IMPROVE Ion Study and Other IMPROVE Special Studies

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Western Resource Advocates
Outline

- The IMPROVE Ion/Nitrate Study
  - Motivation
  - Questions and approach
  - Findings and implications

- Other IMPROVE special studies
  - Yosemite smoke study
  - IMPROVE denuder tests
  - Coarse particle speciation
  - Mobile air quality lab
Ion Study

Motivation

- Nitrate is an important contributor to PM at many locations
- Nitrate may be present in fine or coarse modes
- Sampling methodology issues

\[ \text{HNO}_3(\text{g}) + \text{NH}_3(\text{g}) \leftrightarrow \text{NH}_4\text{NO}_3(\text{p}) \]

\[ \text{HNO}_3(\text{g}) + \text{NaCl}(\text{p}) \rightarrow \text{NaNO}_3(\text{p}) + \text{HCl}(\text{g}) \]

\[ 2 \text{HNO}_3(\text{g}) + \text{CaCO}_3(\text{p}) \rightarrow \text{Ca(NO}_3)_2(\text{p}) + \text{CO}_2 + \text{H}_2\text{O} \]
Nitrate in Big Bend

- High PM$_{2.5}$ nitrate associated with flow from Gulf
- Nitrate replaced chloride in sea salt aerosol
Nitrate in Big Bend

- Nitrate found in coarse mode particles
  - Mode size ~4-5 µm
  - Size distribution similar to Na⁺

- PM$_{2.5}$ includes tail of coarse mode
Yosemite results

- Carbon-dominated aerosol
- \((\text{NH}_4)_2\text{SO}_4\) dominant salt
- \(\text{NO}_3^-\) replaced \(\text{Cl}^-\) in sea salt

2-week excerpt, PILS 15-min data
IMPROVE ion special study goals

- Determine characteristics of ionic aerosol present at selected IMPROVE sites
  - Ionic composition
  - Ion size distributions
  - Gas-particle distribution of $\text{NH}_3(g)/\text{NH}_4^+(p)$ and $\text{HNO}_3(g)/\text{NO}_3^-(p)$

- Evaluate IMPROVE ion sampling and analysis approach
  - Combination of field and lab studies
  - Filter choice, filter extraction method, and denuder protocol
Ion study locations

- San Gorgonio
- Bondville
- Big Bend
- Yosemite
- Sequoia
- Brigantine
- Grand Canyon
Study equipment

- 24 hr URG PM$_{2.5}$ cyclone/annular denuder/filter pack sampler
- MOUDI impactor (10-stage)
- 15 min PM$_{2.5}$ PILS/IC system
  - Particle into Liquid Sampler
  - Ion Chromatograph
Bondville 2/03

- $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ both important
- $\text{NH}_4\text{NO}_3$ in submicron mode
San Gorgonio
4/03

- Large diurnal variability
- Submicron NH$_4$NO$_3$ dominant
San Gorgonio 7/03

- More regular diurnal variability
- Some days sulfate-dominated
- Nitrate in coarse mode
- Appears to be associated with Na\(^+\) and Ca\(^{2+}\)
Sampling and extraction issues

- Does water efficiently extract nitrate from nylon filters?
  - HNO₃ not efficiently recovered with water extraction
  - Typically use NaHCO₃/Na₂CO₃

- What happens to NH₄NO₃ volatilized from nylon filters?
  - HNO₃ trapped? Decrease in water extraction efficiency?
  - NH₃ lost? Bias in measured PM₂.₅ ammonium?
**NO$_3^-$ & NH$_4^+$ on nylon**

- Nylon filter extraction by water showed no bias in first three studies

- Significant NH$_4^+$ lost from nylon filter
  - Nylon recaptures volatilized NO$_3^-$
San Gorgonio July (latest results)

- ~ 25% of nitrate not extracted from nylon filter with water

$\text{NH}_4^+$ loss ~ 20-50%

\[ y = m^2 \times M_0 \]

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Yosemite special study

- July-September 2002
- Focus on smoke
- Aerosol dominated by OC

Study average PM$_{2.5}$ composition

- **POM** 73%
- **Black C** 2%
- **Soil** 6%
- **Ions** 19%
- **Oxalate** 1%
- **Na+** 1%
- **NH4+** 4%
- **K+** 0%
- **Mg2+** 0%
- **Ca2+** 0%
- **NO3-** 3%
- **NO2-** 0%
- **SO42-** 10%
- **Cl-** 0%
- **NO2-** 0%
- **SO42-** 10%
Yosemite special study

- Large changes in OC
  - EC remained small

- "Contemporary" carbon dominant
  - Wood smoke
  - Biogenic production

- Molecular markers indicate presence of wood smoke and secondary biogenic particles
  - Vehicle contribution appears small
Yosemite size distributions

- Size distributions measured with Differential Mobility Analyzer (DMA)
- Two submicron modes present during smoke period

08 Aug 2002 (DOY 220) 03:45 PST

“CLEAN”

16 Aug 2002 (DOY 228) 22:30 PST

SMOKE
Yosemite size distributions - II

- Aerosol Mass Scattering Efficiency
  - increases during smoky periods
Yosemite aerosol hygroscopicity

- Hygroscopicity of 100 and 200 nm particles measured with Hygroscopic Tandem Differential Mobility Analyzer (HTDMA)

- Smoke-dominated aerosol much less hygroscopic than “normal” Yosemite summer aerosol

Equation: $y = A1 \exp(-x/t1) + y0$

$\chi^2/\text{DoF} = 0.001$

$R^2 = 0.723$

$y0 \quad 1.102 \pm 0.007$

$A1 \quad 0.434 \pm 0.067$

$t1 \quad 1.386 \pm 0.201$
DIFFERENT denuder configurations tested
- No performance differences observed
- Lab tests planned at CSU
Coarse particle speciation (UC Davis)

- PM$_{10}$ speciation
- 9 sites
  - Bondville
  - Great Smokies
  - Grand Canyon
  - San Gorgonio
  - Sequoia
  - Brigantine
  - Upper Buffalo
  - Bridger
  - Mount Rainier

- Operational by 1/1/04
  - Several sites already operating
  - Overlap with ion study
- Will run for 1 year
New IMPROVE mobile air quality lab

- Mobile platform
  - Special study deployment
  - Some on-road measurement capabilities

- Measurement capabilities
  - Particle and trace gas composition
  - Aerosol size distributions
  - Particle hygroscopicity
  - Trace gases

Cargo Area: 96" x 102"
Summary

- Nitrate present in
  - Submicron ammonium nitrate particles
    - Bondville, IL
    - San Gorgonio, CA
  - Coarse mode sodium or calcium nitrate particles
    - Big Bend NP, TX
    - Yosemite NP, CA
    - Grand Canyon NP, AZ
- Nylon filter
  - DI water extraction may not always fully recover NO$_3^-$
  - Yields negatively biased NH$_4^+$ concentrations
- Yosemite aerosol dominated by modern carbon
  - Particles slightly hygroscopic
- HNO$_3$ denuder tests show little dependence on coating
- Coarse particle speciation study beginning
- Mobile lab being constructed for future special studies
IMPROVE ion study field campaigns

- 6 one-month campaigns
  - Bondville (midwest) - February 2003
  - San Gorgonio (southern CA) – April and July 2003
  - Grand Canyon – May 2003 (co-sponsored by LAWFR)
    - Brigantine (NE coastal) – November 2003
    - Sequoia (Sierra Nevada) – February 2004

- Measurements
  - MOUDI sampler – ion size distributions
  - 3 Parallel URG denuder/filter-pack samplers running different protocols
  - PILS sampler – 15 minute PM\(_{2.5}\) anions and cations
Mobile laboratory
Nitrate replacement

- NH$_4$NO$_3$ formation not favored thermodynamically in acidic aerosol
  - NH$_3$(g) will first neutralize sulfate
    - H$_2$SO$_4$ → NH$_4$HSO$_4$ → (NH$_4$)$_2$SO$_4$
- Once aerosol is neutralized, NH$_4$NO$_3$ formation may occur
  - f(T,RH)
- If SO$_4^{2-}$ is decreased, NO$_3^-$ may replace it
  - Two NO$_3^-$ replace each SO$_4^{2-}$
  - Sulfate reduction could produce PM mass increase

SO$_4^{2-}$ 98 g/mole

NO$_3^-$ 62 g/mole

NO$_3^-$ 62 g/mole
• Modules 1 and 2
  • Daily, 24 hr samples
  • Compare nylon filter extraction (H₂O vs. carbonate/bicarbonate)
  • Examine loss of HNO₃ and NH₃ from nylon filter
  • Provide gas-particle phase distribution for N(-III) and N(V)

• Module 3
  • Day/night sampling
  • Replicates for precision
  • Aerosol acidity/NH₄NO₃ volatilization
  • Undenuded sampling on Teflon filter
Initial findings

- Nylon filter extraction by water?
  - EPA study of fall filters collected at numerous STN and IMPROVE sites gave average 90% extraction efficiency
  - CSU Fort Collins samples (Spring 2002) yielded no evidence of lower water extraction efficiency

- Fate of volatilized NH$_4$NO$_3$?
  - EPA study indicated significant ammonia loss
IMPROVE sampling approach

- 4 modules
- Module B for PM$_{2.5}$ ions
  - Carbonate-coated denuder removes acidic gases
  - Nylon filter
    - Extracted with carbonate/bicarbonate solution (anion IC eluent) for anion analysis
    - Extracted with water for anion + cation analysis
      - Sodium interference from IC eluent
    - Analyzed by IC