

# Los Angeles and Bakersfield HCl During CalNex: Acid Displacement, Reactive Cl Reservoir and Partitioning

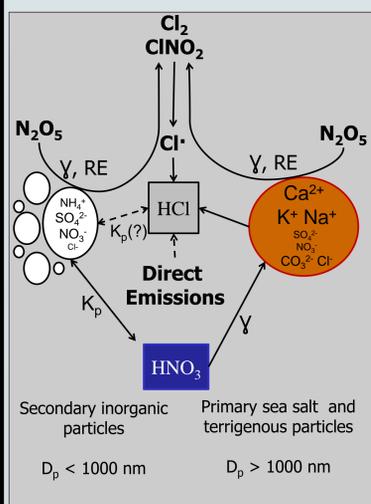
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## Introduction

- Production of HCl in coastal zones has been described through acid displacement by H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> in urban areas (Dasgupta *et al.*, 2007). Constraints on total emissions and displacement chemistry for coastal areas require more observations to improve model accuracy (Kelly *et al.*, 2010).
- HCl is also a product of Cl-radical chemistry, but its contribution to the sustained generation of photo-reactive chlorine species via partitioning is not well understood (Osthoff *et al.*, 2008; Roberts *et al.*, 2008; Roberts *et al.*, 2009; Thornton *et al.*, 2010).
- The partitioning of HCl has large implications in the reactive uptake of N<sub>2</sub>O<sub>5</sub> on aerosols since Cl<sup>-</sup> suppresses the nitrate effect (Bertram and Thornton, 2009; Chang *et al.*, 2011).
- The atmospheric abundance and fate of HCl in mid to central continental locations is uncertain (Thornton *et al.*, 2010).
- Total HCl and soluble Cl<sup>-</sup> measurements with appreciable time resolution are not routinely included in long term monitoring strategies and are necessary to fully constrain the generation of coastal and continental reactive-Cl budgets

## Chemical Framework

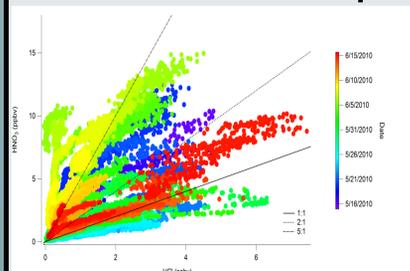


## Objectives

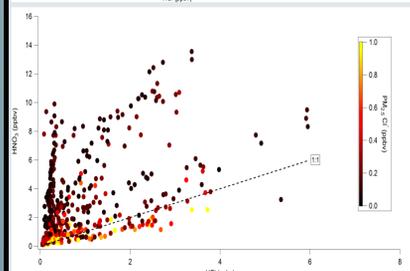
- What is the most important formation mechanism for HCl?
  - Acid displacement by HNO<sub>3</sub>
    - PM<sub>2.5</sub> vs PM > 2.5 μm
  - H-abstraction by Cl-radical
  - Partitioning of semi-volatile NH<sub>4</sub>Cl
  - Direct emissions
- What are the sources of particulate chloride?
  - Direct
    - Terrigenous, sea-spray, biomass burning
  - Partitioning
    - NH<sub>3</sub>, HCl, Temperature, Relative Humidity, Pre-existing aerosol composition
- How important is the observed HCl in the generation of reactive Cl?

## Pasadena (LA) – NH<sub>3</sub> Limited

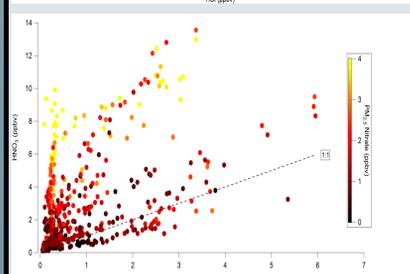
### SOURCES – Acid Displacement and ClNO<sub>2</sub>



(Left Top) Ratio of HCl to HNO<sub>3</sub> changed daily, indicating that the source was variable throughout the campaign. A positive correlation between mixing ratios were seen each day suggesting that acid displacement is the primary source of HCl.

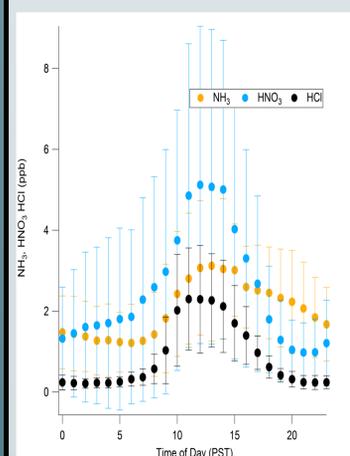


(Left Middle) During the period of highest sea salt loading measured by GPIC, HNO<sub>3</sub>/HCl < 1, indicating that HCl formation by acid displacement dominates the fate of HNO<sub>3</sub>. Additional HCl may be coming from Cl-radical H-abstraction or coarse mode displacement in significant quantity. Fine mode Cl<sup>-</sup> from the GPIC is coincident with high sea salt fractions measured by PALMS.

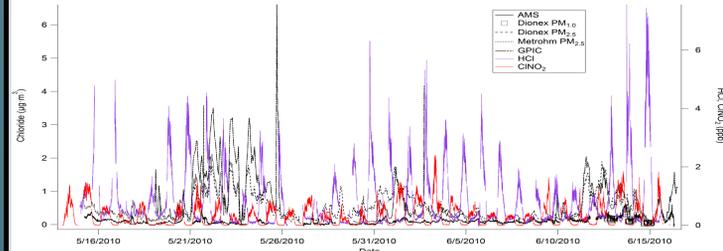
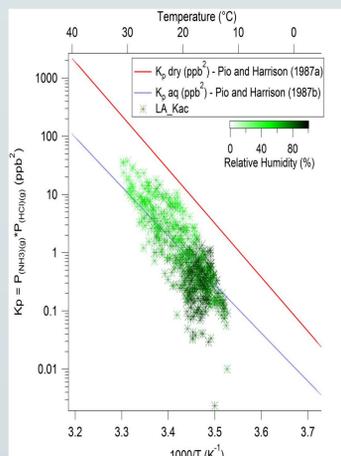


(Left Bottom) HNO<sub>3</sub>/HCl > 1 indicates that other sinks of HNO<sub>3</sub> increase in importance relative to the acid displacement mechanism (e.g. NH<sub>4</sub>NO<sub>3</sub> formation). The importance of the coarse mode and direct emissions of HCl can be determined by mass balance of PM<sub>2.5</sub> and gaseous measurements.

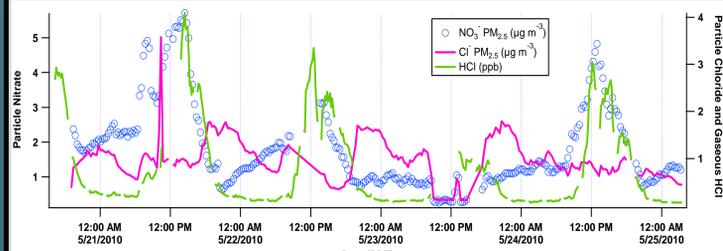
### SINKS – Partitioning, Dry Deposition, Formation of Reactive Cl



(Above Left) Ambient mixing ratios of NH<sub>3</sub> were less than 4 ppbv, but HCl mixing ratios, moderate temperatures and high RH thermodynamically favour homogeneous formation of NH<sub>4</sub>Cl to a small extent at night (Above Right). This can be seen in the AMS Cl<sup>-</sup> measurement (Below). However, the majority of the Cl<sup>-</sup> is only observable by water-soluble methods.



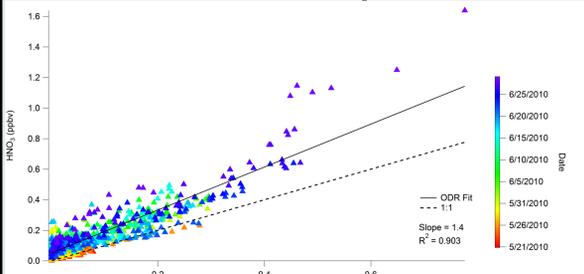
(Above) ClNO<sub>2</sub> photolysis will dominantly terminate in the production of HCl. There is also a general link between the maximum daytime HCl, maximum nighttime ClNO<sub>2</sub> and the local loading of PM<sub>2.5</sub> Cl<sup>-</sup>.



(Above) Evidence for fine mode acid displacement by: HNO<sub>3</sub> + NaCl → NaNO<sub>3</sub> + HCl.  
 • Continuing work is being focused on developing a mass balance of observable HCl production sources to determine the importance of the coarse mode and ground surface acid displacement contributions. Preliminary analysis suggests that contributions from other Cl-radical species and direct emissions are negligible at this site.

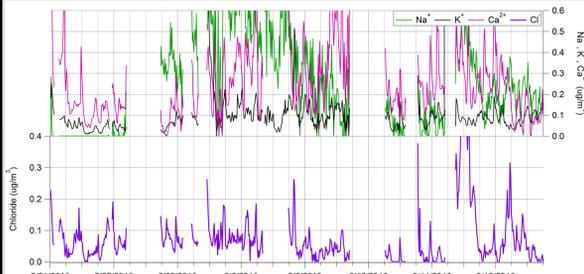
## Bakersfield (SJV) – NH<sub>3</sub> Rich

### SOURCES – Acid Displacement

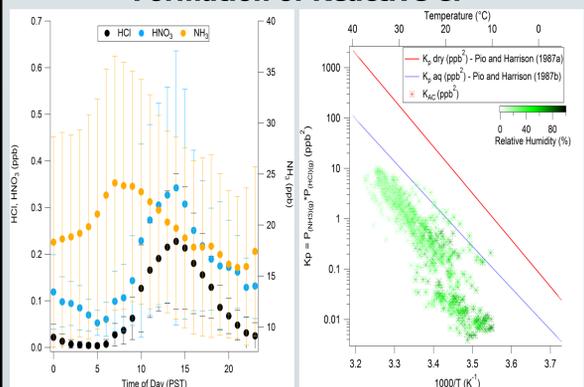


(Above) Ratio of HCl to HNO<sub>3</sub> was seen to be nearly constant throughout the campaign, indicating the source of HCl was essentially constant. Fine mode Cl<sup>-</sup> is more strongly related to fine mode terrigenous mineral cations (Ca<sup>2+</sup> and K<sup>+</sup>) than oceanic Na<sup>+</sup> (below). Implies that local production of HCl was controlled by acid displacement at the ground surface or on lofted super-micron soil rather than displacement from fine or coarse sea-salt aerosol for the majority of the campaign.

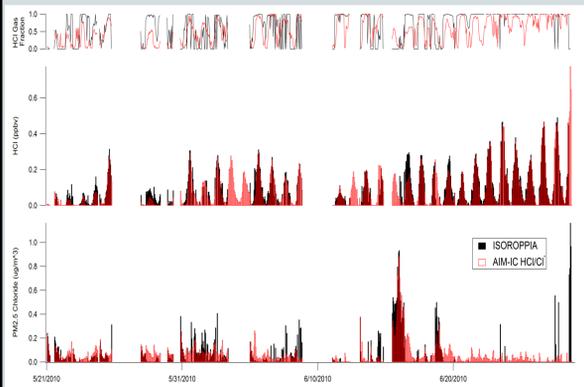
(Below) Elevated mass loadings of Ca<sup>2+</sup> and K<sup>+</sup> are generally coincident with Cl<sup>-</sup> until June 15, when a stronger Na<sup>+</sup> influence emerges. NOAA HYSPLIT back trajectories indicate that air masses with mass loadings of Ca<sup>2+</sup> that exceed Na<sup>+</sup> typically originate within the valley or further inland while long range transport of oceanic air masses through San Francisco bay were uncommon. One distinct episode of KCl observed on June 5 may be derived from biomass burning.



### SINKS – Partitioning, Dry Deposition, Formation of Reactive Cl



(Above Left) Ambient mixing ratios of NH<sub>3</sub> were in excess of 20 ppbv, but low HCl mixing ratios, high temperatures and low RH thermodynamically disfavoured homogeneous formation of NH<sub>4</sub>Cl (Above Right). ISORROPIA constrained only by NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup> observations could not reproduce AIM-IC observations of PM<sub>2.5</sub> Cl<sup>-</sup>.



(Above) ISORROPIA run with mineral cation observations (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> in addition to NH<sub>4</sub><sup>+</sup>) found close agreement with observed mass loadings of PM<sub>2.5</sub> Cl<sup>-</sup>. Periods where Cl<sup>-</sup> is underpredicted may indicate influence from unmeasured particulate species (e.g. additional base cations, alkyl amines). Loss of fine mode Cl<sup>-</sup> during the day suggests acid displacement, but magnitude is insufficient to account for daytime HCl mixing ratios.

### Ongoing Work

- Coarse mode aerosol characterization
- Availability of terrigenous Cl<sup>-</sup> salts (CRH ~ 30 %) for generation of reactive-Cl

### Case Study for June 16

- Could the observed Cl<sup>-</sup> ever generate ClNO<sub>2</sub>? How much?
- P(N<sub>2</sub>O<sub>5</sub>), RH > 60%, Mass Fraction of PM<sub>2.5</sub> Cl<sup>-</sup> available
- Will HCl partition?

## Conclusions

### Pasadena (LA)

- Production of HCl in LA by acid-displacement is dependent on branching in the fate of HNO<sub>3</sub>. During periods of high mass loading of Cl<sup>-</sup> the displacement is near 1:1, due to the fate of HNO<sub>3</sub> being dominated by uptake on sea-salt aerosol. During periods of low mass loading the ratio of becomes higher as the HNO<sub>3</sub> forms NO<sub>3</sub><sup>-</sup>.
- Repartitioning of HCl to fine mode aerosol via NH<sub>3</sub> at night provides a path to sustain the production of ClNO<sub>2</sub> at night.
- HCl loss a competition between partitioning and dry deposition.

### Bakersfield (SJV)

- Production of HCl by acid displacement is dominated by coarse mode aerosol and at the surface
- Repartitioning of HCl with NH<sub>3</sub> to fine mode aerosol is thermodynamically rare at this time of year and unlikely to act as a reservoir for ClNO<sub>2</sub> production
  - Cooler and/or more humid periods are expected to enable partitioning of HCl to the fine mode
- Fine mode chloride is terrigenous in origin and commonly associated with detection of the mineral cations Ca<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>
  - Back trajectories and NH<sub>4</sub><sup>+</sup>-NO<sub>3</sub><sup>-</sup>-SO<sub>4</sub><sup>2-</sup> aerosol neutrality suggest that detected Na<sup>+</sup> was seldom processed sea salt aerosol
- HCl loss dominated by dry deposition

## References

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