Observations of Trace Organic and Inorganic Acids in Coastal California

Photo credit: Doug Day and Shang Liu (SIO)

Timothy Bertram
Timia Crisp
Olivia Ryder
Joel Kimmel
Mike Cubison
Marc Gonin
Doug Worsnop
Motivation: Measurements of HCl in the MBL

Osthoff (2008): HCl partitioning required to sustain observed ClNO₂ mixing ratios in subtropical MBL

Thornton (2010): Elevated ClNO₂ observed in continental air, suggesting a role for HCl gas-particle partitioning as the source of particulate Cl.
Numerous measurements of HCl in the MBL (a few highlights):

1. **Appledore Island:**
   - Strong diurnal cycle, peaking 14-16
   - HCl correlated with HNO$_3$
   - Max HCl >5 ppb

2. **INTEX-B (DC-8):**
   - HCl 20-140 pptv (remote pacific MBL)

**HCl sources:**
1. Acid displacement (HNO$_3$ + Cl containing sea salt)
2. Cl + hydrocarbon reactions
3. Direct emissions

**HCl Sinks:**
1. OH + HCl
2. Deposition

**References:** Keene et al., JGR 2007   Kim et al., ACP 2008
Approach: Negative Ion Chemical Ionization Mass Spectrometry

$CH_3C(O)O^- + HX \rightarrow CH_3C(O)OH + X^-$ \hspace{1cm} R1

$CH_3C(O)O^- + HX \rightarrow CH_3C(O)O^- (HX)$ \hspace{1cm} R2

References: Veres et al., IJMS 2008  Bertram et al., submitted 2010
Detectable Compounds

1. **Organic Acids**: Formic, Acrylic, Propionic, Glycolic, Methacrylic, Butyric, Pyruvic, Lactic, among others

2. **Inorganic Acids**: HCl, HNCO, HONO, HNO₃, H₂SO₄, among others

**References**: Veres et al., IJMS 2008, Bertram et al., submitted 2010
Approach: Negative Ion Chemical Ionization Mass Spectrometry

CalNex Operating Conditions

- Sample collection rate 2Hz
- Mass spectrum 10-200 Th
- Direct calibration of HC(O)OH and HCl
- Relative calibrations for other acids
- Daily inlet characterization
- Routine inlet switching (1-2 days)

References: Bertram et al., submitted 2010
Approach: Inlet Concerns and Calibrations

HCl inlet on lowest platform
5m of sample line
F = 10 L min\(^{-1}\) 0.75 atm
T = 35 C

Current data status:
Data available on select days
Hopeful to have final by (before) May meeting

1. HCl Calibration Standards
   - \(PR(HCl) = 17 \text{ ng min}^{-1}\)

2. Identify Positive Artifacts

3. Characterize Inlet Transmission
General HCl Observations

- HCl is strongly correlated with HNO₃
- Diurnal profile, that tracks HNO₃
- Peak concentration >8 ppb
- Average coastal mixing ratios 1-2 ppb
- Clean marine <200 ppt
General HCl Observations

![Graphs showing HCl observations over time.](image)
Ship emissions: MARGRETHE MAERSK

[Graph showing CO2 and HCl emissions over time]

Julian day (UTC)

[Graph axes showing concentrations in ppmv and ppbv]

[Image of a ship with the Maersk Line logo]
$\Delta \text{HC(O)OH}/\Delta \text{CO} = 0.1 \text{ mmol/mol CO}$

$\Delta \text{HNCO}/\Delta \text{CO} = 0.01 \text{ mmol/mol CO}$
\[\Delta \text{HONO}/\Delta \text{NO}_x < 0.016\]

\[\Delta \text{HONO}/\Delta \text{CO} < 0.7 \text{ mmol/mol CO}\]
OCS does not track:

- HCl
- Formic acid
- HNO₃
- HONO
Next Steps

1. Complete secondary ion chemistry and inlet transmission studies
2. Post FINAL data by May 2011
3. Look in detail at collection of sampled ship plumes
4. Assign unidentified (and potentially useful) peaks
5. Complete analysis of the factors controlling the spatial and temporal distribution of HCl