$PM_{2.5}$ Chemical Speciation Network and Its Challenges

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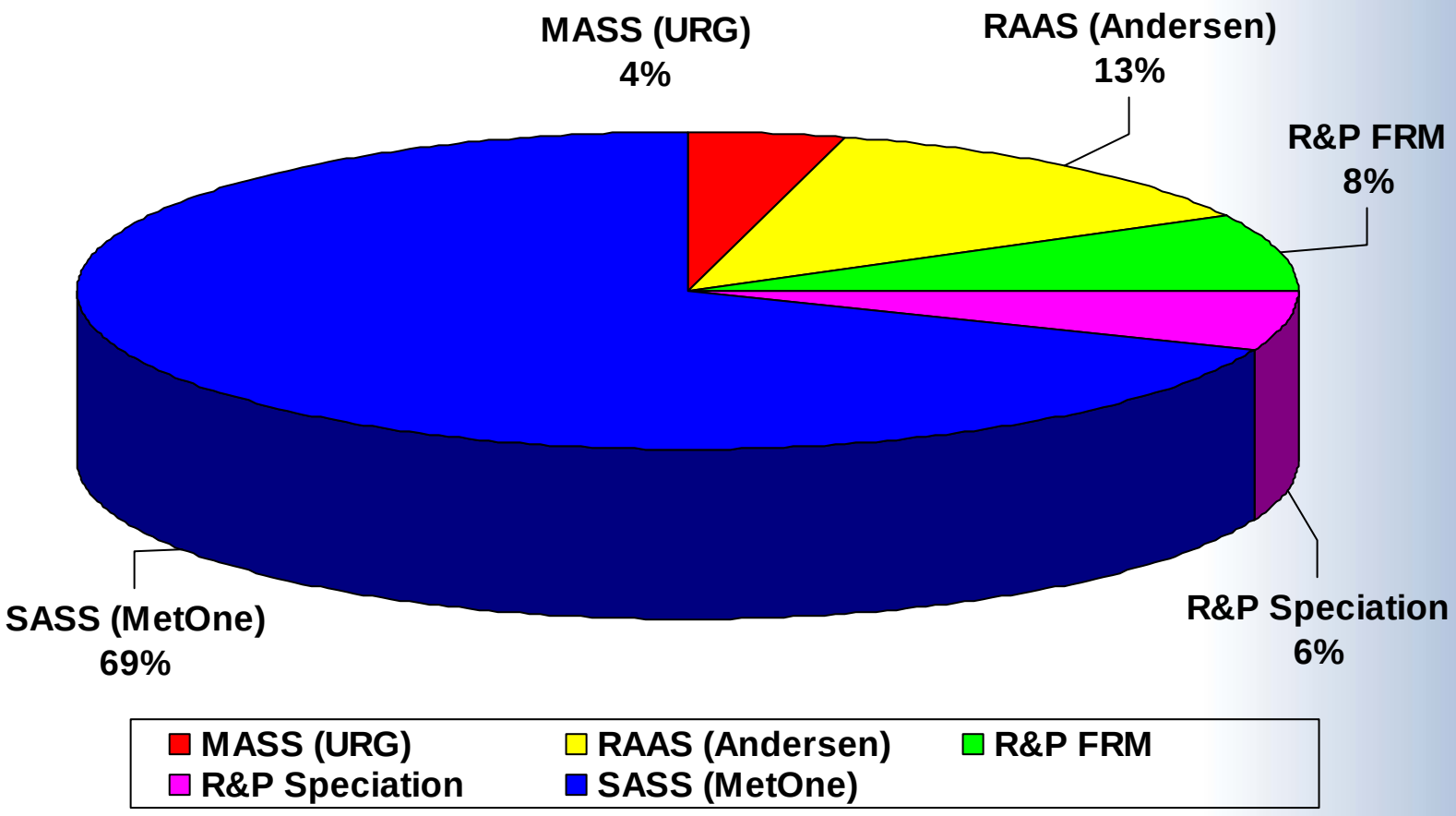
Introduction

- On July 8, 1997, the U.S. Environmental Protection Agency (EPA) promulgated the new national ambient air quality standard (NAAQS) for particulate matter with aerodynamic diameters less than 2.5 μm.
- Today, over 1,000 $PM_{2.5}$ Federal Reference Method (FRM) monitors are operating nationwide to obtain the particulate mass.
- The States, National Academy of Sciences, and scientific community felt that data on the chemical composition of $PM_{2.5}$ would help identify links between observed health effects and $PM_{2.5}$ chemical components.
- EPA decided to establish 250 $PM_{2.5}$ chemical speciation monitoring sites throughout the country.
- In July 1999, EPA implemented a chemical speciation laboratory support contract with RTI to obtain consistent analytical data.

Objectives

- The purpose of the "Chemical Speciation of $PM_{2.5}$ Filters Samples" contract is to provide filter media and analytical support that will help EPA, State, and local agencies operate speciation monitoring network.
- "Analytical support" includes:
  - Analyze sampler filters for mass, selected elements, organic and elemental carbon, anions, and cations.
  - Validate and report analytical data to State agencies on a monthly basis for approval.
  - Enter approved data into EPA's Aerometric Information Retrieval System (AIRS).

Sampler Types and Number in the $PM_{2.5}$ Network



Filter Types and Target Analytes

Filter Type	Target Analytes
Teflon (PTFE)	Gravimetric mass, 48 elements (sodium through lead)
Nylon	Sulfate, nitrate, ammonium, sodium, potassium*
Quartz	Organic, elemental, and carbonate carbon

*In some cases, Teflon filters were used.

Overview of Laboratory Activities

Monitoring site requests laboratory services

Information is entered into RTI's lab database management system (sampler model, site location, sampling schedule, etc.)

Gravimetric Mass Lab	Cations/Anions Lab	OC/EC Lab	Denuder Refurbishment Lab
Provides pre-weighed Teflon filters	Provides cleaned nylon filters	Provides cleaned quartz filters	Provides refurbished denuders

Sample Handling and Archiving Lab (SHAL)
Receives filters/denuders and cleans sampling modules

SHAL assembles modules, packs them into coolers, and ships them overnight

Overview, continued

SHAL personnel receive and unpack coolers, distribute filters for analysis, and enter field sampling data into database

Gravimetric Mass Lab
Post-weighs Teflon filters

XRF Lab.
Measures 48 elements

Cations/Anions Lab
Extracts nylon filters and measures ions

OC/EC Lab
Measures OC/EC and carbonate carbon on quartz filters

Denuder Refurbishment Lab
Refurbishes denuders, if necessary

SHAL
Cleans returned modules and prepares for next sampling event

SHAL archives returned filters and extracts for six months

Analysis lab personnel submit measured values to database

Lab, SHAL, and QA/QC perform validation checks on both field and lab data

Database personnel generate reports and submit to data recipients

Validated data are uploaded into AIRS

Challenges in the Program

- Sample Handling and Archiving Laboratory (SHAL) operations.
- Sampling schedules in the Speciation Network.
- High gravimetric mass blanks (Delrin rings, Kimwipes).
- Elemental analysis (sulfur/sulfate ratio).
- Ion analysis (nylon filter contamination, extraction procedures).
- Organic/elemental carbon (carbon blanks).
- Data validation.
- Data reporting.

SHAL Operations

Receive new sampling modules and denuders from monitoring site

Inventory sample modules and denuders in database

Schedule sampling events

Install new filters into cleaned modules

Ship filters to site for sampling

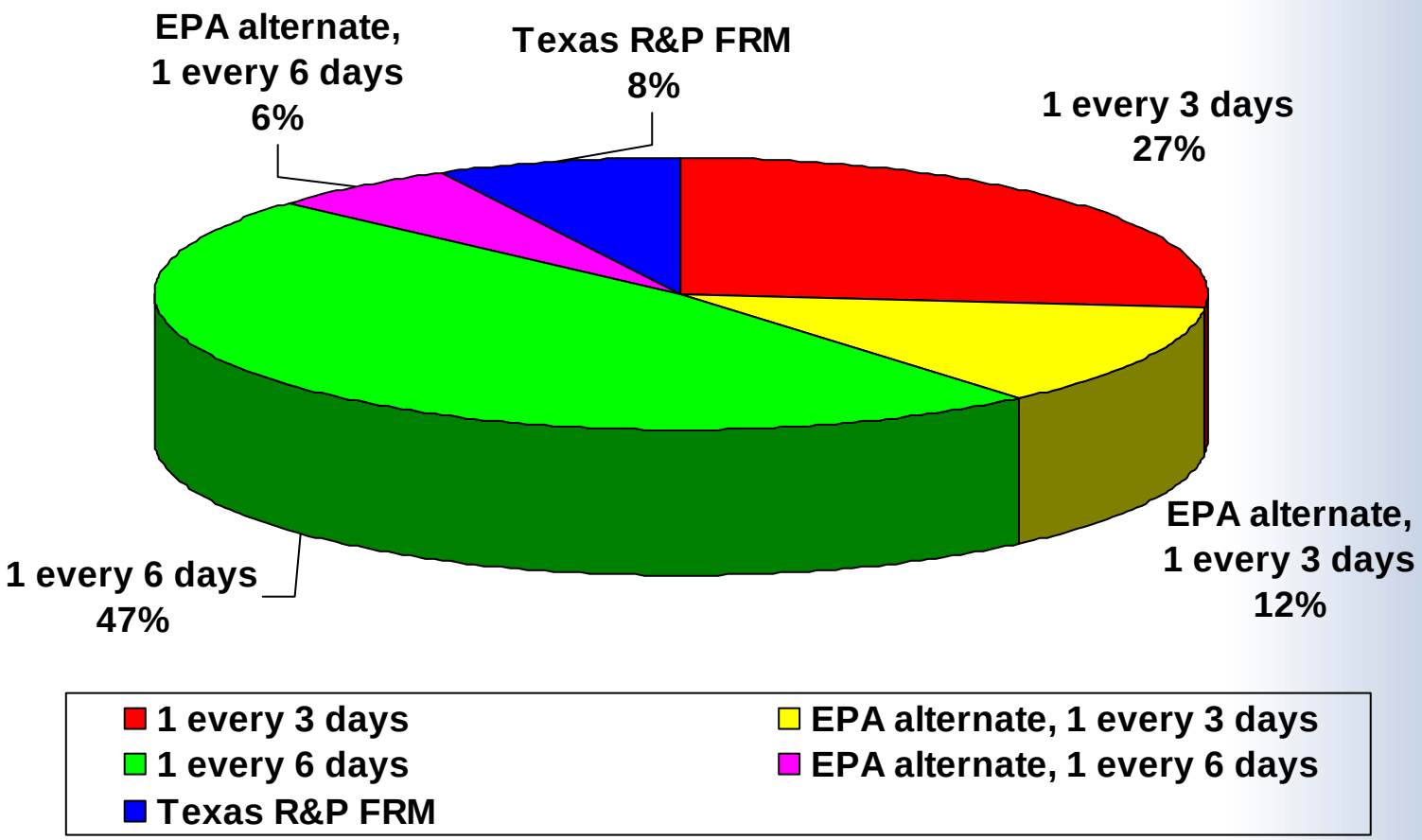
Receive sampled filters back from site

Remove sampled filters from modules and send to analytical labs

Process Field Sampling Chain of Custody form and Level 0 validation

Archive filters and forms

Sampling Schedules in the Speciation Network



Gravimetric Mass

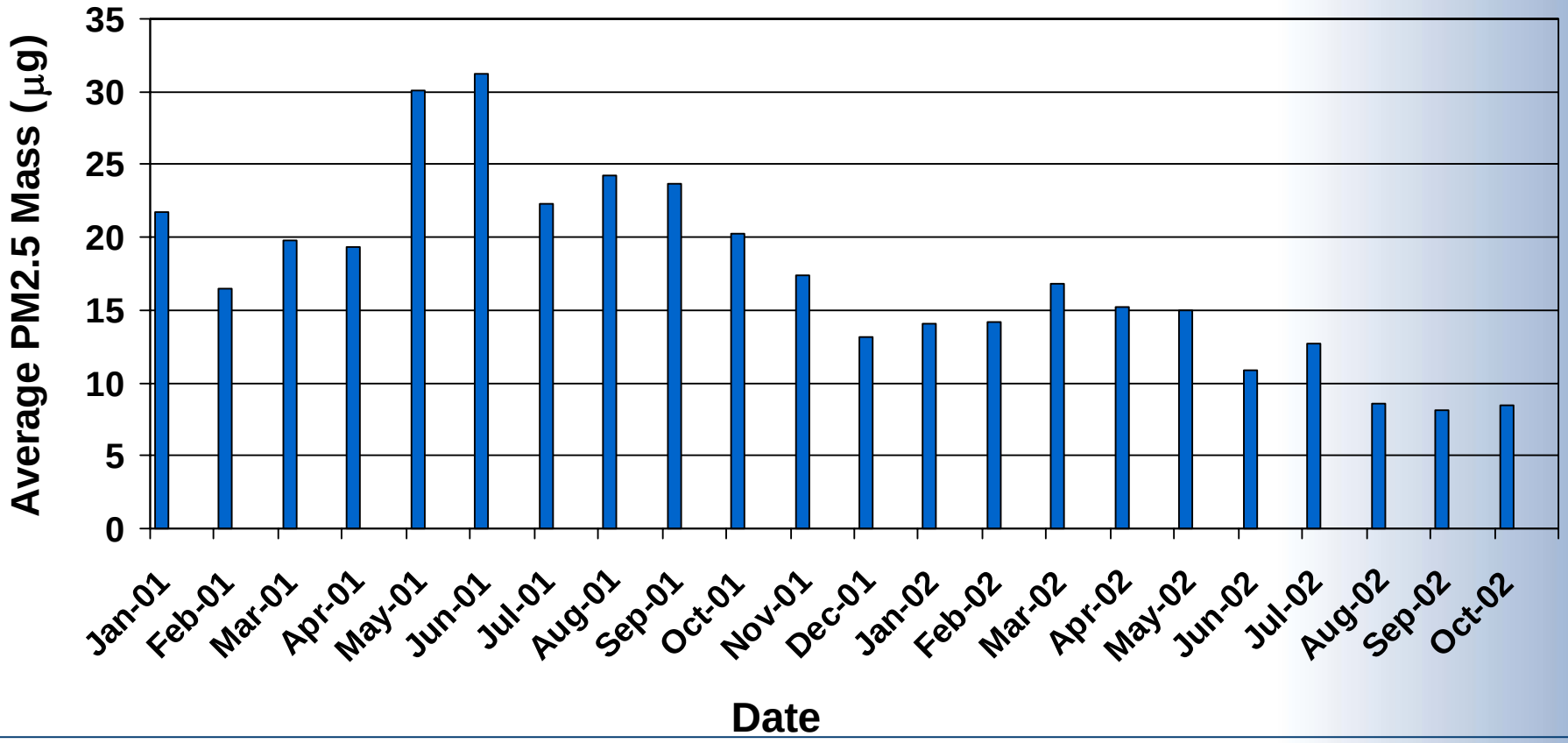
- Teflon filters received from the manufacturer are checked for defects and conditioned in a weighing chamber.
- Weighing is performed with a microbalance having a readability of $\leq 1\ \mu g$.
- Laboratory quality checks include lot stability checks, and trip and field blanks.

Trip and Field Blank Masses

- The average trip and field blank masses were ~30 μg during January through July 2001 (~20% contribution to the actual mass).
- No blank corrections are applied in the program at this time.
- Reasons for high mass blanks were investigated.

Average Trip and Field Blank Masses

(includes all sampler types)



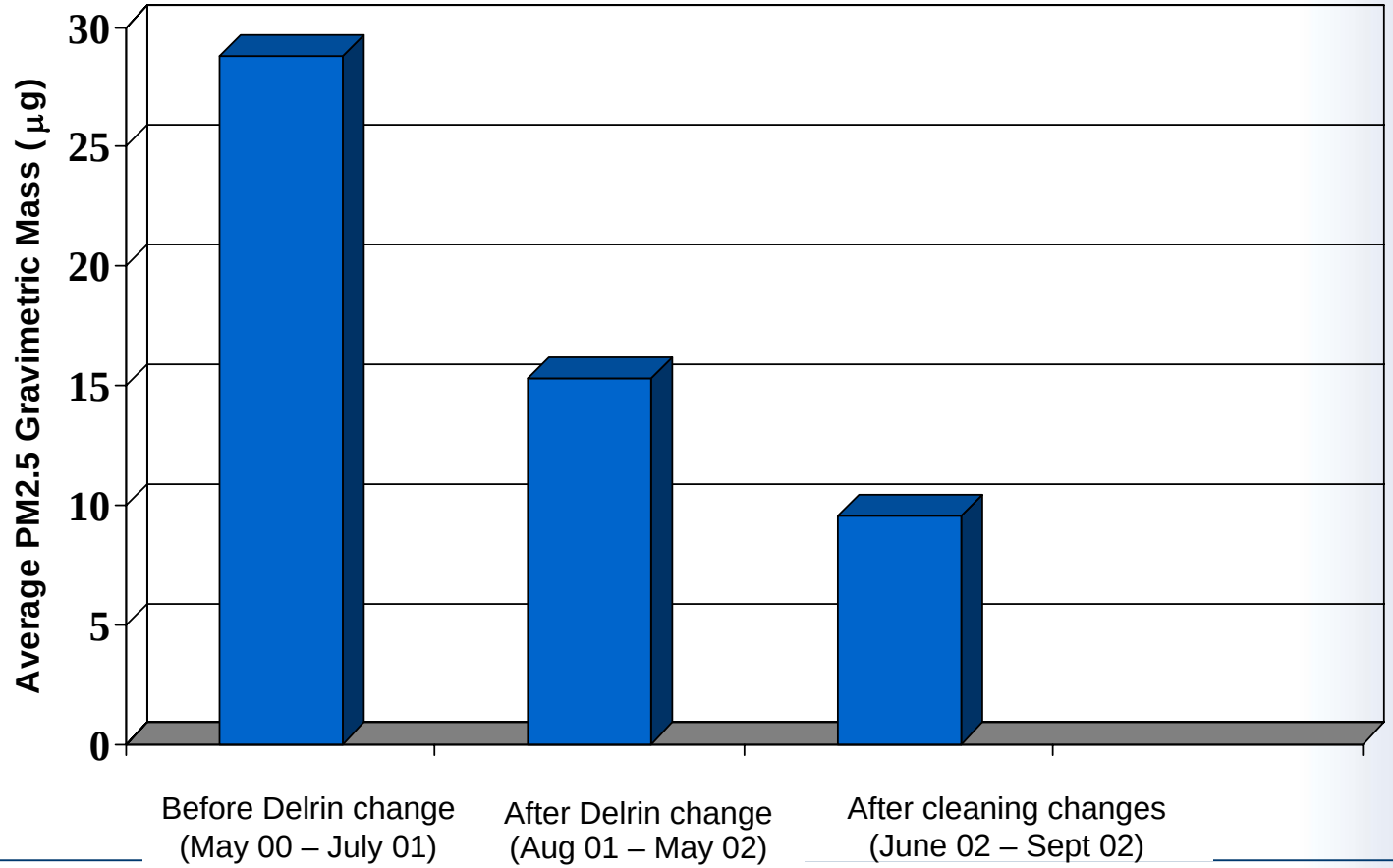
Delrin Rings and Kimwipe Contamination

- Oily materials was observed on a number of Teflon filters.
- This contamination was traced to cassette filter holder rings made of Delrin, a plastic based on polyformaldehyde.
- Heating experiments determined the extent of transfer of materials from the Delrin cassette to the Teflon filter.
- RTI results were confirmed by the U.S. EPA/Montgomery Quality Assurance Laboratory.
- The Delrin filter holder rings in the MetOne sampler (Teflon filter holder only) were replaced with blue rings.
- Kimwipes and plastic trays were eliminated during cleaning of filter holders to further reduce the $PM_{2.5}$ mass blanks.

Teflon Filter Contaminated by Delrin

Met One Module showing Blue and Delrin Rings

Effects of Delrin Rings and Cleaning Procedures on MetOne Samplers
(Includes all trip and field blanks)



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Elemental Analysis

- The method of choice for the determination of 48 elements (sodium through lead) collected on $PM_{2.5}$ filter samples is energy dispersive x-ray fluorescence (XRF).
- The detection limit achieved varies with each element (0.04 to 0.40 μg/filter).
- This analysis method is nondestructive.

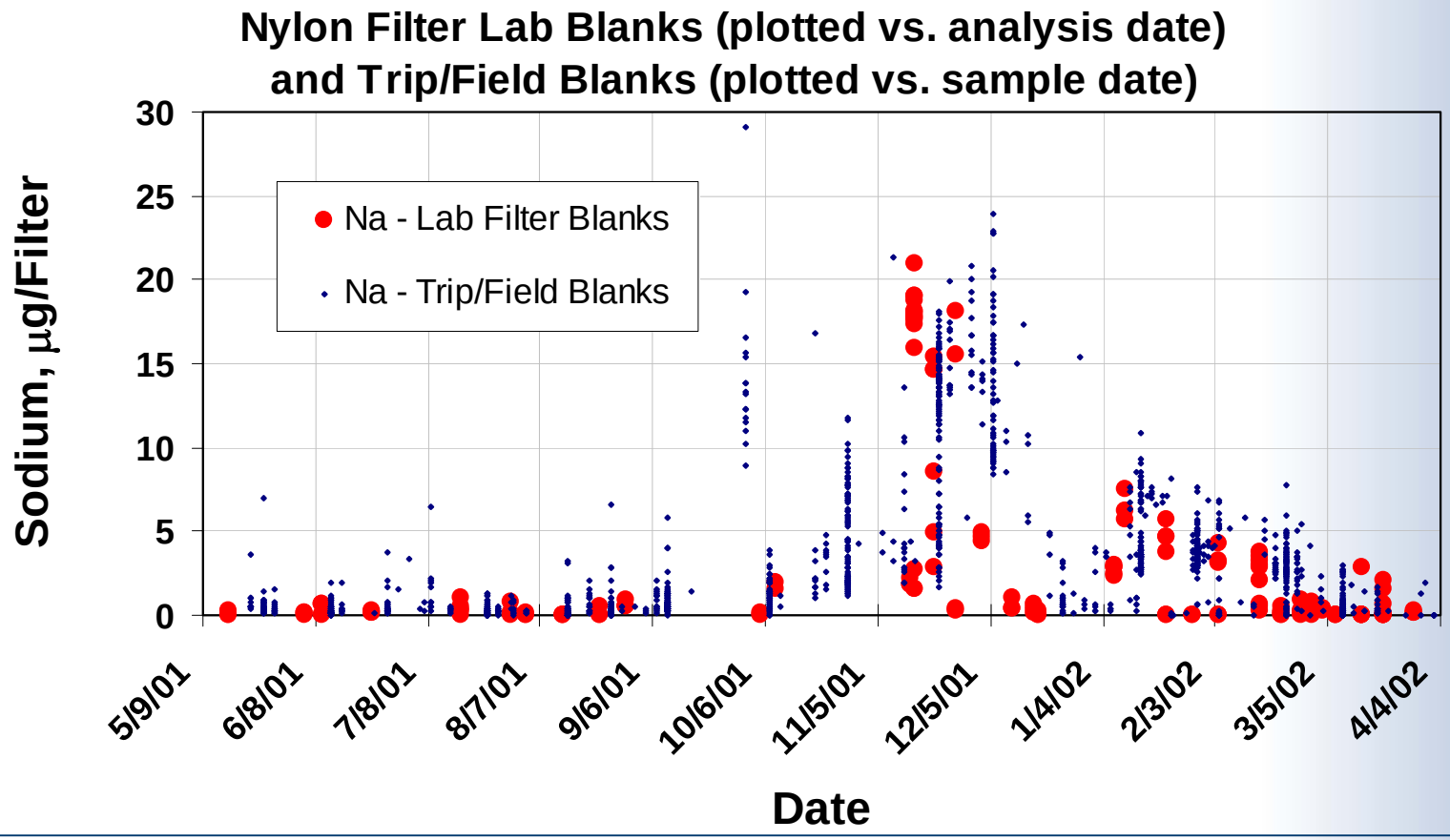
XRF Calibration Problems

- Problems were discovered in September 2002 through excessive number of outliers for sulfur/sulfate ratio check.
- One instrument had drifted about 20% for sulfur.
- The laboratory was notified and all XRF data for the drifting instrument were corrected before data were reported.
- A reference standard for sulfur is now being analyzed weekly.

Ion Analysis

- Water-extractable ions are measured using ion-chromatography.
- The detection limits are low (~0.1 μg/filter).
- Nylon filter blank contamination (sodium and sulfate) is a potential problem; filters must be cleaned before use.
- Nylon filter-cleaning procedures are tedious and time consuming.

Nylon Filter Lab Blanks for Sodium



Nylon Filter-Cleaning Procedures

- Developed a working nylon filter-cleaning procedure before September 2001.
- Recently, a more rigorous procedures was established by rotating the poly bottle with 50 filters in a TCLP apparatus.

TCLP Washing Apparatus

Organic/Elemental Carbon

- Organic, elemental, carbonate, and total carbon in $PM_{2.5}$ are determined by thermal optical analysis based on NIOSH Method 5040.
- Batches of quartz fiber filters (typically 100 filters per batch) are cleaned by heating them in a muffle furnace at 900 °C for at least 3 hours.
- Two percent of filters from a batch are blank-checked.
- The acceptance criteria for total carbon is <1 $\mu g/cm^2$ per filter.
- Ongoing issues include:
  - Filter contamination by ambient volatile organic compounds (VOCs), and
  - Definition of the split point between organic and elemental carbon.

Data Validation

Type	Validation Check
Field data checks	Total volume, elapsed time, operator observations, and validation flags from sampler.
Outlier tests based on prescribed acceptance ranges	Flow rate, elapsed sampling time, holding time(s).
Temperatures	Filter module >4 °C flagged (for information).
Disassembly checks	Shipper received intact, with all components? Temperature in module <4 °C? Evidence of filter damage (ripped, contaminated, creased, etc.)?
Data screening and review: internal consistency checks	Check for correct number and type of samples by date and site. Verification of scheduled vs. actual exposure information.
Analysis lab checks	Laboratory validation flags are assigned by the analysts based on lab QC results.
Other within-sample tests "Level-1 Validation"	Cation/anion ratios, mass conservation, visual and statistical screening.

Data Reporting Challenges

- **Project size** (over 200 sites, 1,800 samples, 200,000 values reported each month).
- **Multiple analysis per event** - Filters from one sample event must be sent to multiple labs and results combined back to one result set.
- **Matching field and laboratory data** from same event to produce results.
- **Extensive QA/QC Needs.**
- **Reporting schedule** – Need rapid turnaround to sites and then rapid delivery of site changes to AIRS.

Meeting Data Reporting Challenges

- **Project size** – Central database allows coordination of all assembly, shipping, and reporting activities.
- **Multiple analysis per event** – Custom reporting programs combine results from all laboratories into a unified monthly report.
- **Matching field and analytical data** – Identifiers assigned to all aspects of operation (sampling event, module, lab sample, etc.). These are linked in the database to permit accurate matching of lab and field data.
- **QA/QC** – Automated programs detect potential outliers in gravimetric mass, anion/cation balance, reconstructed mass balance, sulfur/sulfate ratio, etc.
- **Reporting schedule** – External web site used to deliver reports to sites – e-mail replies for changes. This saves several weeks over paper reports.

Summary and Conclusions

- $PM_{2.5}$ chemical speciation laboratory support includes a complex network of activities that must be performed in a well-choreographed fashion.
- RTI has implemented a successful laboratory analysis and sample processing program to support 225 sites in the nationwide network.
- Several complex challenges involving scheduling, filter blanks, and filter contamination have been identified and addressed to improve data quality.