# An Investigation of Ammonia and Inorganic Particulate Matter in California during the CalNex Campaign

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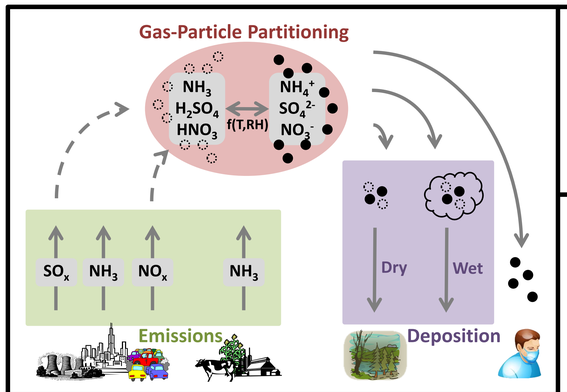
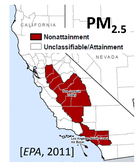
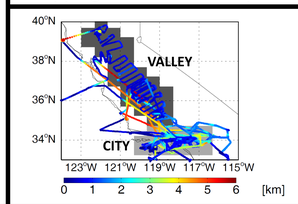
MIT ATMOSPHERIC CHEMISTRY




## Inorganic PM formation in California

Areas of California have high ambient concentrations of surface-level particulate matter. Both the Los Angeles Basin and the Central Valley are often in exceedance of the EPA's air quality standards for fine PM, which have been established to diminish negative health effects caused by atmospheric particles. The PM in these areas of high human population and large agricultural production is largely composed of inorganic aerosol formed through acid-base neutralization, where urban centers emit ammonia and $NO_x$ from mobile sources which mix with ammonia from fertilizer and animal waste in agriculturally productive areas. Sulfur dioxide is emitted from power generation and shipping near the coast. The topography of California also plays an important role in controlling PM levels as the numerous valleys and mountain ranges allow for trapping and diversion of pollutants. Thus, **it is particularly critical in California to understand inorganic PM formation and the role of precursor emissions in achieving air quality compliance.**

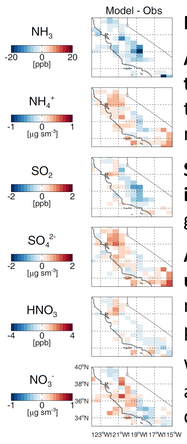



CalNex Field Study Campaign
WP-3D Aircraft and Ground Site Observations
May - June 2010

GEOS-Chem v9-01-01 w/ NEI-2005 Anthro Emissions + FINN Biomass Burning Emissions
0.5 ° x 0.667 ° Nested Horizontal Resolution over NA

## Investigate model sensitivities using airborne observations




**Initial comparison:**

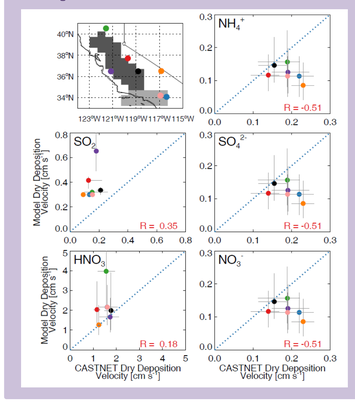
**Ammonia is low throughout CA** – by up to 20 ppb gridded median in Valley.

**$SO_2$ is underestimated in Valley** by up to 1 ppb gridded median.

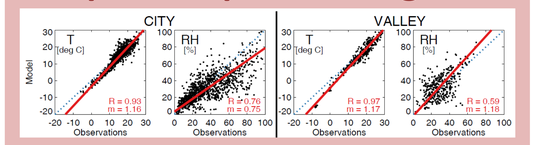
**Ammonium nitrate (AN) underestimated in City** region, overestimated in parts of Valley.

What model processes are contributing to these discrepancies?

### Deposition



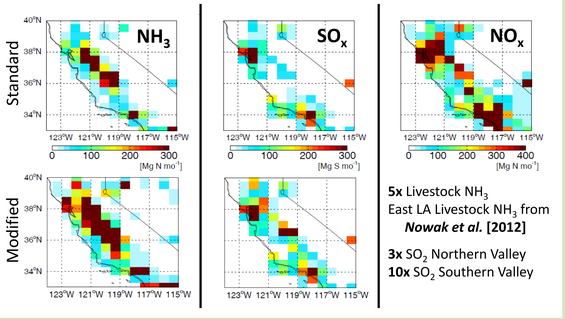

### Gas-particle partitioning




AN partitioning is largely controlled by temperature (T) and relative humidity (RH). Sensitivity studies of +/- 1° C and +/- 10 % RH (consistent with model bias) show **little change** in near-surface simulated AN concentrations.

Wet deposition not a factor given little summertime rainfall. Decreasing $SO_2$ dry deposition velocity reproduces $SO_2$ in City but **discrepancies remain** for other species and regions.

## Emissions

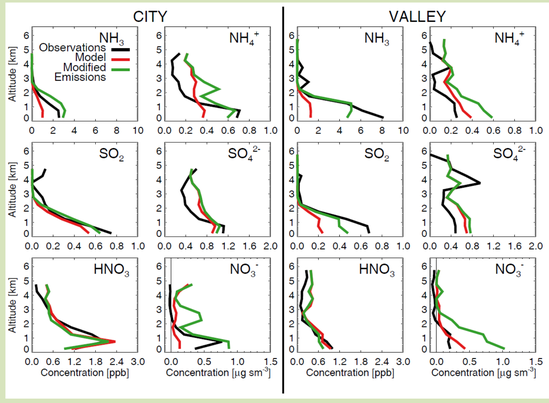


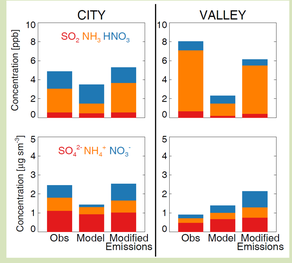

**5x** Livestock $NH_3$
East LA Livestock $NH_3$ from ***Nowak et al.* [2012]**

**3x** $SO_2$ Northern Valley
**10x** $SO_2$ Southern Valley

*Nowak et al.* [2012] show that livestock ammonia emissions were dramatically underestimated in the LA region. Ammonia emissions are dominated in NEI-2005 by livestock emissions throughout the Valley, so it is not unreasonable to consider that this underestimate may explain the model bias here as well.

We test this using a **5-fold increase of livestock ammonia emission throughout California.** Similarly, large underestimates in $SO_2$ motivate increasing these emissions throughout the Valley.

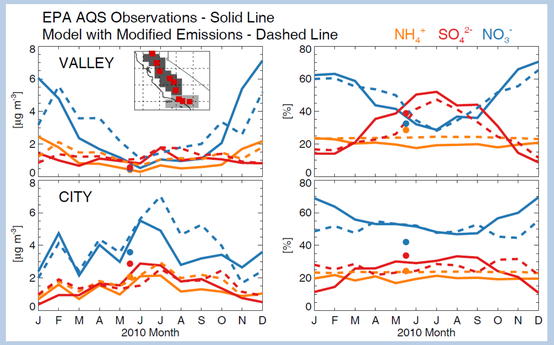



**The modified emission simulation decreases the discrepancies** between ammonia in both regions, $SO_2$ in the Valley and AN in the City. The remaining discrepancy is in AN in the Valley, which is now even more overestimated. Possible reasons for this over-prediction include a missing loss-mechanism such as uptake on dust or a poor representation of ventilation from the region due to insufficiently resolved terrain.

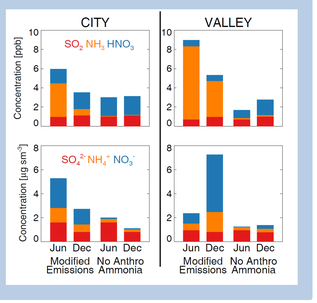
## What are the implications of modified emissions on surface air quality in California?

### Regional difference in seasonal PM variability




Comparison of observed inorganic PM surface concentrations throughout California with the simulated values using increased emissions shows **good agreement throughout the year**. The agreement is greater in the summertime, where the emissions have been adjusted based on the CalNex analysis. Additional examination using widespread **wintertime observations could further constrain these emissions**.

The concentration of **surface inorganic PM decreases in the City** region from summer to winter. The cause of this remains under investigation.

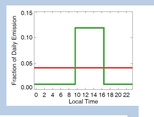


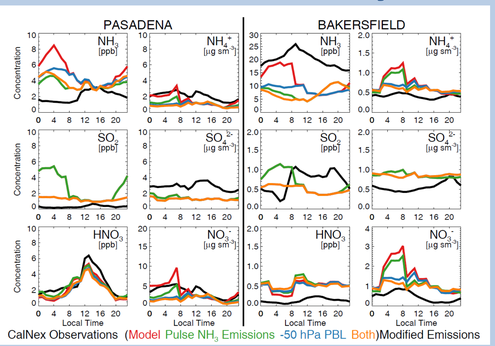

Surface inorganic **PM mass, namely AN, increases greatly in the Valley during the winter** compared to summer. About 75 % of this increase is due to a lower wintertime PBL height, while the remainder is due to colder temperatures enhancing AN formation balanced with lower ammonia emissions.

**Anthropogenic ammonia makes contributions to** about 50 – 60 % of surface inorganic PM in CA during the summer and **up to 80 % in the Valley in the winter.**

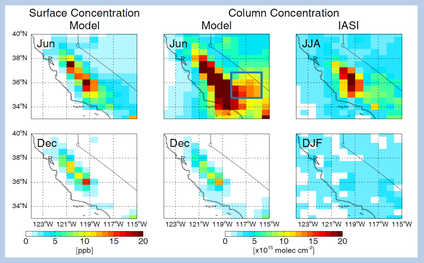
## Effects of emissions timing and PBL on diurnal variability

Ground site observations during CalNex from Pasadena (City) and Bakersfield (Valley) allow for **insight into the diurnal variability** of the relevant gas-precursor and PM species and their comparison to the simulated values.




While providing an improvement over the standard simulation, the model with modified emissions is **generally too high during the overnight periods** for ammonia, $SO_2$ and AN compared to the observations. Adjustments such as emitting ammonia in a daytime pulse (rather than uniformly throughout the day) and raising the overnight PBL height by 50 hPa begin to address these discrepancies. Although we cannot reproduce the diurnal cycle for all species, **the simulated surface concentrations of ammonia, $SO_2$ and AN are highly sensitive to these changes**. For example, the adjustments lead to a concentration decrease in some cases by more than 50 %.




## Potential for future PM enhancement

Higher emissions and warmer temperatures favor export of excess ammonia out of the Valley in summertime. In addition to deposition of this ammonia in the export regions (blue box), which causes environmental degradation, inorganic PM is formed in limited amounts. The remaining reservoir of ammonia in the Valley, present even during winter when inorganic PM formation is favored, indicates that this **formation and the associated air quality degradation could dramatically increase should the emissions of atmospheric acids increase**. This seems possible given current projections of southern Valley human population increase.