

# Effect of Sea Salt PM and Nitryl Chloride on Ozone Formation

Presented to the  
South East Texas Photochemical Modeling  
Technical Committee  
April 23, 2008



# Effect of Sea Salt PM on Ozone Formation

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- Research
  - Nitryl Chloride Observations
  - Sea Salt & Nitryl Chloride Chemistry
  - Effect of Sea Salt & Nitryl Chloride Chemistry
  - CAMx Model Performance
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- Implications
  - Scientific Implications
  - Modeling Implications
  - Regulatory Implications



# Summary: Effect of Sea Salt PM on Ozone Formation

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- Recent NOAA paper suggests overnight reactions of Sea Salt PM can lead to more ozone
- Misunderstandings abound
  - Refines our understanding of early morning Ozone production
  - Does not question the observations, imply new emissions, or control strategies
- Significance
  - Potential to form additional ozone quickly
  - Other factors usually limit ozone formation, so it could be minor
- **Its too soon to base regulatory decisions on this research**



# Nitryl Chloride Observations

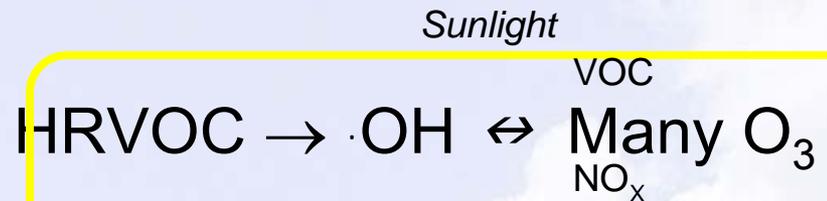
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- **TexAQS Discovery**
  - Jim Roberts, NOAA Ship Ron Brown
  - April 7 published in Nature Geoscience, Ostoff et. al., “High Levels Of Nitryl Chloride In The Polluted Subtropical Marine Boundary Layer”  
<http://www.nature.com/ngeo/journal/vaop/ncurrent/abs/ngeo177.html>
- **Presence of Sea Salt PM in a polluted atmosphere**
  - Causes Nitryl Chloride ( $\text{ClNO}_2$ ) accumulation overnight
  - Which accelerates early morning Ozone formation
  - This Ozone comes from overnight reaction of
    - Onshore or offshore emissions, depending on conditions
    - $\text{NO}_x$  emissions from any source
  - Don't know how much it increases afternoon maximum Ozone concentration

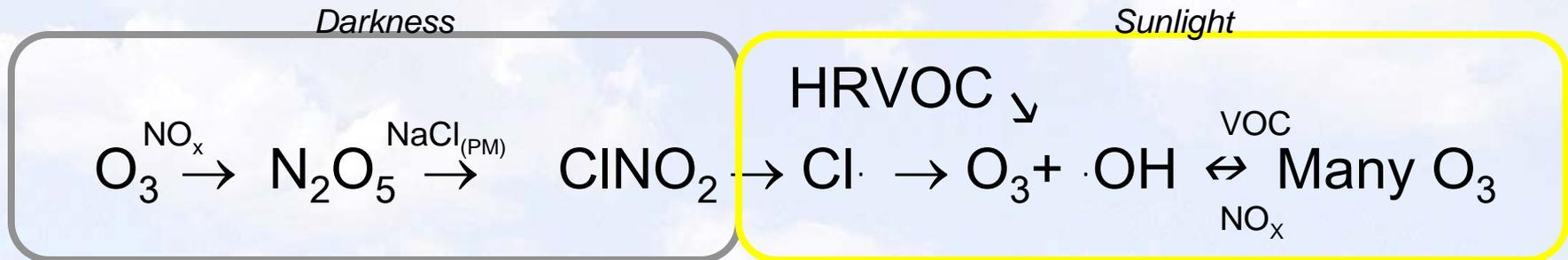


# Sea Salt & Nitryl Chloride Chemistry

- Current Mechanism



- Sea Salt Mechanism



*Early start*

*Faster*

*Same old cycle*

*An early, fast start means you win, unless there is a traffic jam...*



# Effect of Sea Salt & Nitryl Chloride Chemistry

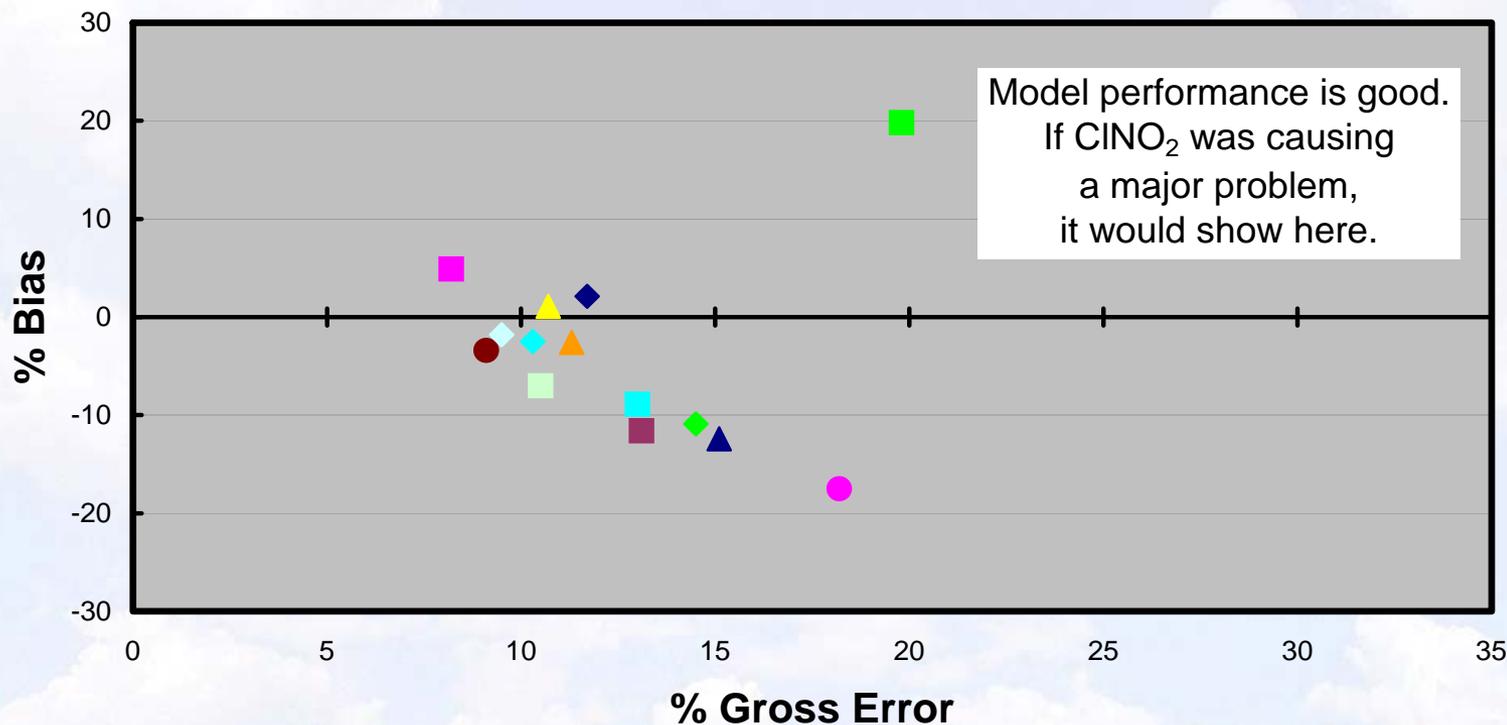
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- $\text{Cl}\cdot$  is much more reactive than  $\cdot\text{OH}$ 
  - $\text{Cl}\cdot$  reacts much faster
  - One time reaction
  - Potential to produce more ozone quickly
- But other factors usually limit Ozone formation
  - VOC limited
  - $\text{NO}_x$  limited
  - Transport limited
  - Sunlight limited
  - Radical limited, then  $\text{Cl}\cdot$  important
- $\text{Cl}\cdot$  has the potential to produce more Ozone
- Does that extra Ozone actually form?



# CAMx Model Performance

## HG June 2005 Performance One Hour Ozone



6/17/2005 6/18/2005 6/19/2005 6/20/2005 6/21/2005 6/22/2005 6/23/2005 6/24/2005  
6/25/2005 6/26/2005 6/27/2005 6/28/2005 6/29/2005 6/30/2005



# Houston Chronicle Article

## “Sea Salt May Be Adding To Houston's Air Pollution”, April 6, 2008

Chronicle Said	Roberts Said ☆
Sea salt may increase ozone 30%	Observed 30% increase in Nitryl Chloride, but the ozone increase is unknown
Sea salt causes ozone	Sea Salt provides another way for known emissions to make ozone
<p style="text-align: center;"><b>Roberts Also Said ☆</b></p> <p><b>It's “much too soon” to base regulatory decisions based on this line of research.</b></p>	

☆ Phone conversion with Jim Neece, TCEQ, April 7, 2008



# Houston Chronicle Editorial

**Editorial: “A pinch of salt / Research indicates a natural culprit is aggravating Houston's air pollution”, April 10, 2008**

**Chronicle Said**

**TCEQ Said ☆**

“Levels of ozone could be substantially higher here than officially measured, with sea salt worsening the situation by as much as 30 percent.”

This research does not question the ozone observations.

It merely helps explain where the ozone came from.

☆ Jim Neece, TCEQ, April 14, 2008



# Scientific Implications

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- Scientific Importance
  - New instruments allowed 1<sup>st</sup> field measurements of Nitryl Chloride
  - Emphasize importance of
    - Overnight recirculation of onshore emissions
    - Overnight transport of offshore emissions
    - Overnight reactions
    - NOx emissions from all sources
- Need more research to fully understand sea salt PM
  - More measurements both in Texas and elsewhere
  - Nitryl Chloride has the potential to form Ozone quickly
  - Does that extra Ozone actually form?



# Modeling Implications

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- Need detailed SIP quality modeling - Major project
  - Add the CINO<sub>2</sub> mechanism to CAMx & thoroughly test it
  - Need observations to validate revised mechanism
  - Model the extent & magnitude of the sea salt effect
  - Model the effect of proposed control strategies
- The effect of this chemistry may turn out to be small
- If we had a major problem, we already would know it



# Regulatory Implications

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- **Too early to base regulatory decisions on this research**
- **Effect of Sea Salt PM on Nitryl Chloride and ozone**
  - Better understanding of how known emissions form ozone
  - Does not imply new or under reported emissions
- **Using this chemistry, the CAMx model might**
  - Predict more ozone, by emphasizing
    - Overnight recirculation of onshore emissions
    - Direct reaction of onshore emissions
    - Overnight transport of offshore emissions
  - Predict little change – other factors may limit ozone production



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