Ion Analysis for the IMPROVE Program

IMPROVE Steering Committee Meeting

Mammoth Cave NP

September 26-28, 2006

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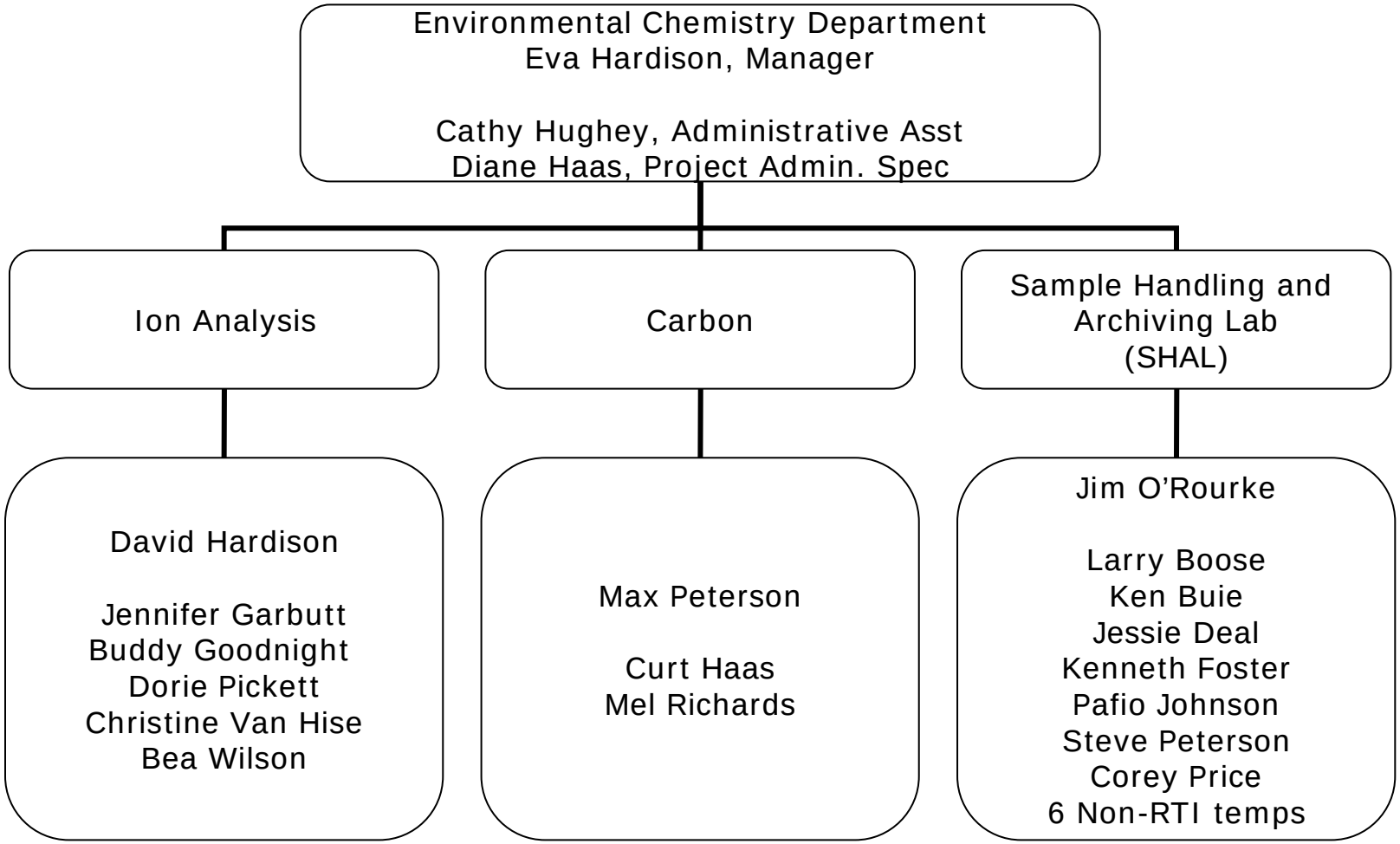
ECD Organizational Structure



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Environmental Chemistry Department Mission

Our mission is to provide air monitoring services and analytical data of the highest quality and in a timely manner:

- to our clients so they can make the best possible decisions about their programs.
- to policy makers so they can develop regulations needed to preserve our natural resources and our health.

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RTI's Analytical Support for IMPROVE 1985-Present

- 1985 – 1990: Ions and SO_2
- 1990 – 1995: SO_2
- 1995 – Present w/option yrs thru 2011: Ions, SO_2, and Passive Ozone (3 contracts)

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Ion Analysis Laboratory Overview

- Professional staff degreed in chemistry and biology
- Stable and experienced workforce
- Strong spirit of teamwork recognized by clients
- State-of-the-art instrumentation and facilities: 10 Dionex ion chromatographs; Lachat Flow Injection Analyzer (newly acquired to enhance the capabilities for the Ogawa passive sampling/analysis program)

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Ion Analysis Team

L to R: Buddy Goodnight, Bea Wilson, David Hardison, Jennifer Garbutt, Eva Hardison, Dorie Pickett, Christine Van Hise

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Ion and Passive Ozone Analyses of IMPROVE Filters

RTI provides the following services:

1. Analysis and reporting of anion loadings (Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}) on nylon filters from the IMPROVE network (~22,000 filters/yr) and of cation loadings (NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) for special studies.
2. Preparation of impregnated filters for SO_2 sampling, and analysis and reporting of sulfate mass (~250 filters/yr)
3. Loading and shipping of passive samplers for ozone, analysis of exposed collection pads, and reporting of nitrate ion loadings for calculation of average weekly ozone concentrations (~1200 samples/ozone season)

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Nylon Filter Receipt

- RTI receives filters from the PMCC in batches of 400 every 7-10 days.
- Electronic files provided by the PMCC are used to prepare labels for sample vials and to prepare autosampler queues.
- Filters are stored in a freezer in a locked sample custody room until they are extracted.

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Nylon Filter Extraction

- Using tweezers, each filter is placed in a disposable centrifuge tube that has been labeled with the sample ID.
- 20.0 mL of DI H_2O is added using a calibrated electronic pipette.
- Tubes are placed in a rack and into an ultrasonic bath, sonicated for 30 minutes, and allowed to sit one night at RT and another night in the refrigerator prior to analysis.

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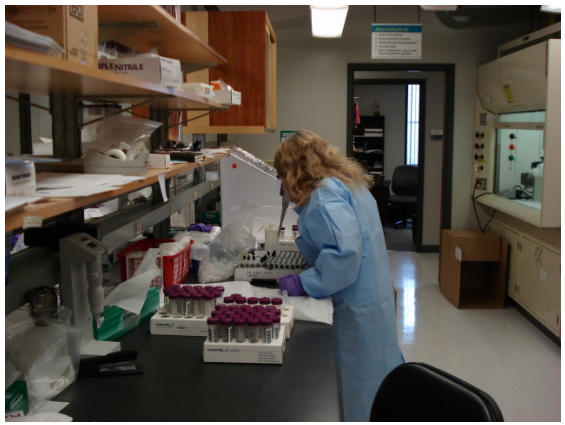
Analysis of Filter Extracts

- Autosampler vials are loaded according to the queues prepared from the e-files.
- Vials are loaded into the autosampler.
- Chromatograms, including those for QA/QC samples, are monitored to insure that the ICs are operating properly.
- Extracts are analyzed for Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}



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Anion Analysis Queue

- Full calibration each day of analysis
- Calibration checked with QA samples at various concentrations
- ~5% duplicate injections and ~5% spiked extracts

Sample Set: R24 - DAY 1 Date:

Directory: IC Model No.:

Method Name: Column:

Comments:

Sample ID	C	P	I	Comments
BLANK 1	1	1	1	
BLANK 2	1	2	2	
AUTOCAL 1R	1	3	3	0.01 ppm Cl; 0.05 ppm NO2, NO3, SO4
AUTOCAL 1A	1	4	4	0.01 ppm Cl; 0.05 ppm NO2, NO3, SO4
AUTOCAL 2R	1	5	5	0.02 ppm Cl; 0.1 ppm NO2, NO3, SO4
AUTOCAL 2A	1	6	6	0.02 ppm Cl; 0.1 ppm NO2, NO3, SO4
AUTOCAL 3R	2	1	7	0.04 ppm Cl; 0.2 ppm NO2, NO3, SO4
AUTOCAL 4R	2	2	8	0.1 ppm Cl; 0.5 ppm NO2, NO3, SO4
AUTOCAL 5R	2	3	9	0.2 ppm Cl; 1.0 ppm NO2, NO3, SO4
AUTOCAL 6R	2	4	10	0.6 ppm Cl; 3.0 ppm NO2, NO3, SO4
AUTOCAL 7R	2	5	11	2.0 ppm Cl; 10.0 ppm NO2, NO3, SO4
AUTOCAL 8R	2	6	12	5.0 ppm Cl; 25.0 ppm NO2, NO3, SO4
QA-MED	3	1	1	0.5 ppm Cl; 1.0 ppm NO2, 1.5 ppm NO3, 3.0 ppm SO4
QA-LOW	3	2	2	0.2 ppm Cl; 0.4 ppm NO2, 0.6 ppm NO3, 1.2 ppm SO4
QA-CPI_LOW	3	3	3	0.2 ppm Cl; 0.4 ppm NO2, 0.6 ppm NO3, 1.2 ppm SO4
PRIS1 7/19/06	3	4	4	
PRIS1 7/22/06	3	5	5	
PRIS1 7/25/06	3	6	6	
PRIS1 7/28/06	4	1	7	
PRIS1 7/31/06	4	2	8	
QUVA1 7/13/06	4	3	9	
QUVA1 7/16/06	4	4	10	
QUVA1 7/19/06	4	5	11	
QUVA1 7/19/06 DUP	4	6	12	
QUVA1 7/22/06	5	1	13	
QUVA1 7/25/06	5	2	14	
QA-HIGH	5	3	15	2.0 ppm Cl; 4.0 ppm NO2, 6.0 ppm NO3, 12.0 ppm SO4
QUVA1 7/28/06	5	4	16	

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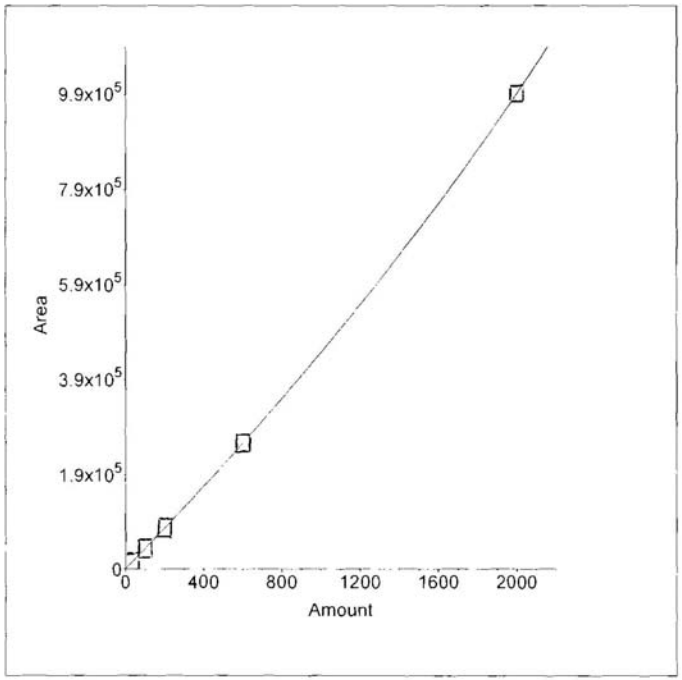
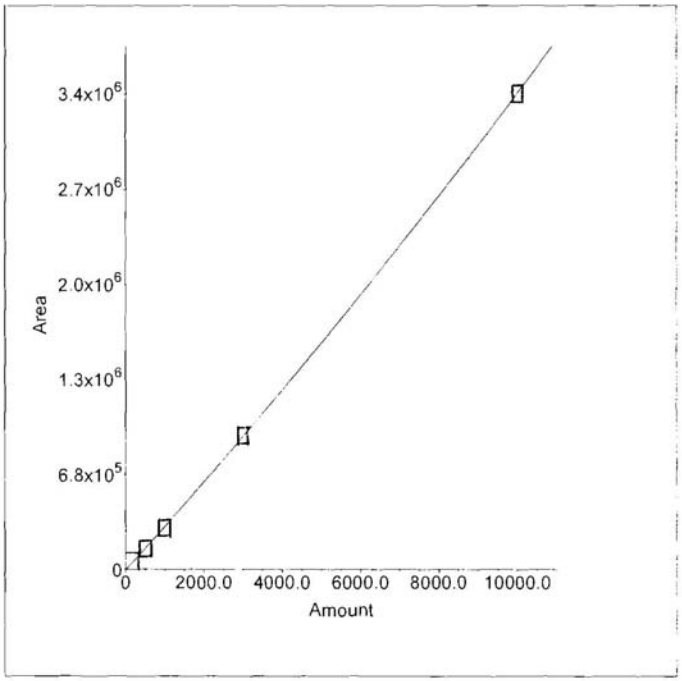
Cl^- and NO_2^- Calibration Data

1. Component:CHLORIDE
Standard:External Fit Type:Quadratic
Origin:Ignore Calibration:Area
r^2=0.999999
Amt=-3.593840e-010*Resp^2+
2.369085e-003*Resp+-1.034

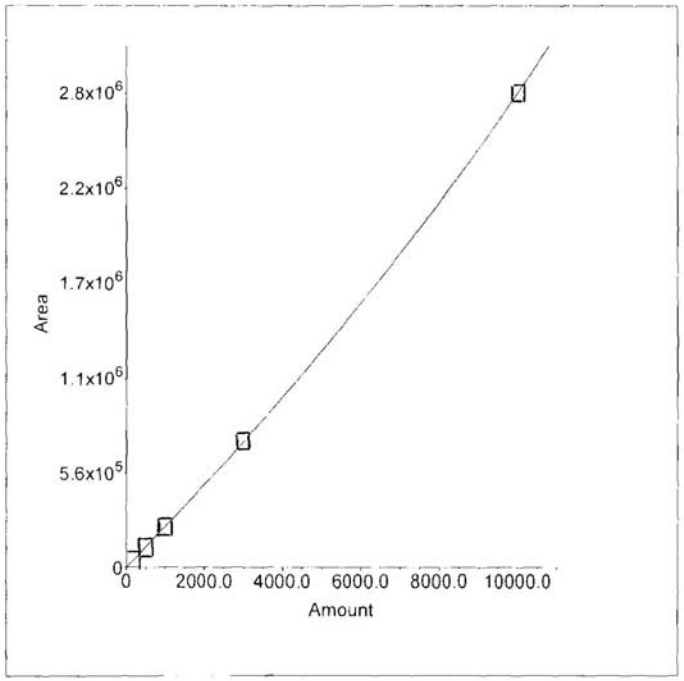


2. Component:NITRITE
Standard:External Fit Type:Quadratic
Origin:Ignore Calibration:Area
r^2=0.999985
Amt=-7.950817e-011*Resp^2+
3.200461e-003*Resp+21.4

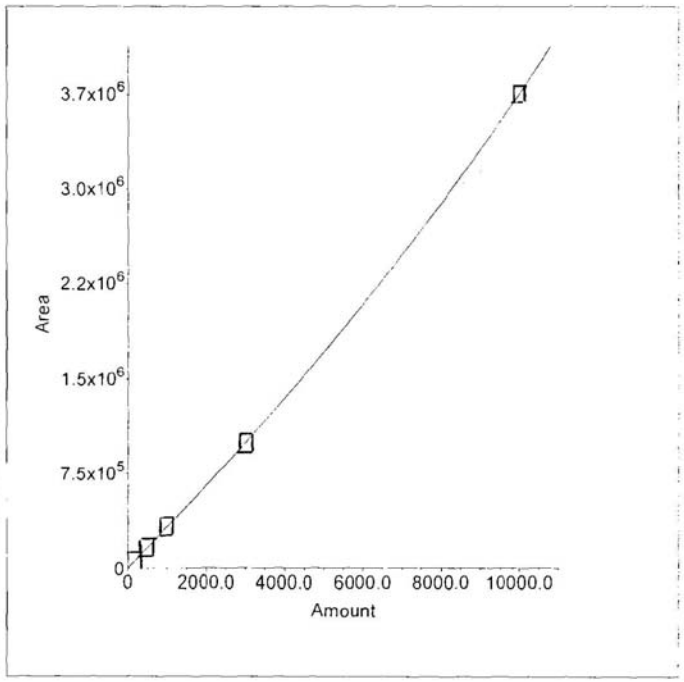


NO_3^- and SO_4^{2-} Calibration Data

3. Component:NITRATE
Standard:External Fit Type:Quadratic
Origin:Ignore Calibration:Area
r^2=0.999998
Amt=-2.138297e-010*Resp^2+
4.121447e-003*Resp+8.016



4. Component:SULFATE
Standard:External Fit Type:Quadratic
Origin:Ignore Calibration:Area
r^2=0.999999
Amt=-1.252508e-010*Resp^2+
3.122605e-003*Resp+4.179



Ion Chromatography Detection Limits

Ion	Extract MDL, µg/mL	Filter MDL*, µg
Cl^-	0.002	0.04
NO_2^-	0.002	0.03
NO_3^-	0.004	0.09
SO_4^{2-}	0.007	0.14

* Extraction volume = 20 mL

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Anion Recoveries – QA/QC Samples A06 Quarter (March-May 2006)

	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
Average	99.5%	97.9%	100.0%	100.7%
Maximum	113.8%	105.0%	104.7%	105.2%
Minimum	93.6%	94.1%	96.7%	96.5%
N	620	620	620	620

Recovery, % = (analyzed conc/calculated conc) X 100

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Anion Recoveries – Spiked Extracts A06 Quarter (March-May 2006)

	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
Average	101.1%	98.2%	101.2%	101.3%
Maximum	108.3%	106.7%	109.0%	107.9%
Minimum	96.4%	91.5%	93.3%	94.5%
N	181	181	181	181

Recovery, % = (analyzed conc/calculated conc) X 100

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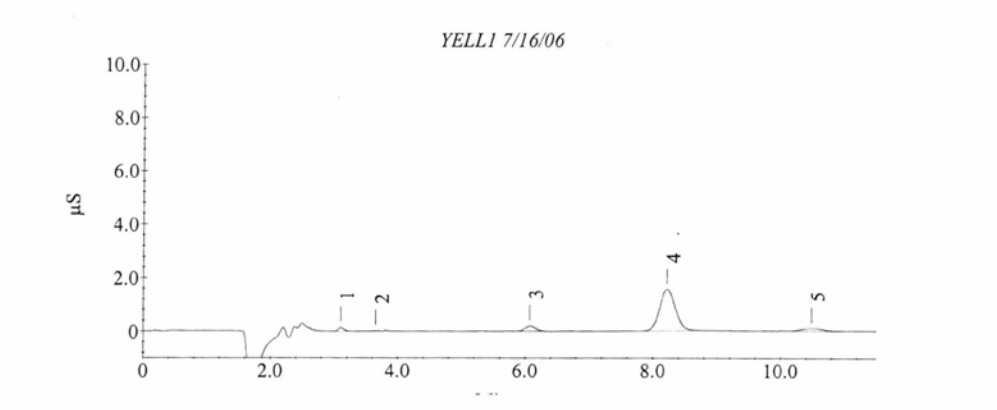
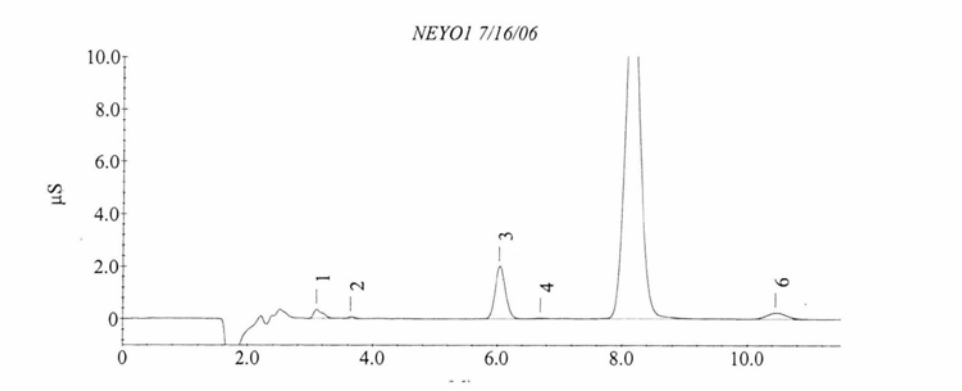
IMPROVE Anions: Rural vs. Urban

- Pk1: Cl^-, 0.431 µg
- Pk2: NO_2^-, 0.584 ug
- Pk3: NO_3^-, 2.043 ug
- Pk4: $SO_4^=$, 16.685 ug



- Pk1: Cl^-, 1.569 µg
- Pk2: NO_2^-, 0.777 ug
- Pk3: NO_3^-, 18.985 ug
- Pk5: $SO_4^=$, 122.112 ug



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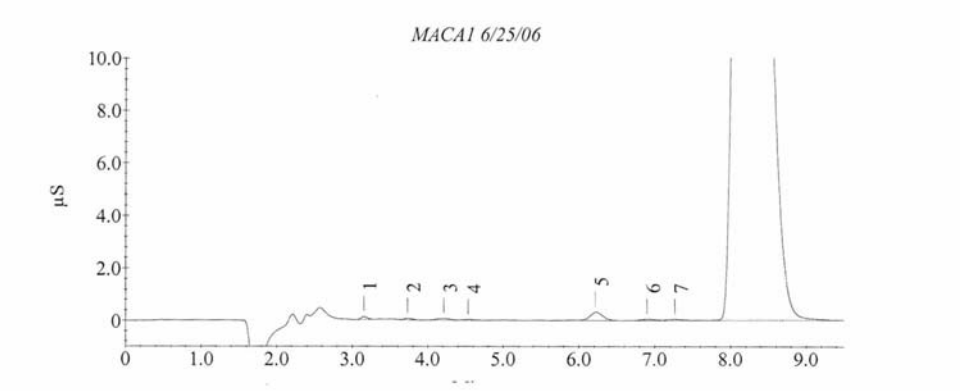
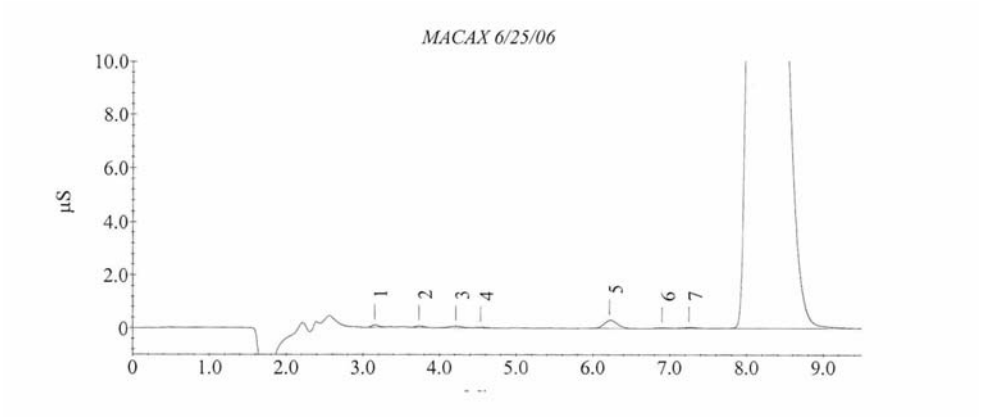
MACA Anions

- Pk1: Cl^-, 0.308 µg
- Pk2: NO_2^-, 0.705 ug
- Pk5: NO_3^-, 3.303 ug
- Pk8: $SO_4^=$, 670.302 ug



- Pk1: Cl^-, .253 µg
- Pk2: NO_2^-, 0.727 ug
- Pk5: NO_3^-, 3.226 ug
- Pk8: $SO_4^=$, 662.516 ug



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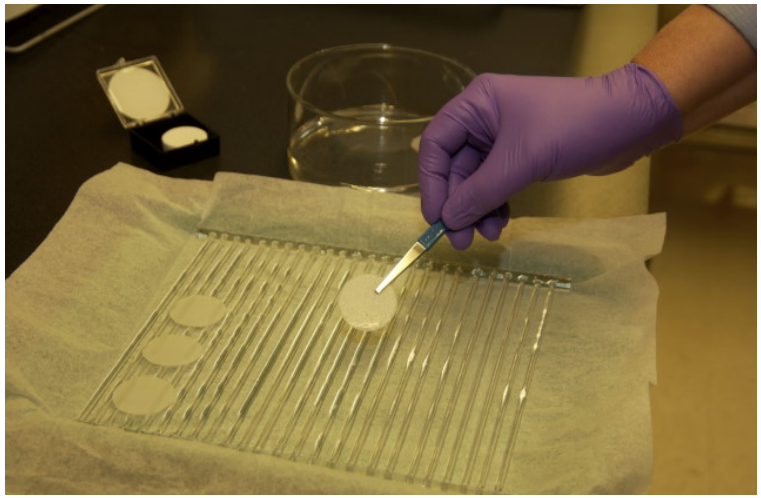
Quartz Filter Prep for SO_2 Collection

- 37-mm quartz fiber filters are purchased (Pallflex No. 3700 QAT-UP).
- Filters are coated with a K_2CO_3/glycerol solution.
- Filters are dried under vacuum at 60°C for 30 min or until dry.



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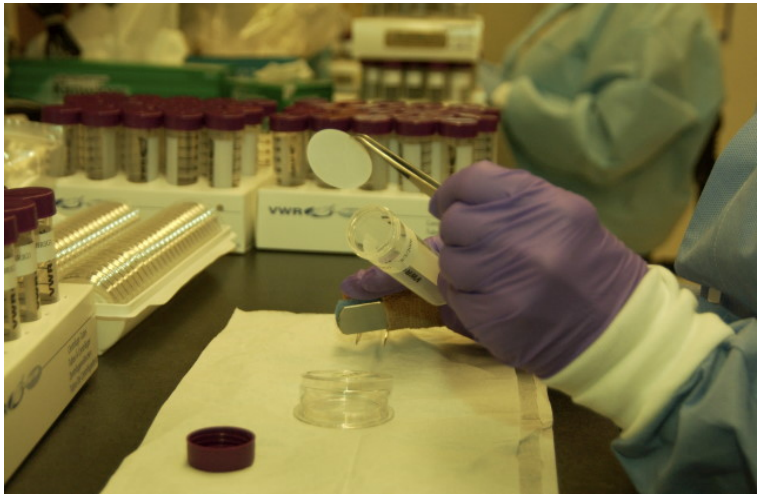
SO2 Filter Extraction

- Using tweezers, each filter is placed in a disposable centrifuge tube that has been labeled with the sample ID.
- 20.0 mL of 0.1% H_2O_2 is added using a calibrated electronic pipette.
- Tubes are placed in a rack and into an ultrasonic bath, sonicated for 30 minutes, and allowed to sit one night at RT and another night in the refrigerator prior to analysis.



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SO_2 Analysis Queue

- Full calibration each day of analysis
- Calibration checked with QA samples at various concentrations
- ~5% duplicate injections and ~5% spiked extracts

Sample Set: X7 - DAY 1 SO2 Date:

Directory: IC Model No.:

Method Name: Column:

Comments:

Sample ID	C	P	I	Comments
BLANK 1	1	1	1	
BLANK 2	1	2	2	
AUTOCAL 1R	1	3	3	0.05 ppm NO3, SO4
AUTOCAL 1A	1	4	4	0.05 ppm NO3, SO4
AUTOCAL 2R	1	5	5	0.1 ppm NO3, SO4
AUTOCAL 2A	1	6	6	0.1 ppm NO3, SO4
AUTOCAL 3R	2	1	7	0.2 ppm NO3, SO4
AUTOCAL 4R	2	2	8	0.5 ppm NO3, SO4
AUTOCAL 5R	2	3	9	1.0 ppm NO3, SO4
AUTOCAL 6R	2	4	10	3.0 ppm NO3, SO4
AUTOCAL 7R	2	5	11	10.0 ppm NO3, SO4
AUTOCAL 8R	2	6	12	25.0 ppm NO3, SO4
QA-MED	3	1	1	1.5 ppm NO3, 3.0 ppm SO4
QA-LOW	3	2	2	0.6 ppm NO3, 1.2 ppm SO4
QA-CPI_LOW	3	3	3	0.6 ppm NO3, 1.2 ppm SO4
HANCS 9/1/05	3	4	4	All Samples diluted 1ml sample + 4 ml DI H2O
HANCS 9/4/05	3	5	5	
HANCS 9/7/05	3	6	6	
HANCS 9/10/05	4	1	7	
HANCS 9/13/05	4	2	8	
HANCS 9/16/05	4	3	9	
HANCS 9/19/05	4	4	10	
HANCS 9/22/05	4	5	11	
HANCS 9/22/05 DUP	4	6	12	

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SO_4^{2-} Recoveries – Spiked Extracts of SO_2 Filters A05-C05 Quarters (March-November 2005)

	SO_4^{2-}
Average	100.2%
Maximum	101.8%
Minimum	99.3%
N	3

Recovery, % = (analyzed conc/calculated conc) X 100

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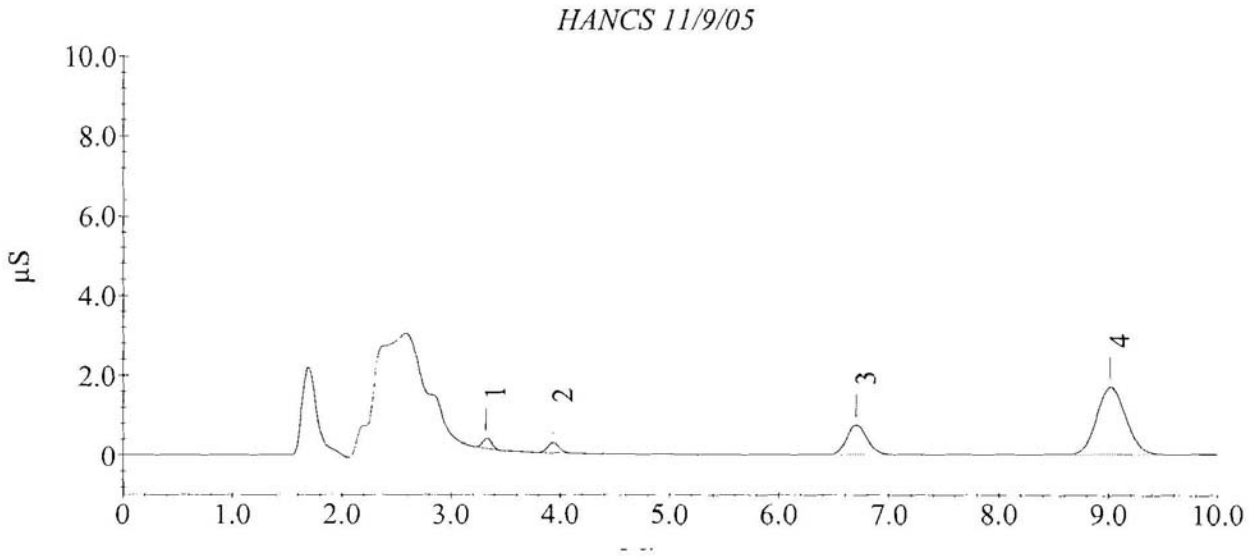
HANCS SO2

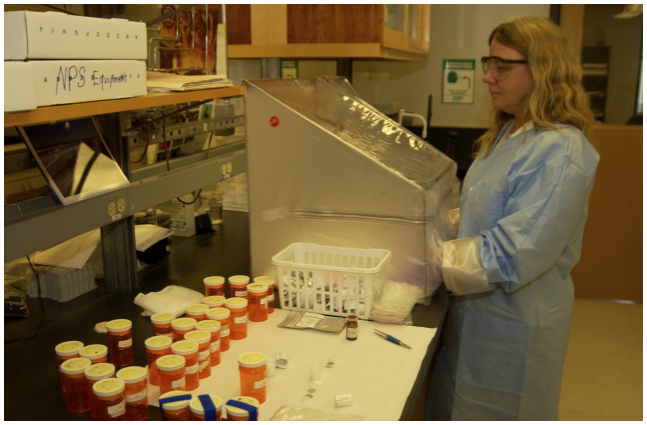


Pk4: $SO_4^{=}$, 100.138 µg/filter

(Extract diluted 5-fold)

Summer Passive Ozone Studies

- May thru September
- Ozone collection pads purchased from Ogawa
- Passive samplers loaded and shipped to individual parks each month



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Passive Sample Collection

- Samplers are deployed on sample poles under rainshields
- Samplers are exposed for 1 week
- Start/stop dates and times recorded on Sampler Report

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National Park Service

Air Resources Division

Sampler Report

Passive Ozone Sampler Program

2004

Park Code: _____ **Site name & number** _____ **Operator Name:** _____

Please fill out the sampler record and return with the exposed samplers at the end of the month. Thanks.

Week of the month	Date of start	Time of start	Date of stop	Time of stop	Sampler Code Number
	MMM / DD	HH : MM	MMM / DD	HH : MM	
1					
2					
3					
4					
5					

(Note: Use 24-hour clock and local standard time)

SAMPLING NOTES: _____

_____

_____

Form No. NPS/AQD-FSS-4 2004STUDY SITEFORM.DOC

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Ozone Sample Recovery

- Samplers are returned to RTI using a prepaid label.
- Each sampler is unloaded in a glove box and the 2 collection pads are placed in a clean 8-mL HDPE bottle for extraction in 5 mL DI H_2O.

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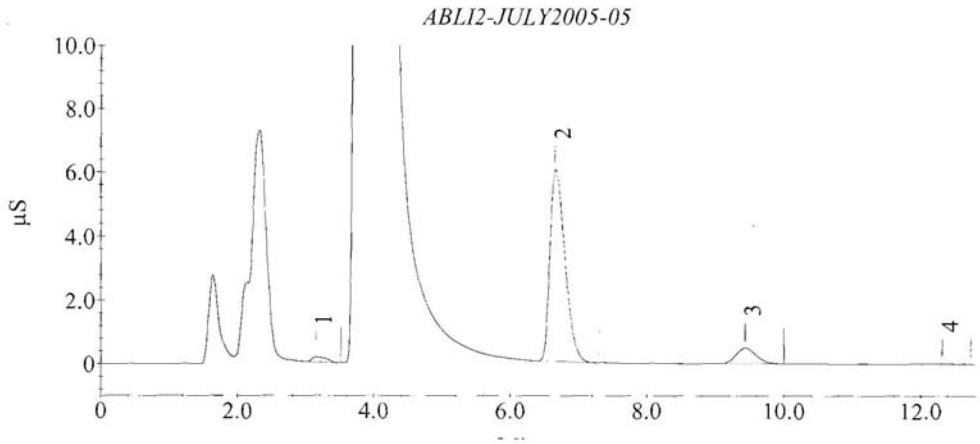
Cumberland –Piedmont 2005 Study



- Pk2: NO_3^-, 20.282 µg/sample (28.8 ppb ozone in air)
- Large peak at ~4 min: NO_2^- from collection pad coating

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Future Directions

- Build upon work with long-term clients
  - Explore the possibilities for unsolicited proposals to the NPS (modeling, etc.)
  - Become more involved with the NPS IMPROVE Steering Committee
  - Continue to develop our capabilities for analysis of IMPROVE samples to accommodate changes in the EPA PM2.5 contract
  - Investigate gas-phase ammonia, especially in in agricultural areas, for the PM2.5 network
  - Data “mining” for PM2.5 (SVDAT tool)

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Future Directions (continued)

- Promote the use of passive sampling
  - Developing and under-developed countries
  - Health studies
- Develop new capabilities for ions in water

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