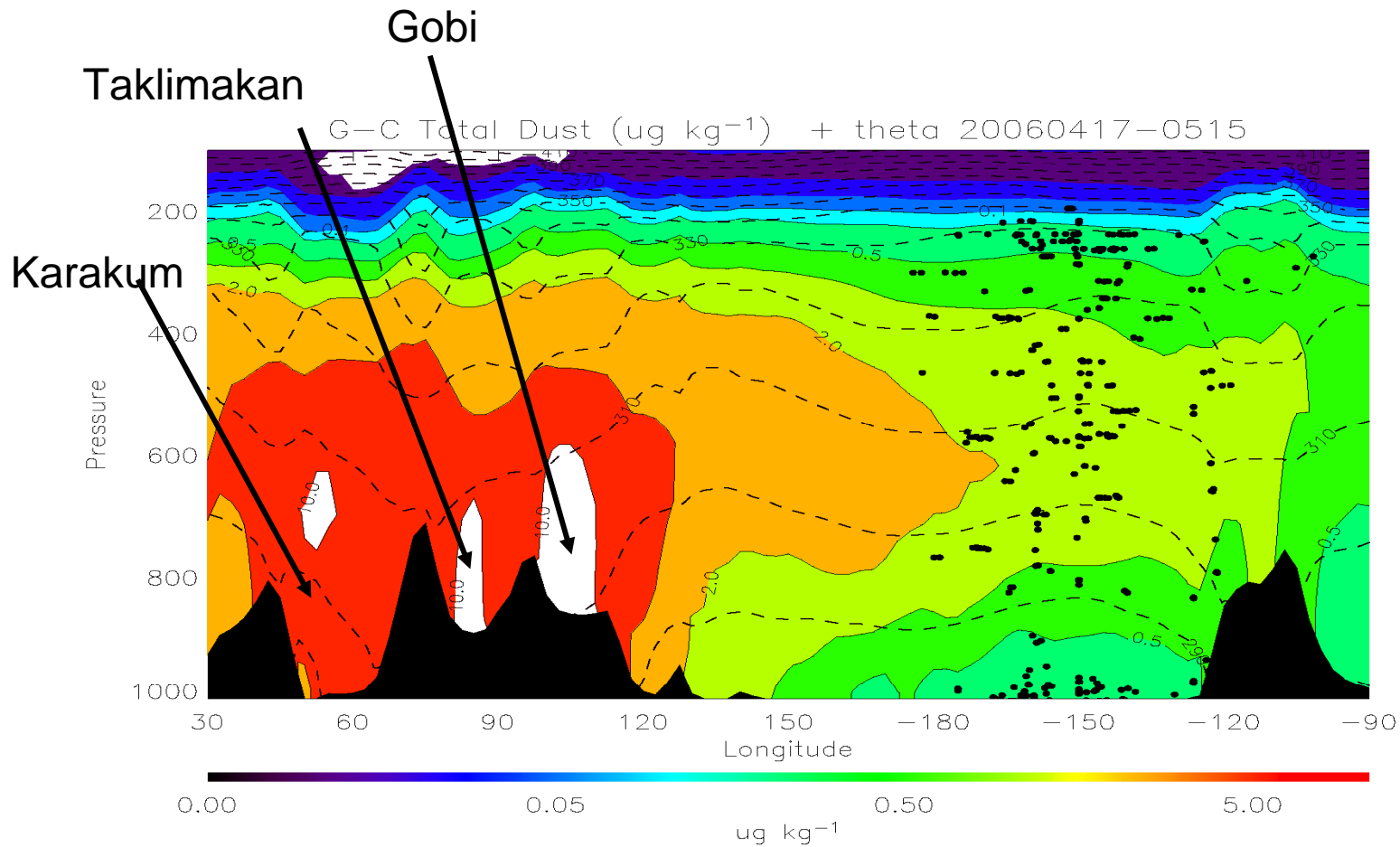
NB: Comparisons of simulated and observed Ca(2+) indicate that simulated dust concentrations are 4 times too large. The results shown here show simulated dust (Ca²⁺) scaled by a factor of 1/4.

Simulated April/May 2006 dust emissions, average load, dry and wet depositions
[145 Tg; 14.5 Tg; 53 Tg; 94 Tg, respectively



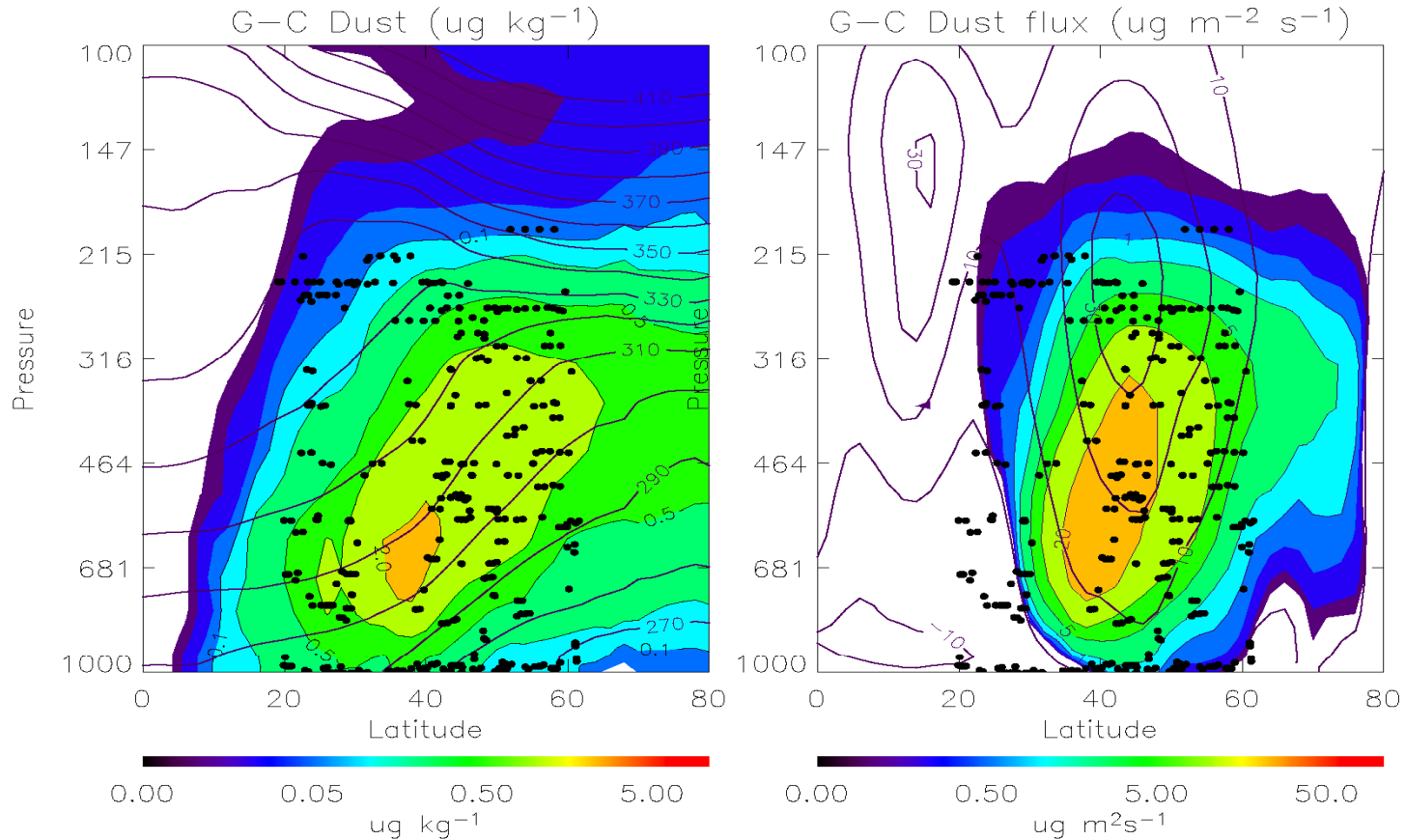


Dust AOD and surface concentration averaged for the Pacific deployment (20060417-0515). Contours of average mean sea level pressure are also shown. The map shows the mean transpacific transport of mineral dust from Asia dust storm activity to North America during April-May 2006. SAGA data points along the DC8 flight tracks (black dots) were well positioned to sample the transpacific dust transport.



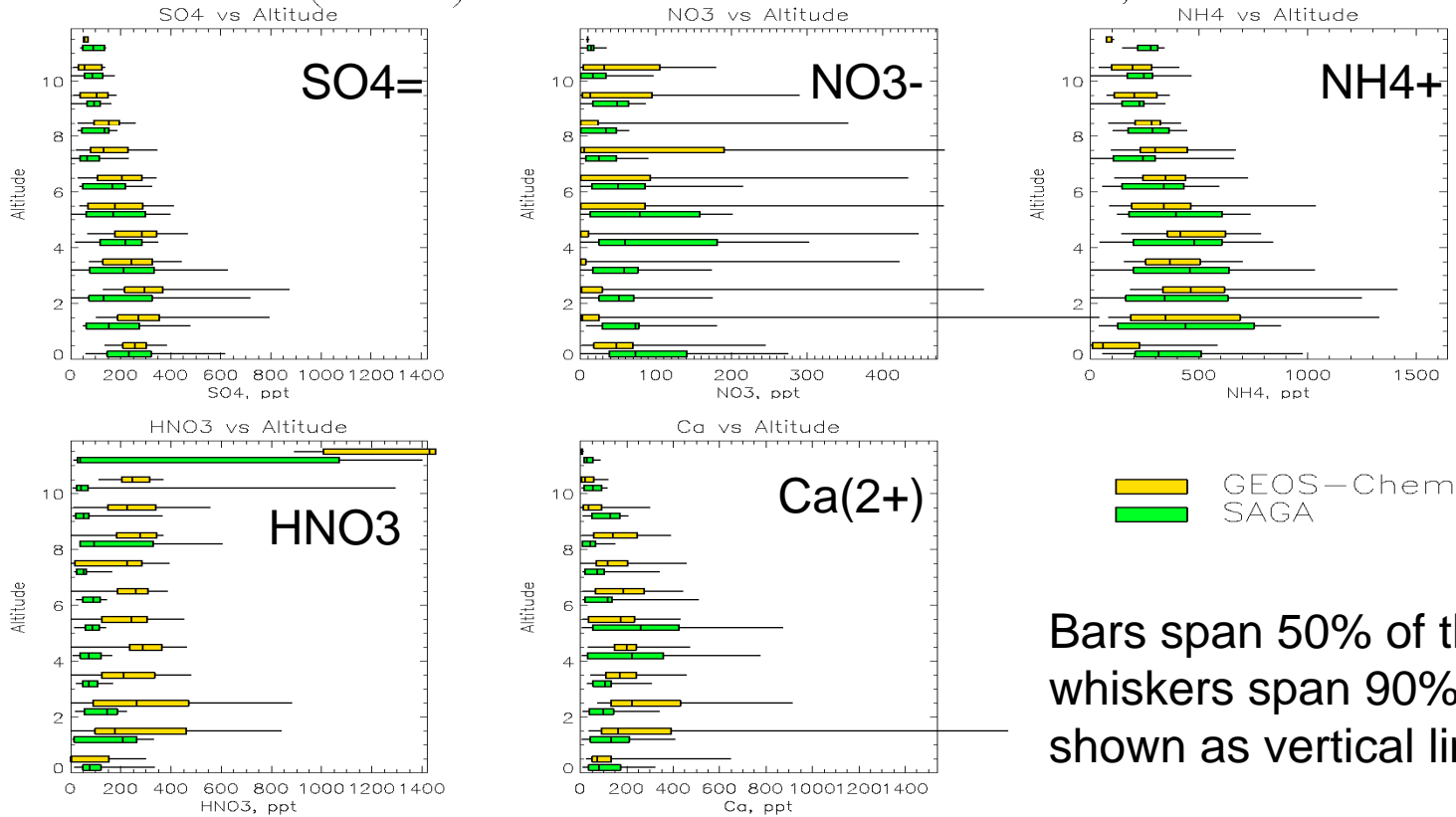
Dust mixing ratio at 40°N averaged for the INTEX-B Pacific deployment (20060417-0515). The section highlights the principal source regions and the mean transport across the Pacific during April-May 2006. In addition to dust emissions from the Gobi and Taklimakan deserts, the model indicates upstream contributions to transpacific transport.

INTEX-B Pacific 20060417-0515



Latitude-altitude cross-sections of mean simulated dust mixing ratio and eastward dust flux at 180°W during the Pacific deployment (20060417-0515). Isopleths of potential temperature and zonal wind speed are also shown. The sections show the bulk of the dust between 30 and 60°N , with the largest eastward flux around 40°N . SAGA data points along the DC8 flight tracks are also shown (black dots).

INTEX-B (SAGA): 20060417 – 20060515, Pacific

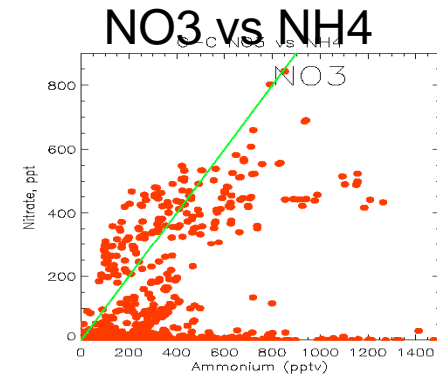
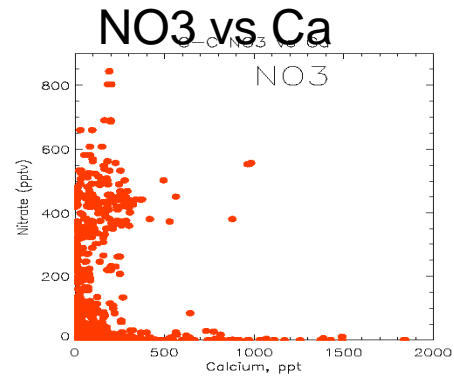
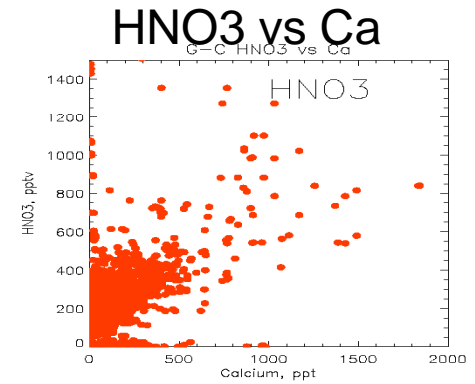
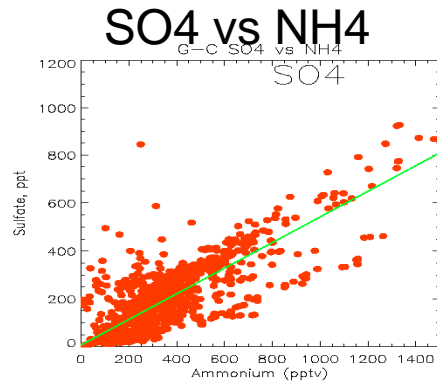
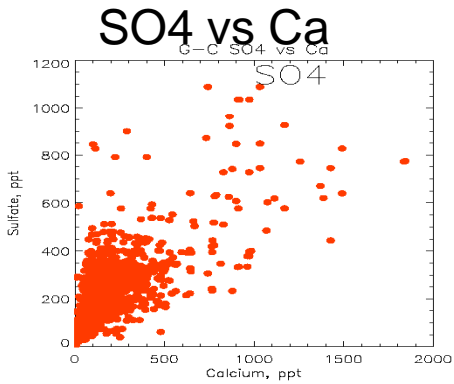


Bars span 50% of the data;
whiskers span 90%; medians
shown as vertical lines

Altitude distribution of **SAGA ion data** vs. **G-C model** data.

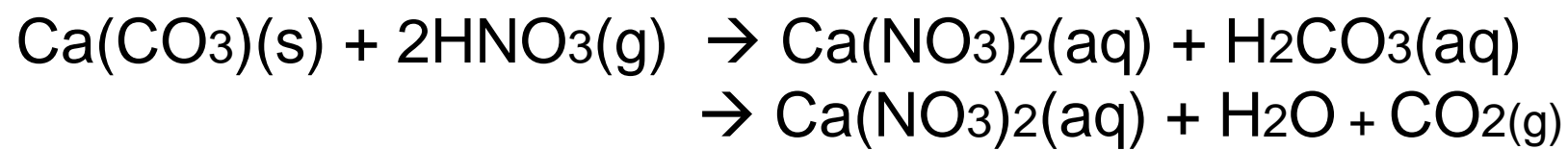
- Medians of simulated SO4 and NH4 generally fall between the quartiles of the observations throughout the troposphere.
- Simulated NO3 is biased low in the low to mid troposphere, whereas HNO3 is biased high throughout the troposphere.
- Modeled Ca(2+) shows the dust peak between 1 and 3 km whereas SAGA indicates the peak between 4 and 5 km.

INTEX-B (GEOS-Chem): 20060417 – 20060515, Pacific



- Scatter plots from the model corresponding to those shown earlier for the SAGA data.**
- Like SAGA, the model shows a positive association between SO₄⁼ and Ca(2+).
 - SO₄⁼ vs. NH₄⁺ shows a slope of about 0.5 indicating (NH₄)₂SO₄.
 - Some indication of excess NH₄⁺ and evidence for (NH₄)NO₃, in contrast with SAGA.
 - Positive association of Ca(2+) with HNO₃, in contrast with SAGA.
 - Lacks of the positive association between NO₃⁻ and Ca(2+) that was found in obs.
 - Differences between the simulated and observed NO₃ partitioning indicates the importance of HNO₃ uptake on dust.

Simple representation of uptake of HNO₃ on dust:



$$d [\text{HNO}_3] / dt = -2K [\text{Ca}]_a [\text{HNO}_3]$$

$$d [\text{NO}_3] / dt = 2K [\text{Ca}]_a [\text{HNO}_3]$$

$$d [\text{Ca}]_a / dt = -K [\text{Ca}]_a [\text{HNO}_3] \quad \text{where } [\text{Ca}]_a \text{ is the available Ca(2+);}$$

Keeping [Ca]_a constant yields

$$[\text{HNO}_3] = [\text{HNO}_3]_0 \exp(-\gamma)$$

$$[\text{NO}_3] = [\text{NO}_3]_0 + [\text{HNO}_3]_0 (1 - \exp(-\gamma)) \quad \text{where } \gamma = 2K [\text{Ca}]_a t ;$$

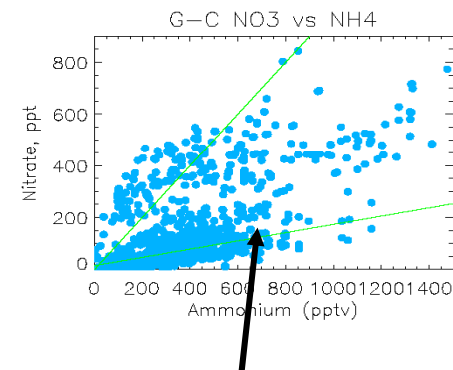
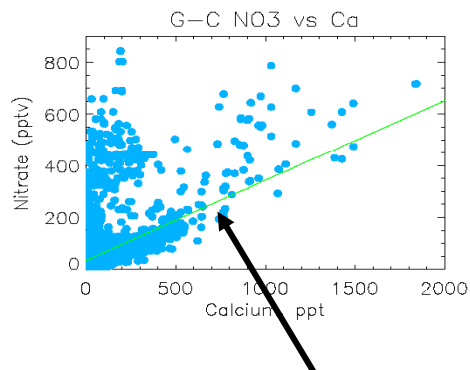
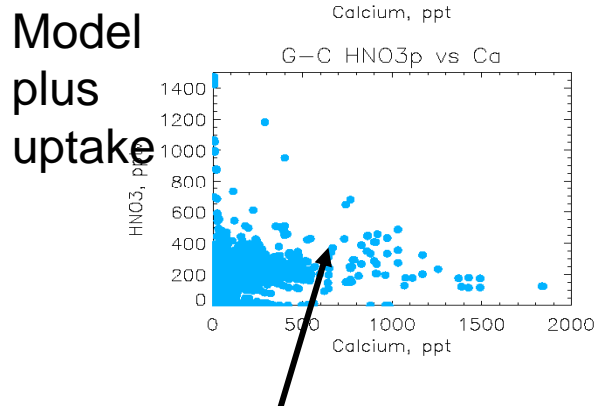
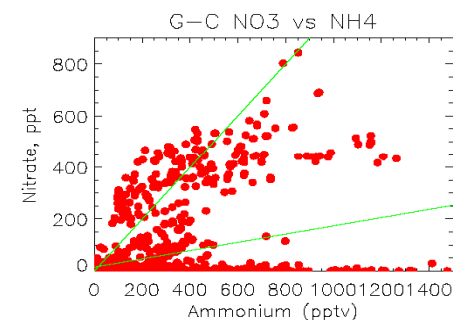
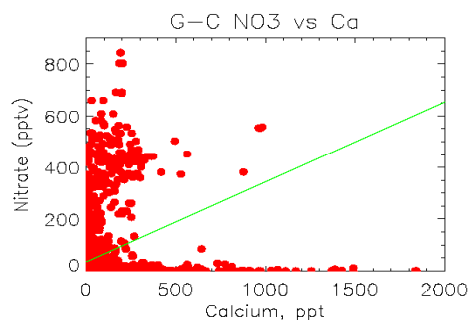
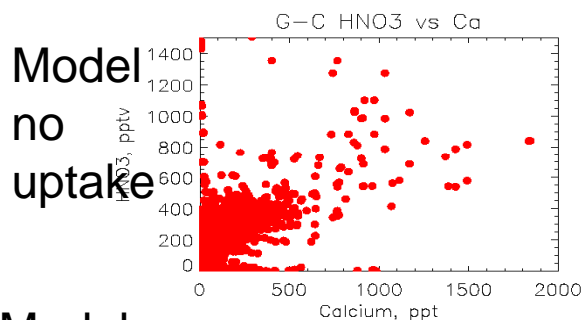
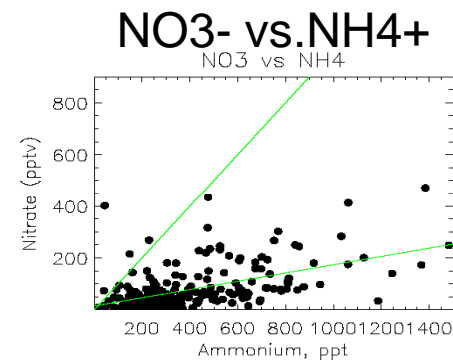
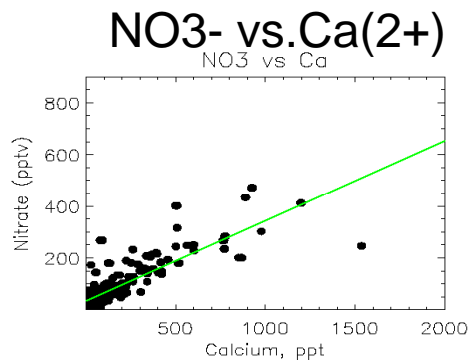
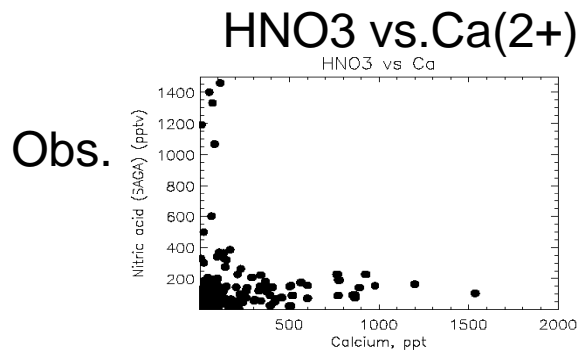
$$[\text{HNO}_3](t+\delta t) = [\text{HNO}_3](t) - 2K [\text{Ca}]_a [\text{HNO}_3](t) \delta t$$

$$[\text{NO}_3] (t+\delta t) = [\text{NO}_3] (t) + 2K [\text{Ca}]_a [\text{HNO}_3](t) \delta t$$

$$[\text{Ca}]_a (t+\delta t) = [\text{Ca}]_a (t) - K [\text{Ca}]_a [\text{HNO}_3](t) \delta t$$

$$\text{Let } \gamma = 2K [\text{Ca}]_a t = 0.0006$$

Impact of simple representation of HNO₃ uptake on dust



Impact (i) reduces HNO₃ at high Ca(2+) values

(ii) raises NO₃⁻ at high Ca(2+) values

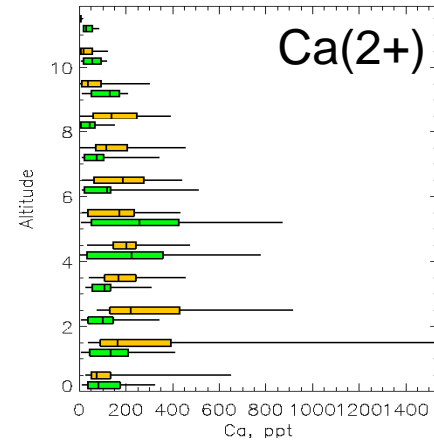
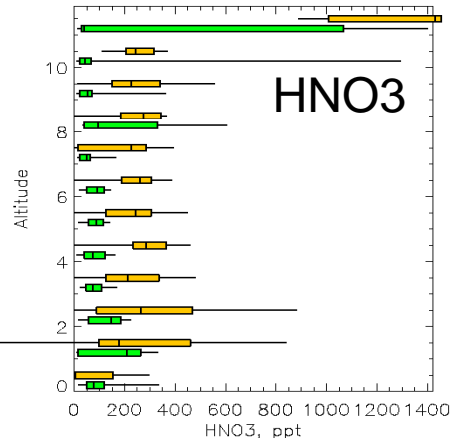
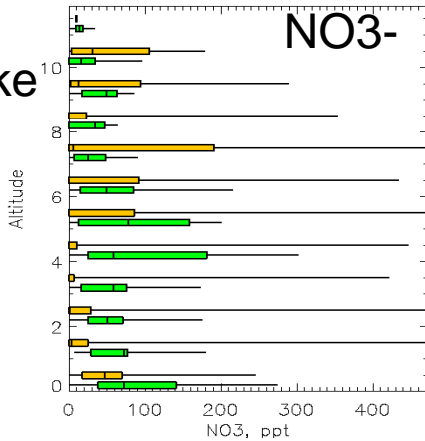
(iii) raises NO₃⁻ vs. NH₄⁺
Closer to observations

INTEX-B (SAGA): 20060417 – 20060515, Pacific

NO₃ vs Altitude

HNO₃ vs Altitude

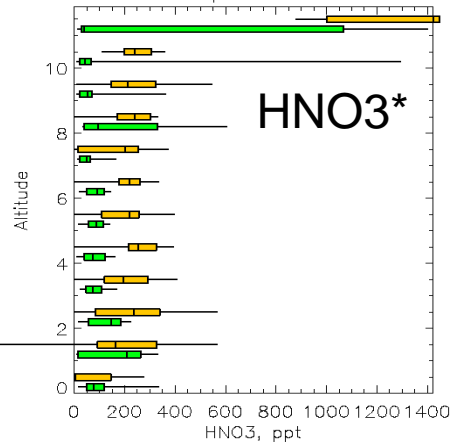
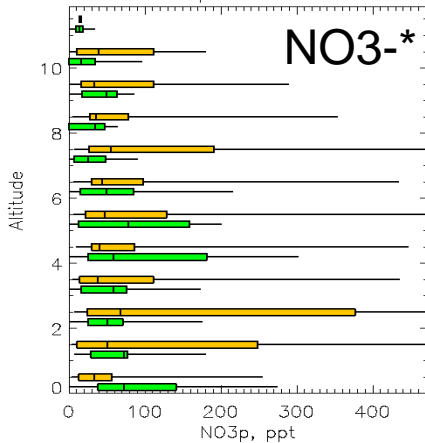
Ca vs Altitude



No uptake

NO₃p vs Altitude

HNO₃p vs Altitude



Uptake

█ GEOS-Chem
█ SAGA
 Bars span 50% of the data;
 whiskers span 90%; medians
 shown as vertical lines

Simple scheme:

➤ raises NO₃⁻ mixing ratios in the mid-upper trop. comparable with observations; larger between 1 and 4 km coincident with peak dust.

➤ We do have a total NO₃⁻ (= [NO₃⁻] + [HNO₃]) high bias in the model in the trop.

Conclusions

- The SAGA observations indicate sulfate to be primarily in the form of $(\text{NH}_4)_2\text{SO}_4$. A positive relationship between $\text{Ca}(2+)$ and NO_3^- , together with an inverse relationship between HNO_3 and $\text{Ca}(2+)$, and little evidence for NH_4NO_3 , suggest that NO_3^- is associated with mineral dust surfaces.
- 3-d model simulations conducted with GEOS-Chem indicate that transpacific transport was principally responsible for the dust observed from the aircraft over the Pacific. The model shows a very different partition with respect to NO_3^- : elevated HNO_3 and substantial evidence for NH_4NO_3 .
- Simple representation of HNO_3 uptake raises NO_3^- mixing ratios in the lower troposphere coincident with the simulated dust peak, and improves simulated ion correlations.
- These results indicate that the uptake of HNO_3 on dust surfaces, missing from *this* model formulation, is an important process in accounting for the partitioning of NO_3^- in the INTEX-B data.
- Stick around for Fabien's presentation

Questions

- [Typically for seawater: $\text{Na}^+ = 0.469$;
 $\text{Mg}(2+) = 0.0528$; $\text{SO}_4(=) = 0.0283$;
 $\text{Ca}(2+) = 0.0183$ (mol/kg)].
- Dust
- $\text{Ca}:\text{Na} \sim 5:2$; $\text{K}:\text{Na} \sim 1:4$; $\text{Mg}:\text{Ca} \sim 3:10$
- [Na^+ is also a component of dust, Na_2O , typically 2% by weight].