Source-Oriented Sampling of Ambient Fine and Ultrafine PM

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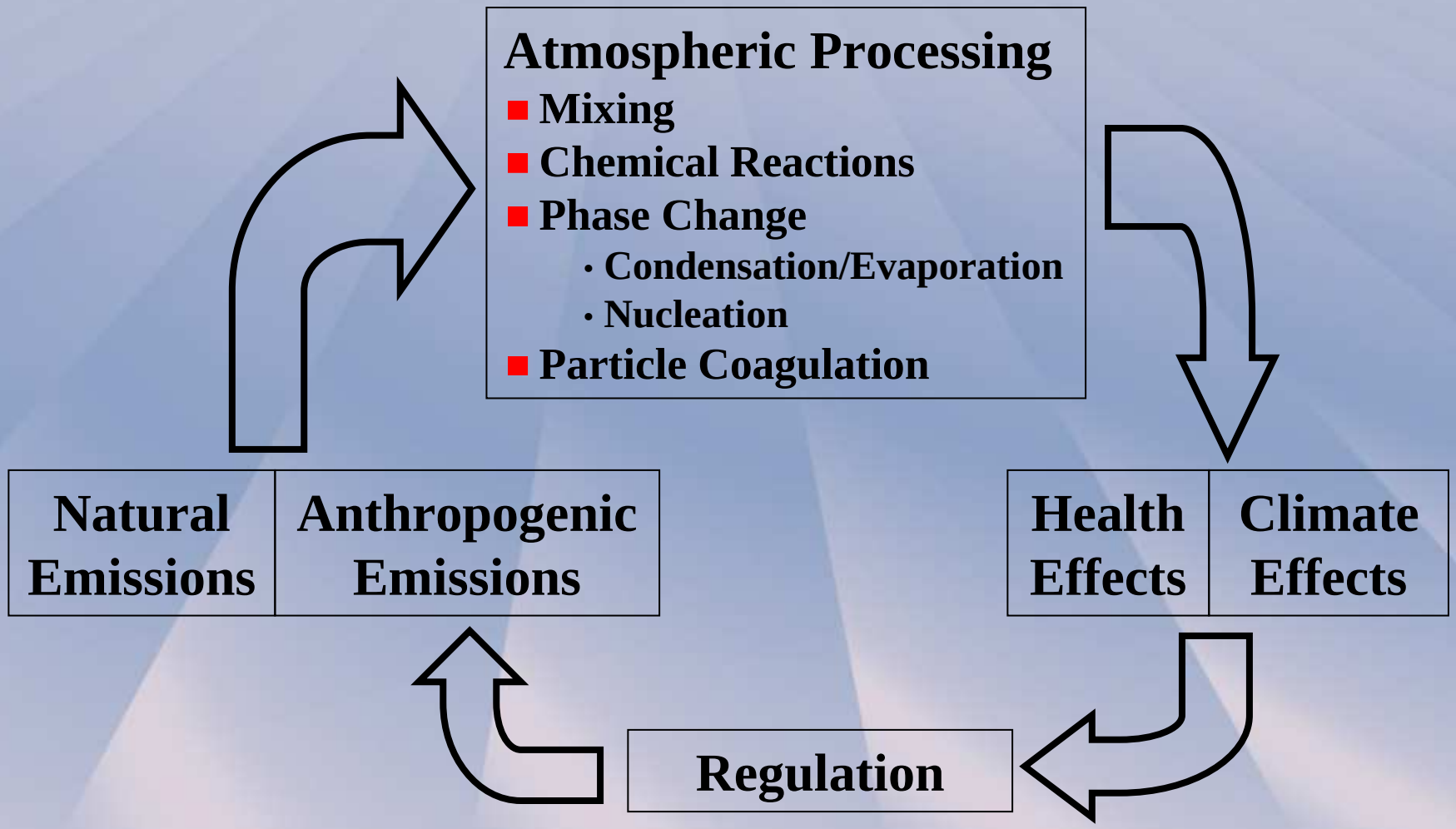
Many Thanks to

Keith Bein, UC Davis

Yongjing Zhao, UC Davis

Kent Pinkerton, UC Davis

The Air Pollution Life Cycle



Future Regulatory Imperatives

Is all PM created equal?

Is some PM more equal than others?

(apologies to George Orwell)

-- Do sea spray and diesel exhaust have same toxicity?

-- Current mass-based NAAQS treats them the same

-- More cost-effective to regulate more toxic emissions

Source-based Regulation may be the future

Future Regulatory Imperatives

How do we deduce health effects of different sources?

Epidemiologically

-- Kids growing up near freeways
-- Kids growing up downwind of coal fired power plants
-- Many other studies
-- But correlation, not causative

Future Regulatory Imperatives

How do we deduce health effects of different sources?

Toxicologically directly from sources

-- Well how about those nasty secondary compounds?

-- And how about the atmosphere changing the toxicity?

-- Can we collect source-oriented PM from the atmosphere?

-- Isn’t the atmosphere well mixed?

Source-Oriented Sampling

The atmosphere is not well mixed on short time scales

-- Consider plumes hitting a sampling site

-- Single particle mass spectrometer observations in Atlanta, Houston, Baltimore and Pittsburgh

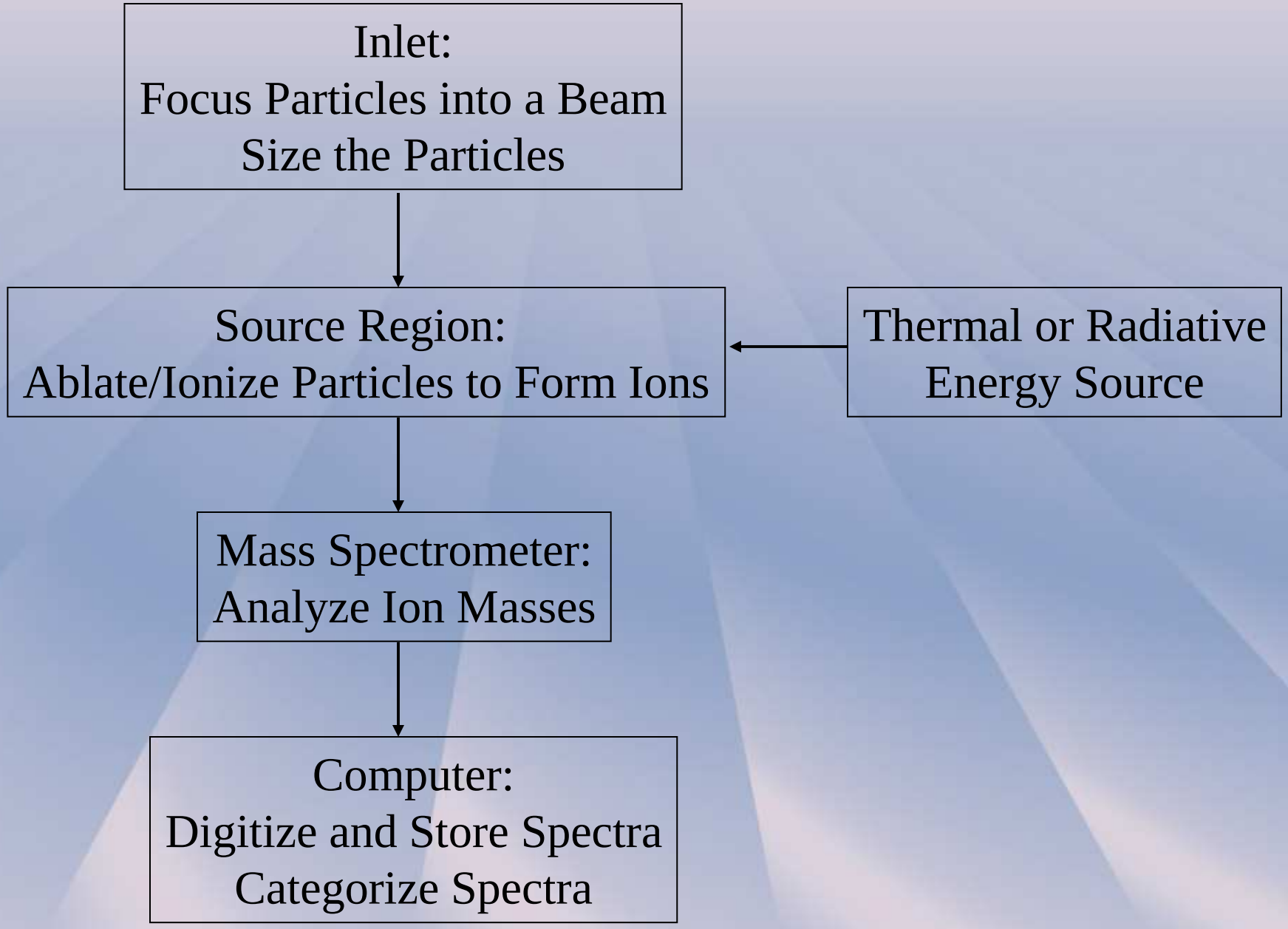
Source-Oriented Sampling

So what's the big idea?

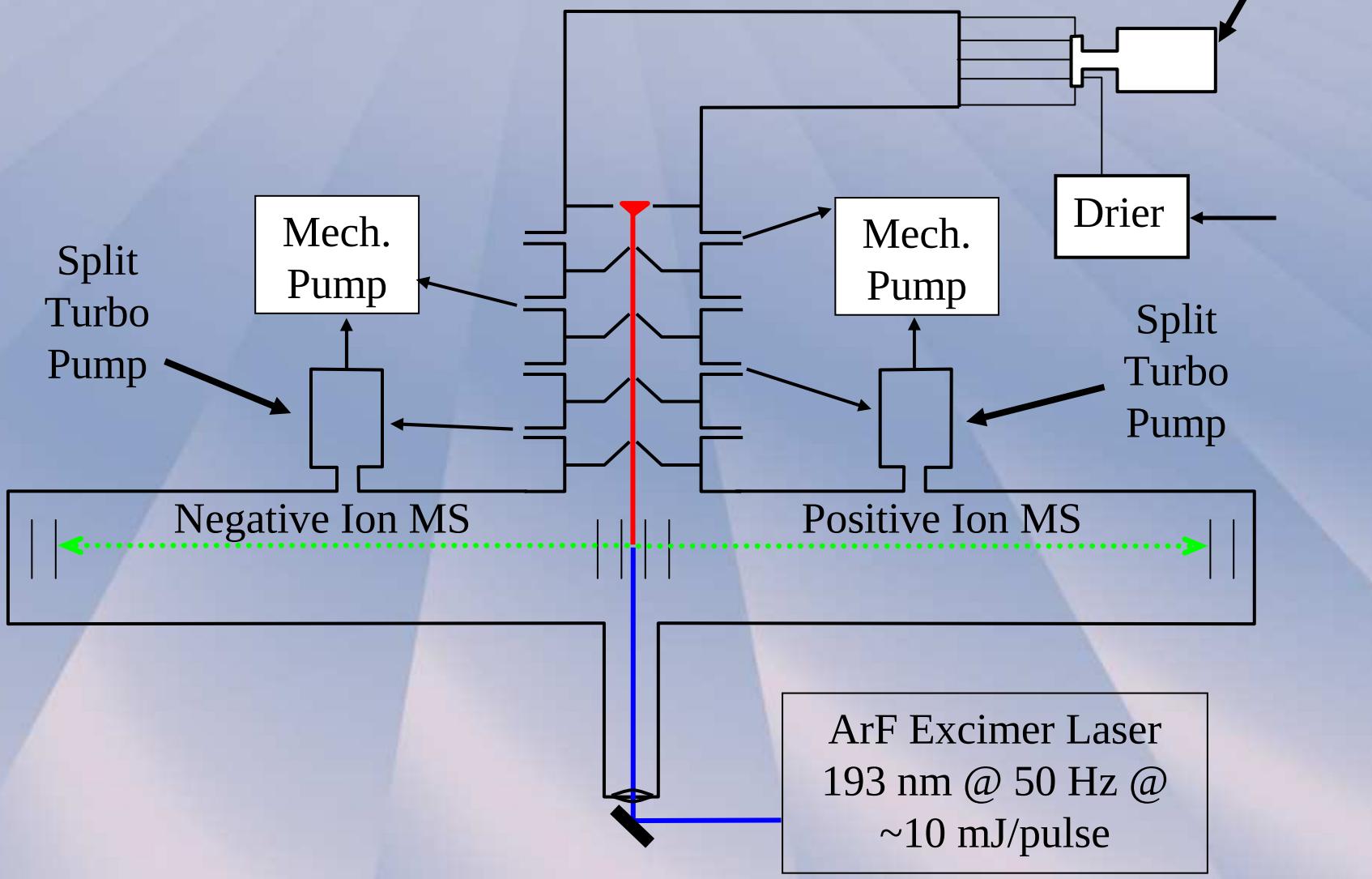
-- Run a single particle mass spectrometer to characterize the mixing state of the atmosphere

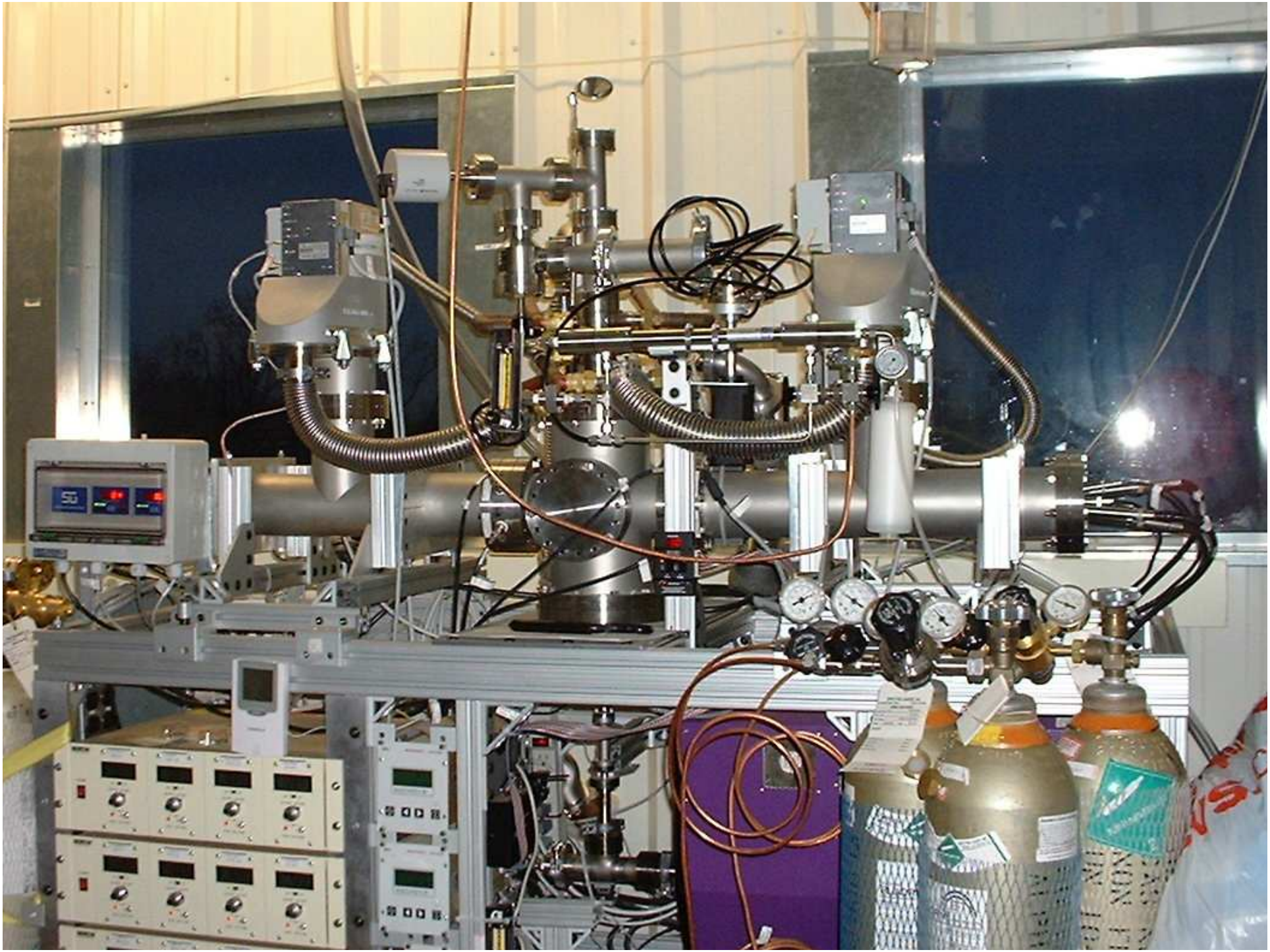
-- Assign prevailing sources or source combinations to each of 10 high-volume ChemVol samplers

-- Use the single particle mass spectrometer to select which ChemVol samples depending on the sources or source combinations affecting the site


Inlet:
Focus Particles into a Beam
Size the Particles
Source Region:
Ablate/Ionize Particles to Form Ions
Thermal or Radiative
Energy Source
Mass Spectrometer:
Analyze Ion Masses
Computer:
Digitize and Store Spectra
Categorize Spectra

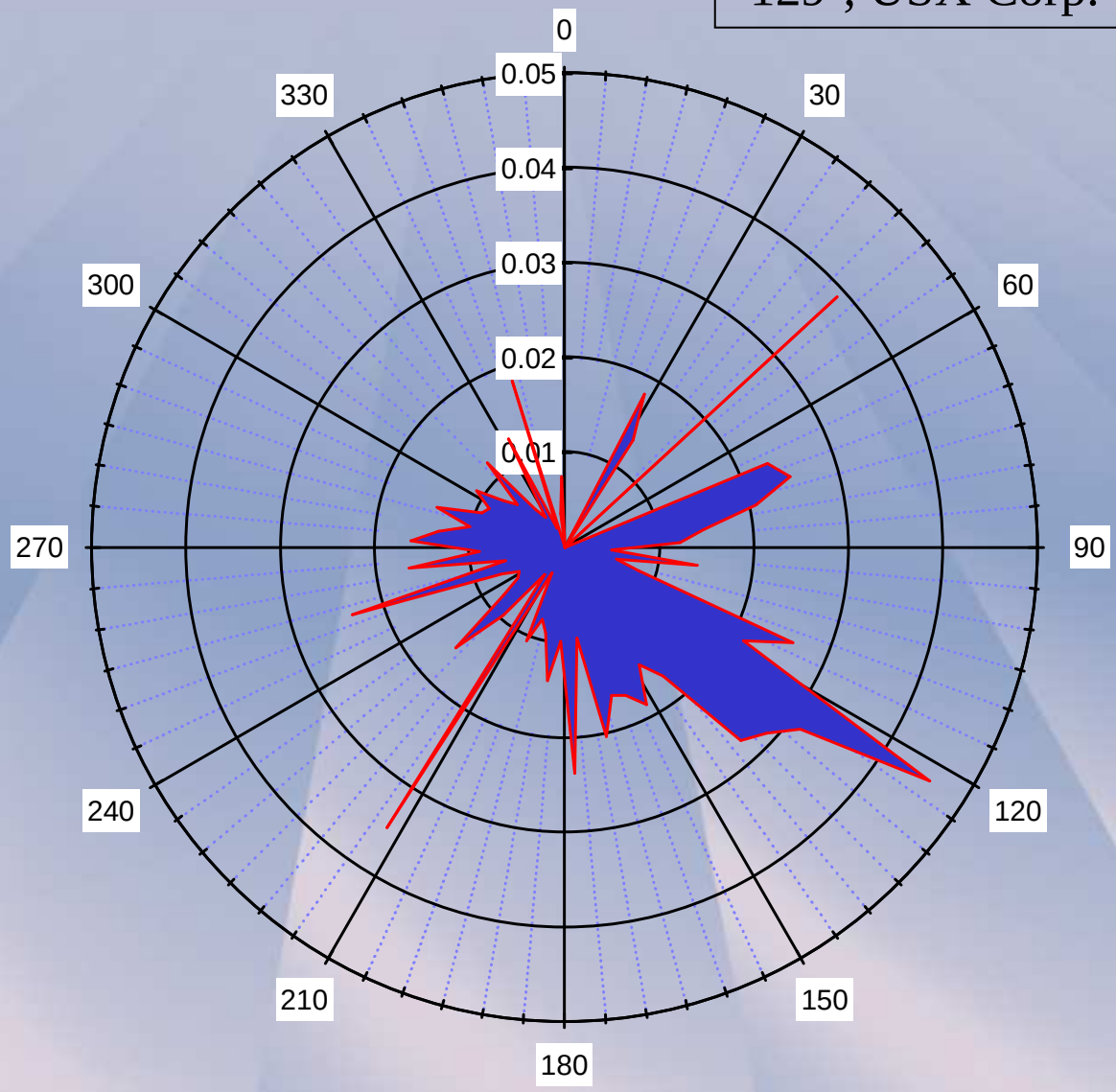
Rapid Single-ultrafine-particle Mass Spectrometer (RSMS-III)



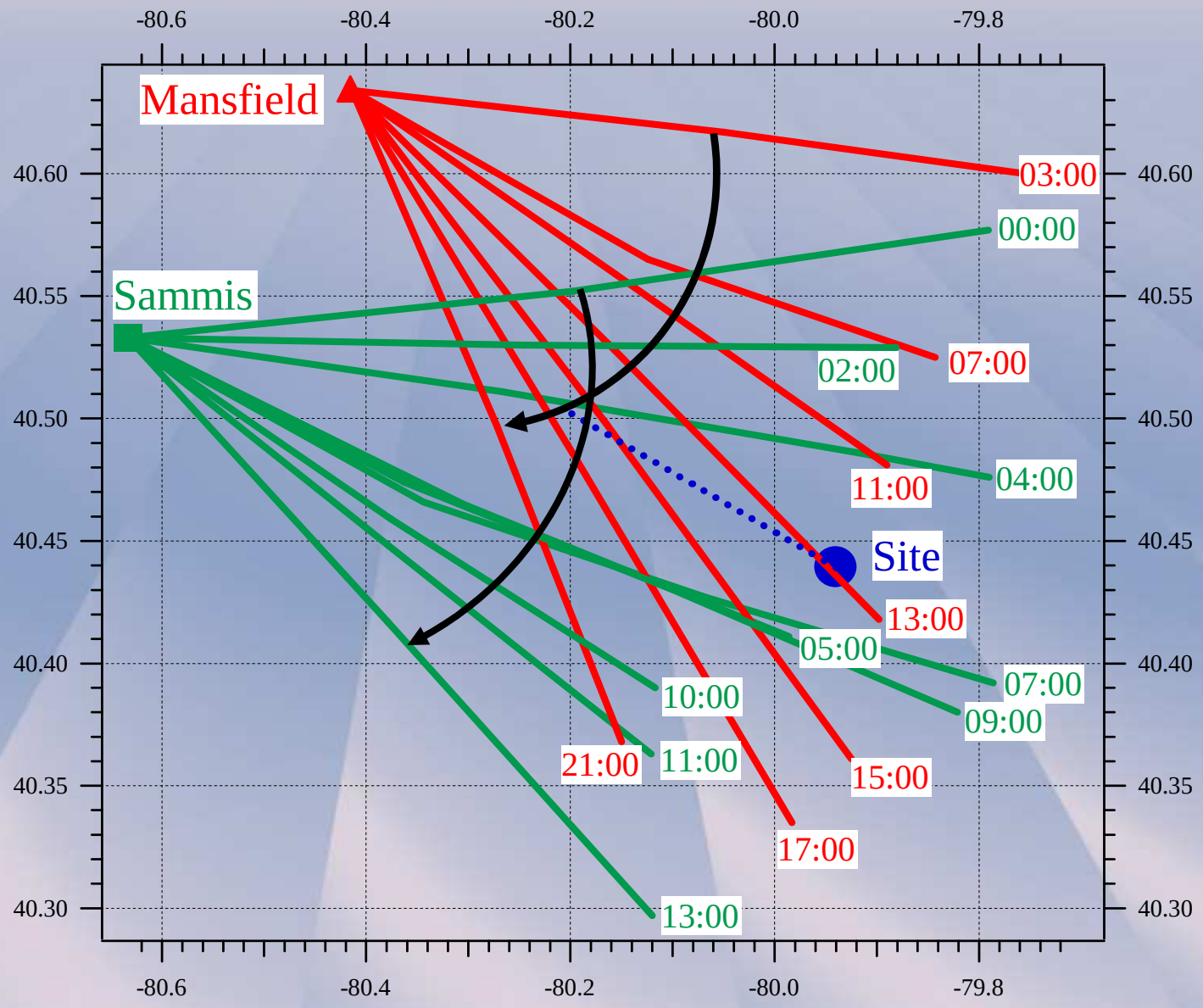


Correlating with Wind Direction: Steel Mills

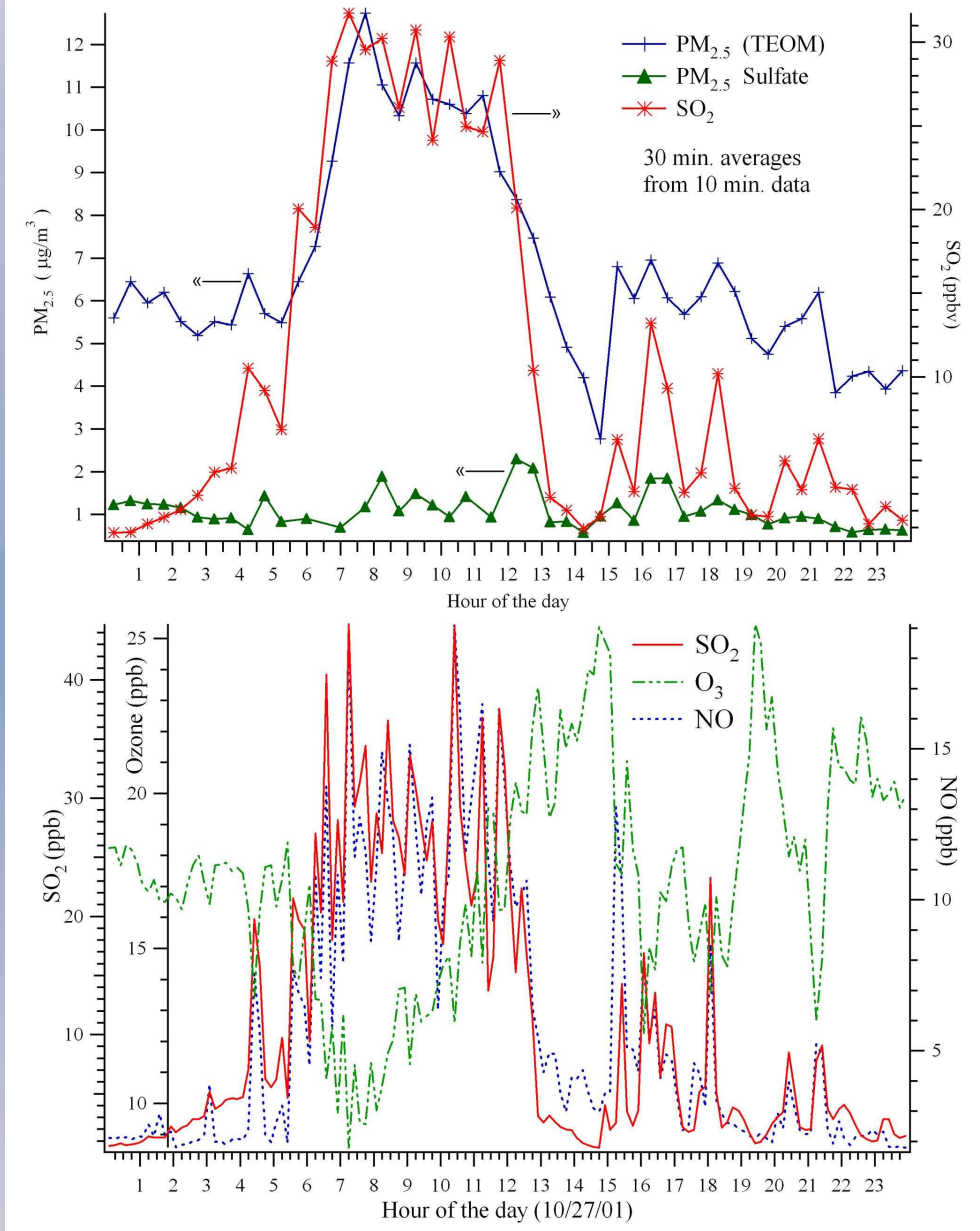
129º, USX Corp. –ET, 426 tons/yr



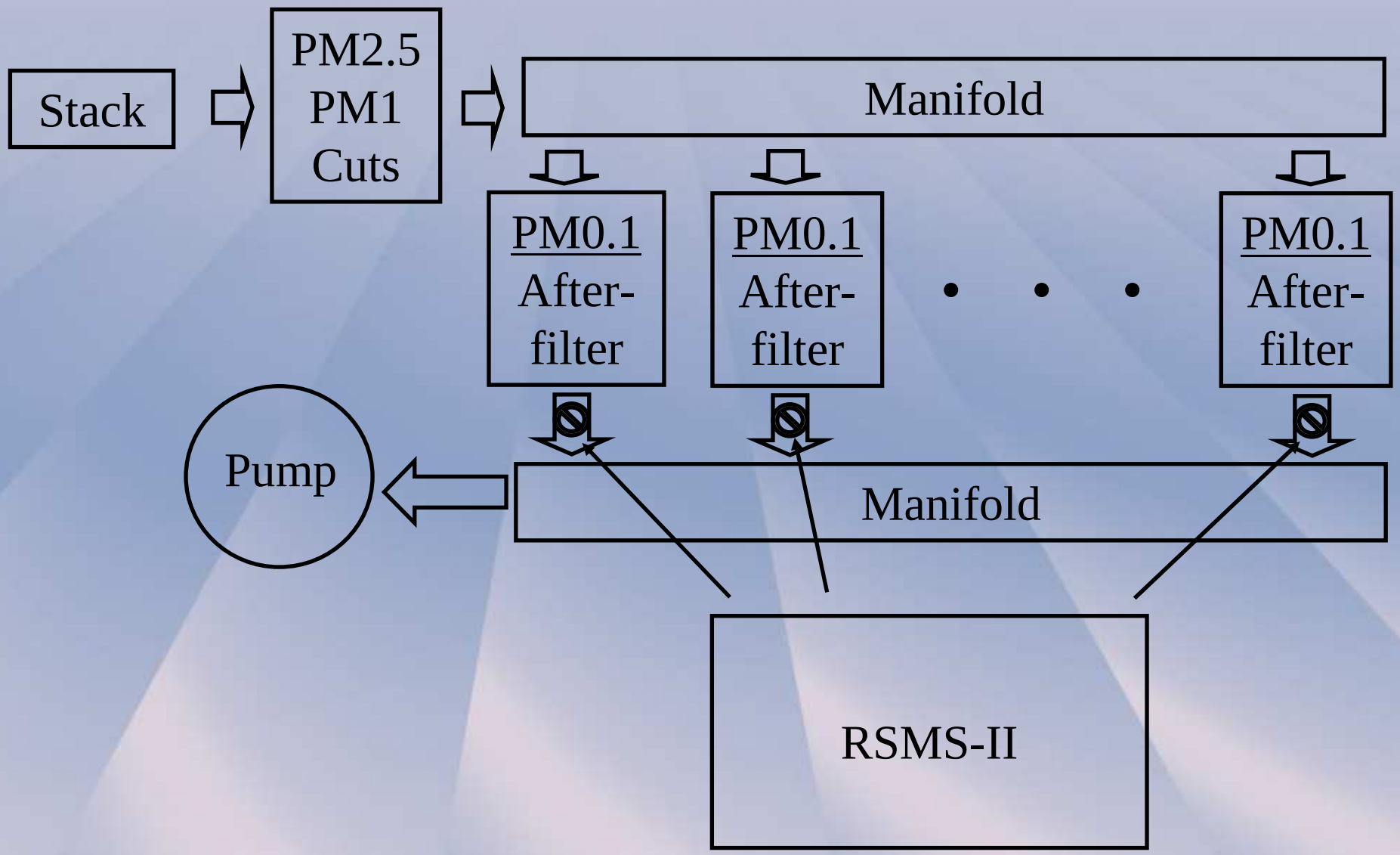
Coal Fired Power Plants



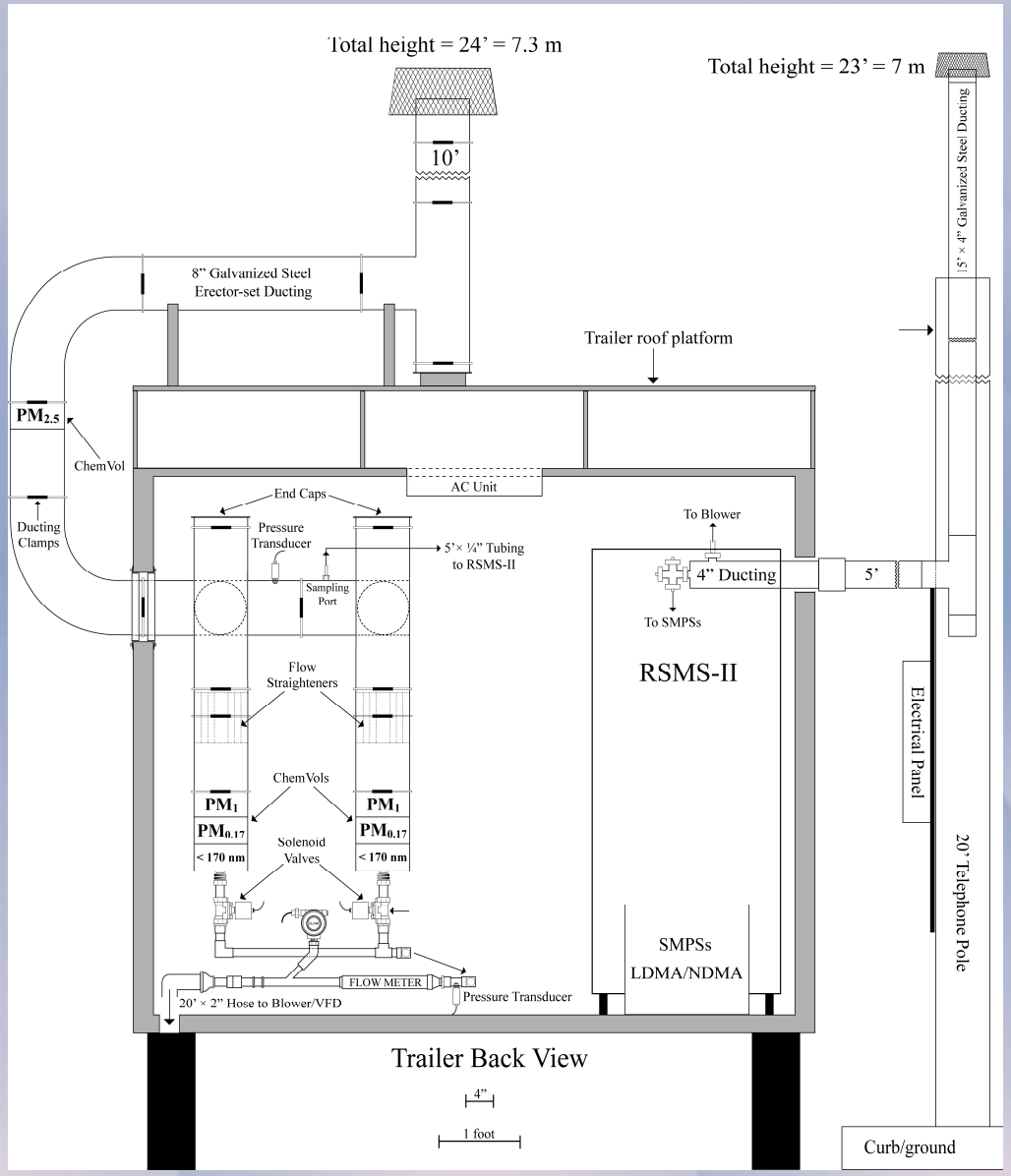
Coal Fired Power Plants



Conditional Source-Oriented Sampling



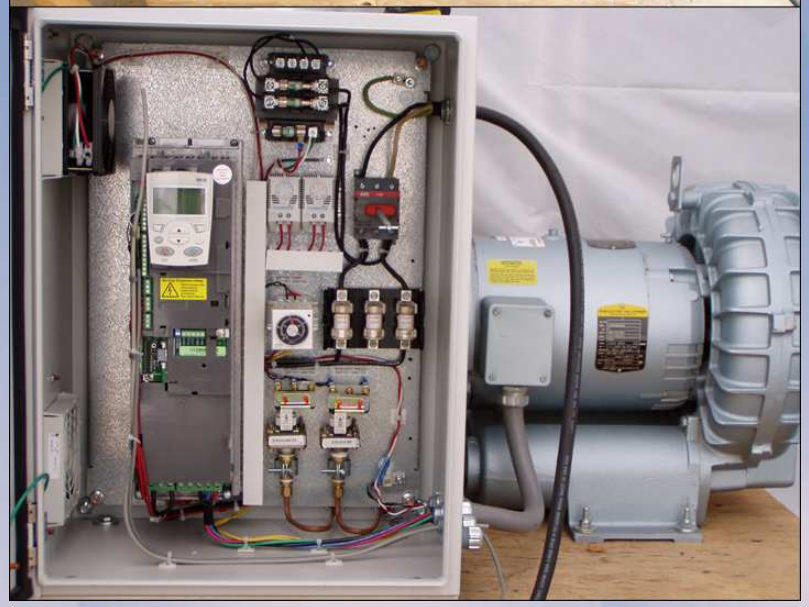
Sampling Train Schematic



RSMS-II

Sampling Train

Blower Assembly

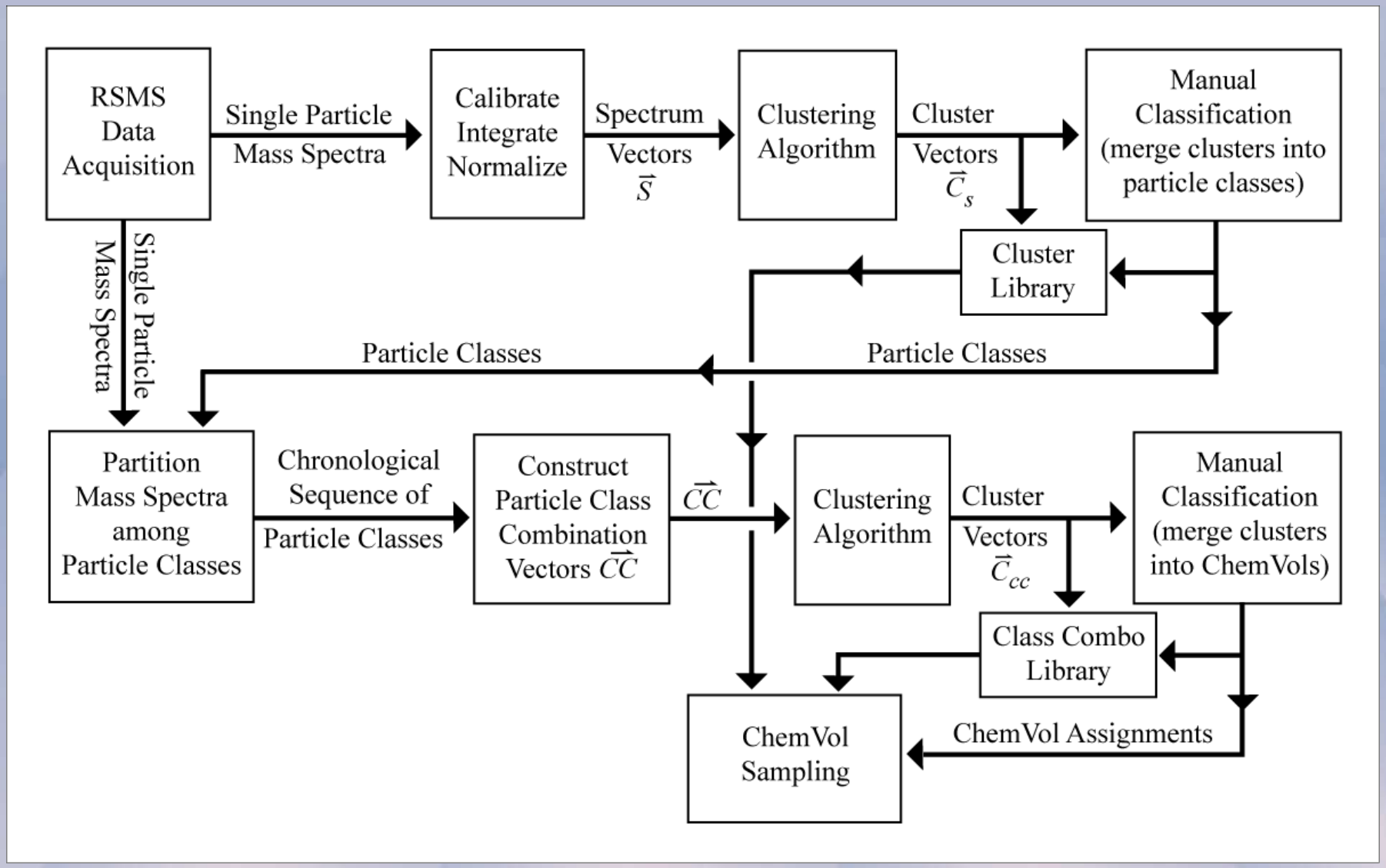


Conditional Source-Oriented Sampling

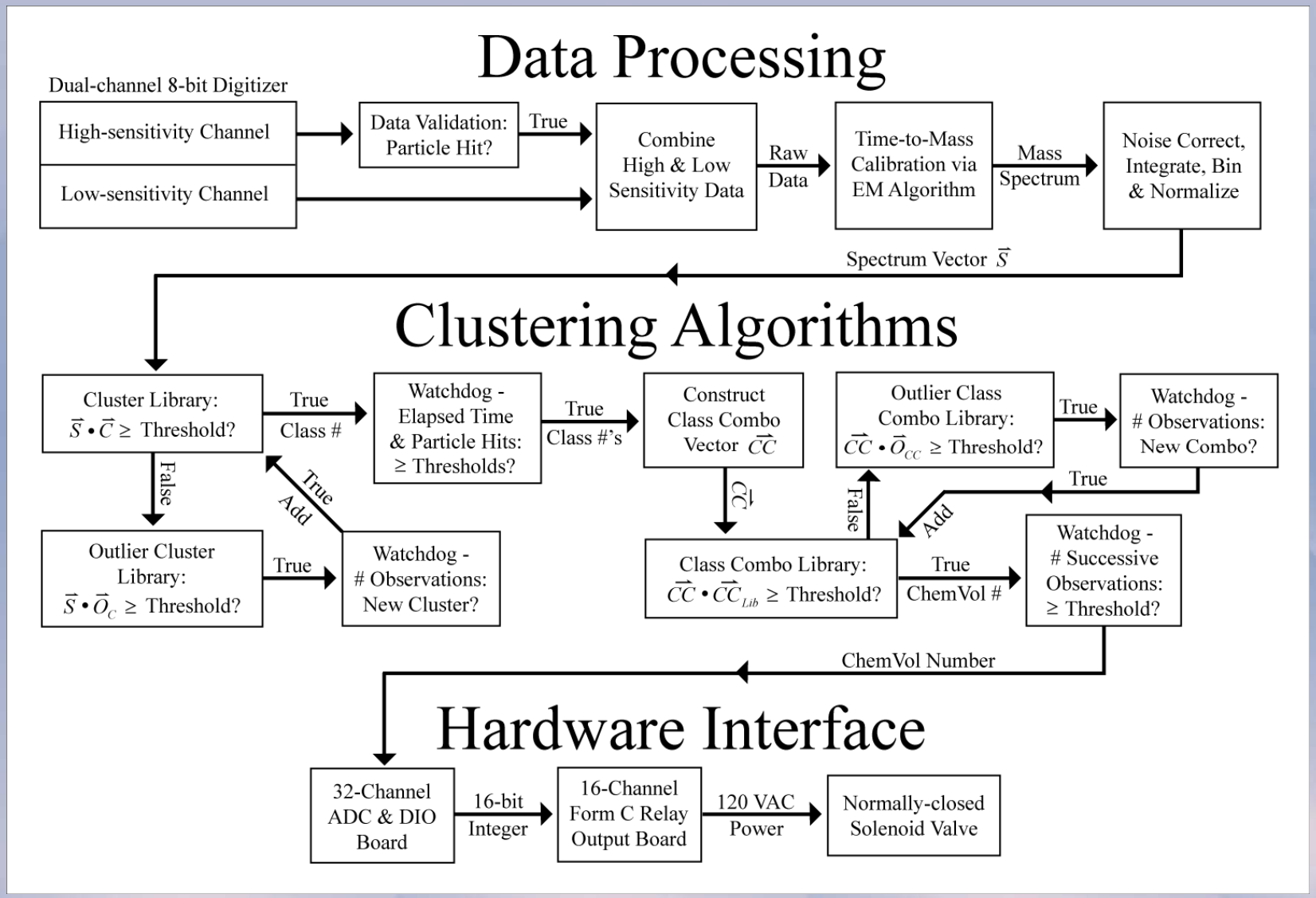
Anthony Wexler and coworkers

photosynth.net search wexler

Pre-study Data Analysis

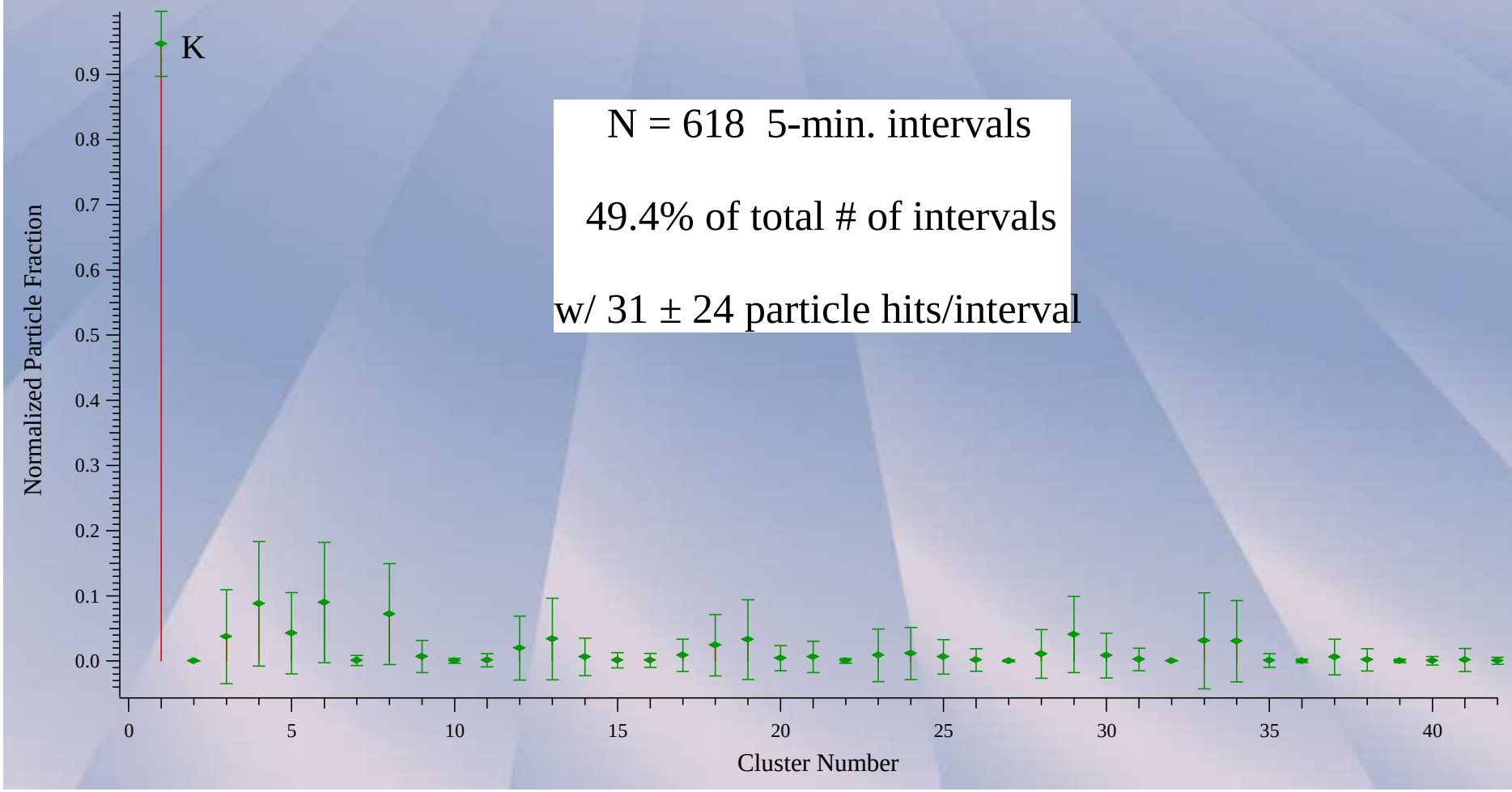


Real-time Data Flow



Source Combination 1 (D_p ~ 70-93 nm)

Relatively clean separation of primary wood smoke emissions



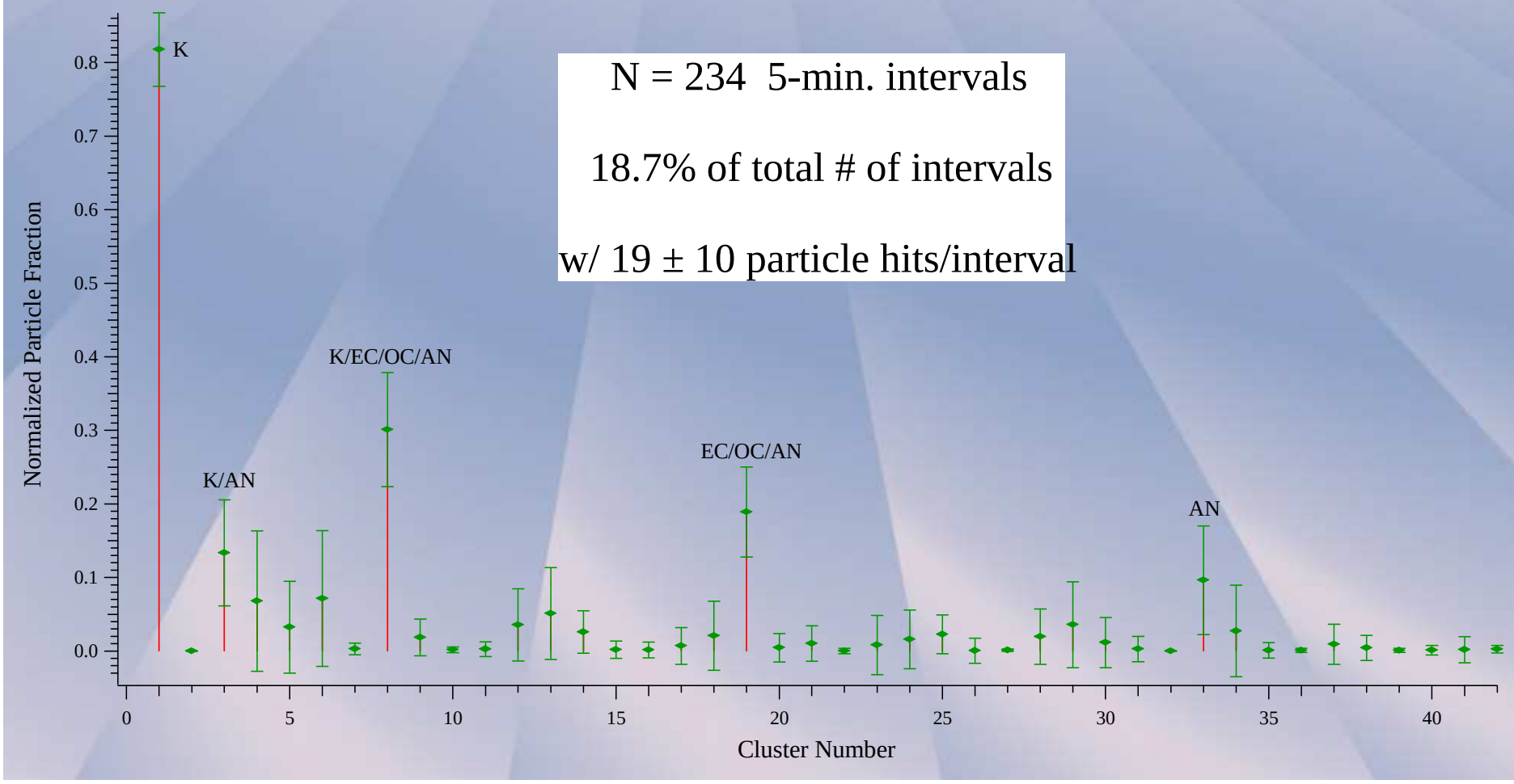
N = 618 5-min. intervals

49.4% of total # of intervals

w/ 31 ± 24 particle hits/interval

Source Combination 2 (D_p ~ 70-93 nm)

Mixture: wood smoke emissions (primary and w/ammonium nitrate), carbonaceous aerosol, and ammonium nitrate (AN) particles



Runtime Parameters

Runtime Parameter	Summer 2008	Winter 2009
Vacuum Aerodynamic Diameter Scanned (nm)	70	150
Particle Class Library – Similarity Threshold (dot product)	0.8	0.84
Outlier Cluster Library – # Observations for New Particle Class	5	15
Maximum Time between Successive Single Particle Observations (s)	90	30
Class Combination Library – Similarity Threshold (dot product)	0.6	0.81
Class Combination Vector – Time interval (s)	300	60
Class Combination Vector – Minimum # Single Particle Observations	5	3
# Single Particle Observations between Successive Class Combination Vectors	3	3
ChemVol Switching – Minimum # Successive Observations	1	2

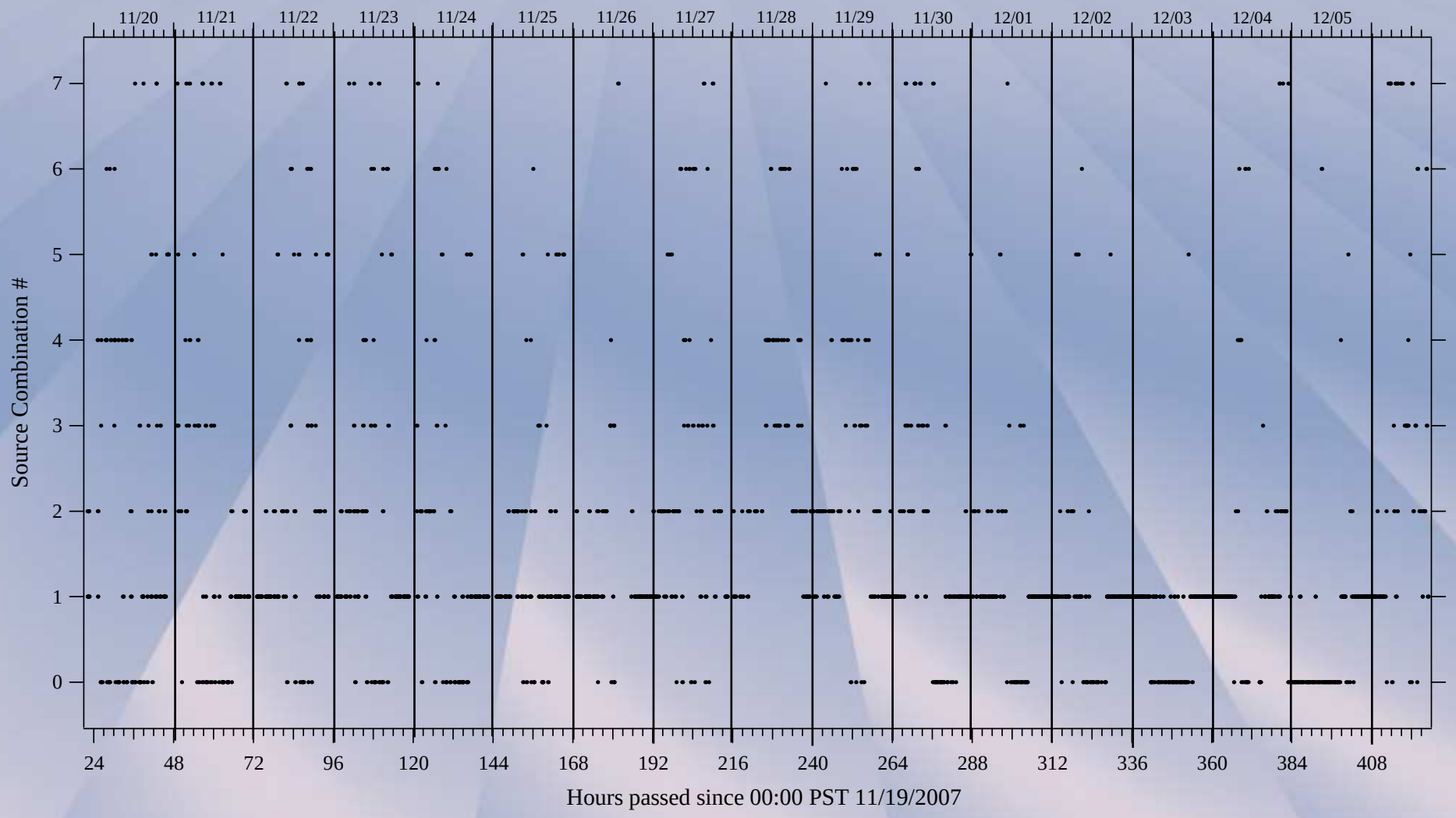
Fresno Metadata

Experiment		Start Date	End Date	Total Sampling Hours	Total # Mass Spectra	Total # Particle Classes	Total # Class Combination Vectors
Summer 2008	Pre-study	8/13/2008	9/2/2008	446	21,906	12	4689
	ChemVol Sampling	9/11/2008	10/21/2008	741	35,266		8785
Winter 2009	Pre-study	1/9/2009	2/11/2009	522	100,242	6	30,810
	ChemVol Sampling	3/1/2009	4/6/2009	712	46,286		10,274

Temporal Trend in Source Combinations

Source combinations are temporally separated

Seven source combinations account for 91% of the 5-min intervals.



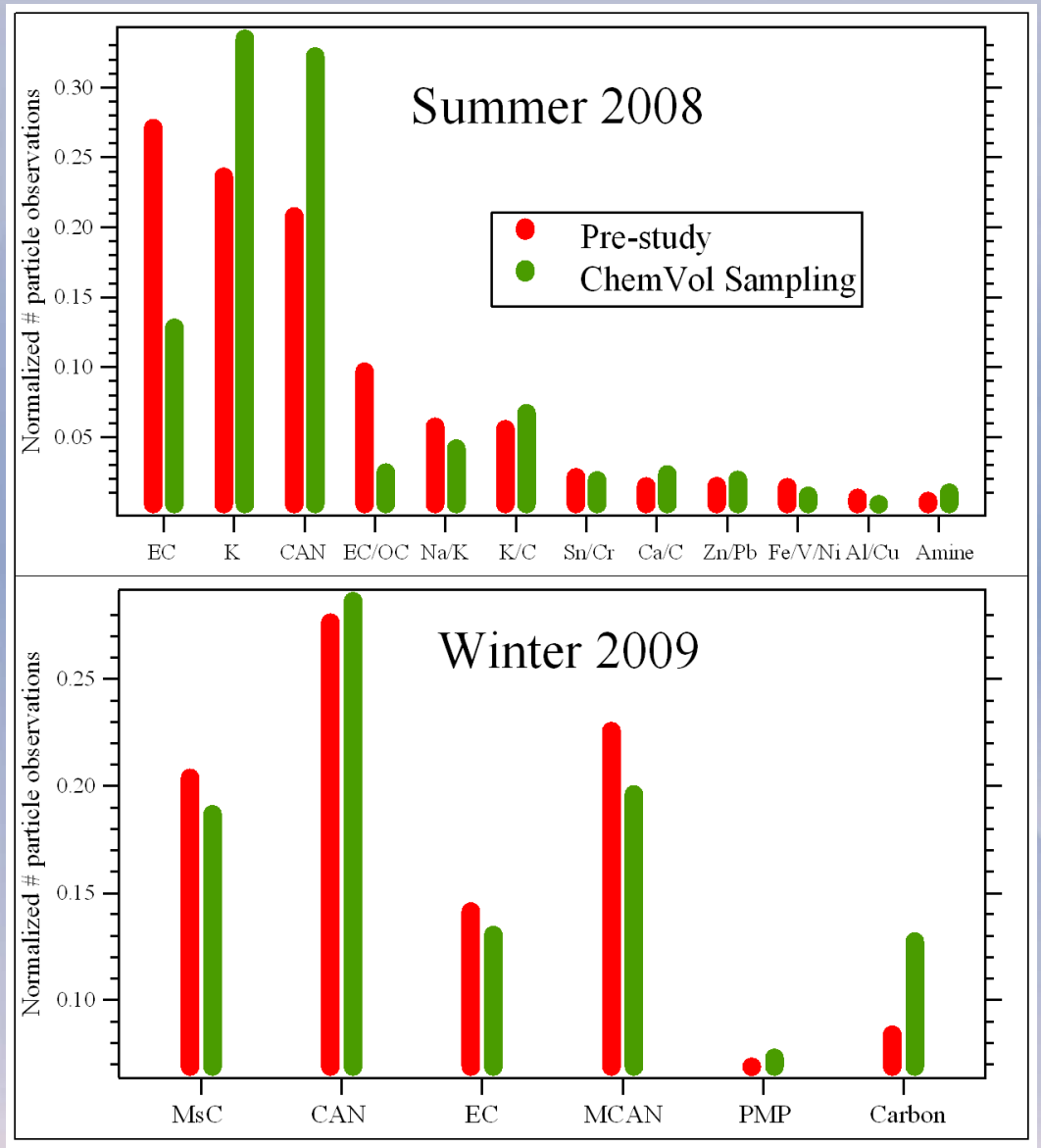
Single Particle Summary Statistics

Summer 2008 Experiment							
ChemVol	Total Sampling Time (hrs)	Total # Particle Hits	Total # Sampling Intervals	Class Combo Vectors		Scaled Estimates – Collected Mass (mg)	
				Total #	Average # Particles/	Ultrafine	Fine
1	85.55	15283	991	4327	14 ± 8	14 ± 3	36 ± 10
2	63.69	13304	742	3844	24 ± 20	12 ± 2	41 ± 12
3	2.60	426	62	83	7 ± 2	0.42 ± 0.08	1.3 ± 0.4
4	2.26	400	61	76	8 ± 3	0.41 ± 0.07	1.1 ± 0.3
5	0.51	88	13	18	8 ± 3	0.10 ± 0.02	0.21 ± 0.06
6	5.85	1106	133	242	11 ± 6	1.1 ± 0.2	2.9 ± 0.8
7	1.45	240	38	45	7 ± 3	0.16 ± 0.03	0.4 ± 0.1
9	139.60	-	29	-	-	17 ± 3	47 ± 14
10	468.27	4419	1344	139	8 ± 7	63 ± 11	197 ± 56
Totals:	770	35266	3413	8785	-	109 ± 12	328 ± 60

Single Particle Summary Statistics

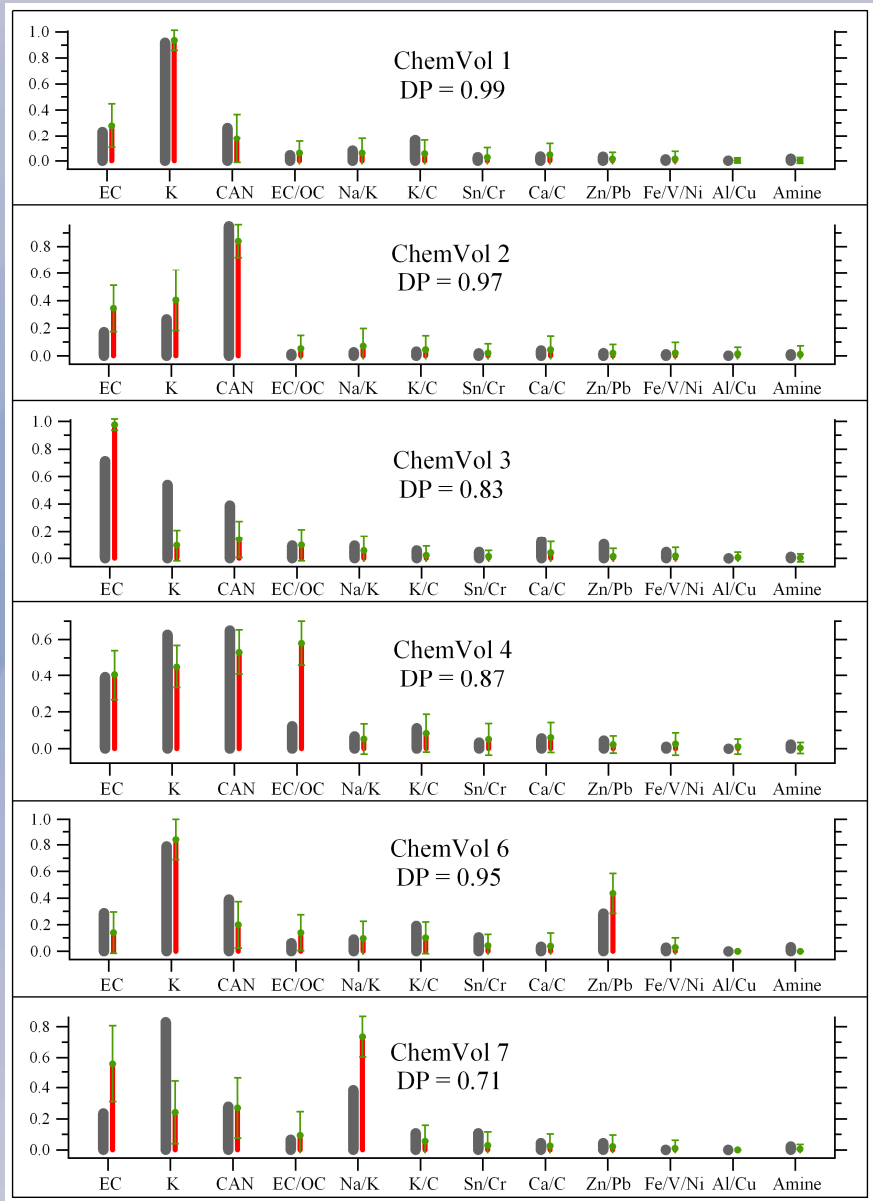
Winter 2009 Experiment							
ChemVol	Total Sampling Time (hrs)	Total # Particle Hits	Total # Sampling Intervals	Class Combo Vectors		Measured Mass (mg)	
				Total #	Average # Particles/	Ultrafine	Fine
1	6.91	7478	477	2148	12 ± 7	2.58 ± 0.06	3.21 ± 0.04
2	6.04	4087	402	1479	7 ± 2	1.30 ± 0.05	3.02 ± 0.03
3	4.41	3605	363	1239	8 ± 5	1.01 ± 0.08	2.0 ± 0.5
4	1.65	1879	137	536	11 ± 5	0.73 ± 0.04	0.8 ± 0.2
5	4.72	4423	422	1421	8 ± 3	1.33 ± 0.06	1.66 ± 0.08
6	1.98	2519	191	691	11 ± 7	0.88 ± 0.07	1.23 ± 0.04
7	8.75	-	3	-	-	1.07 ± 0.06	1.88 ± 0.06
8	92.49	-	32	-	-	11.26 ± 0.06	15.48 ± 0.05
9	257.82	-	33	-	-	27.22 ± 0.07	32.82 ± 0.08
10	356.51	22295	2081	2760	6 ± 1	37.16 ± 0.07	47.26 ± 0.09
Totals:	741	46286	4141	10274	-	85	107

Particle Class Distributions

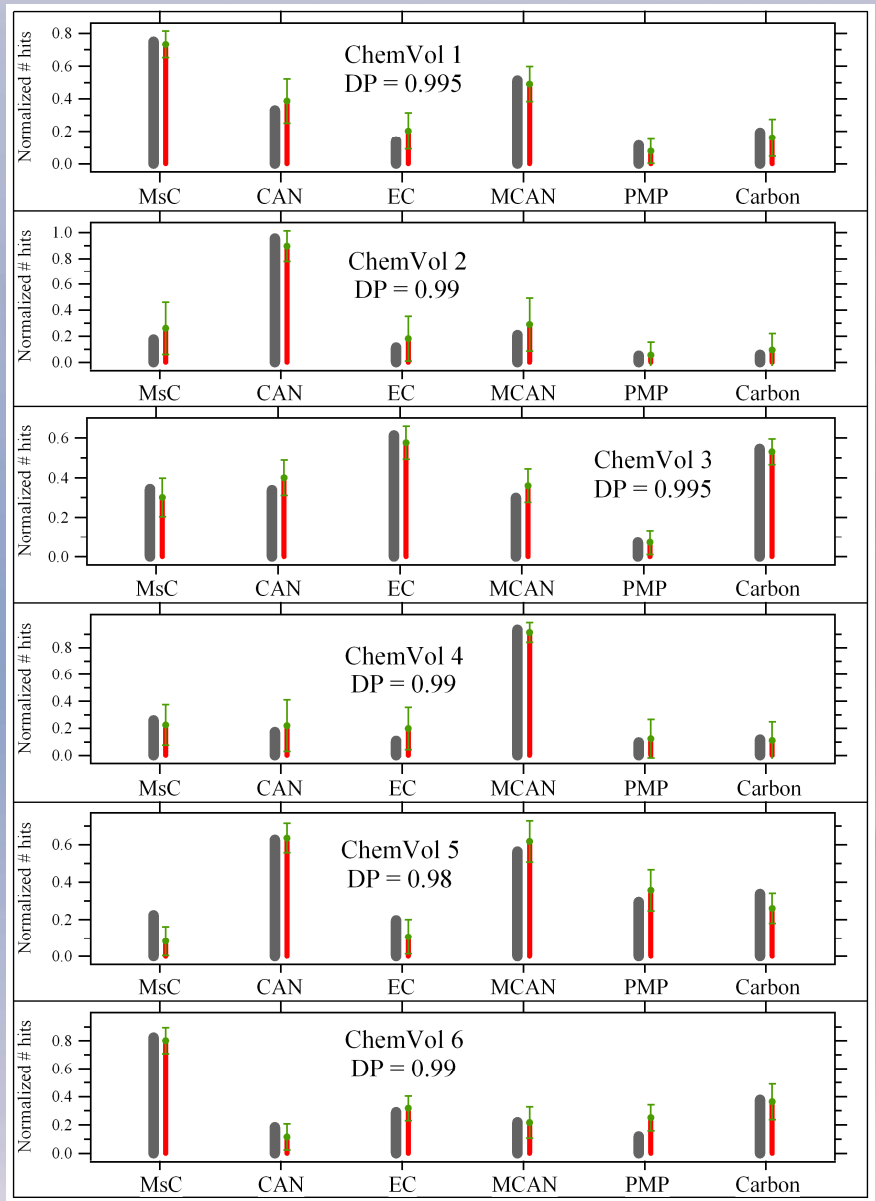


Fidelity

Summer 2008



Winter 2009



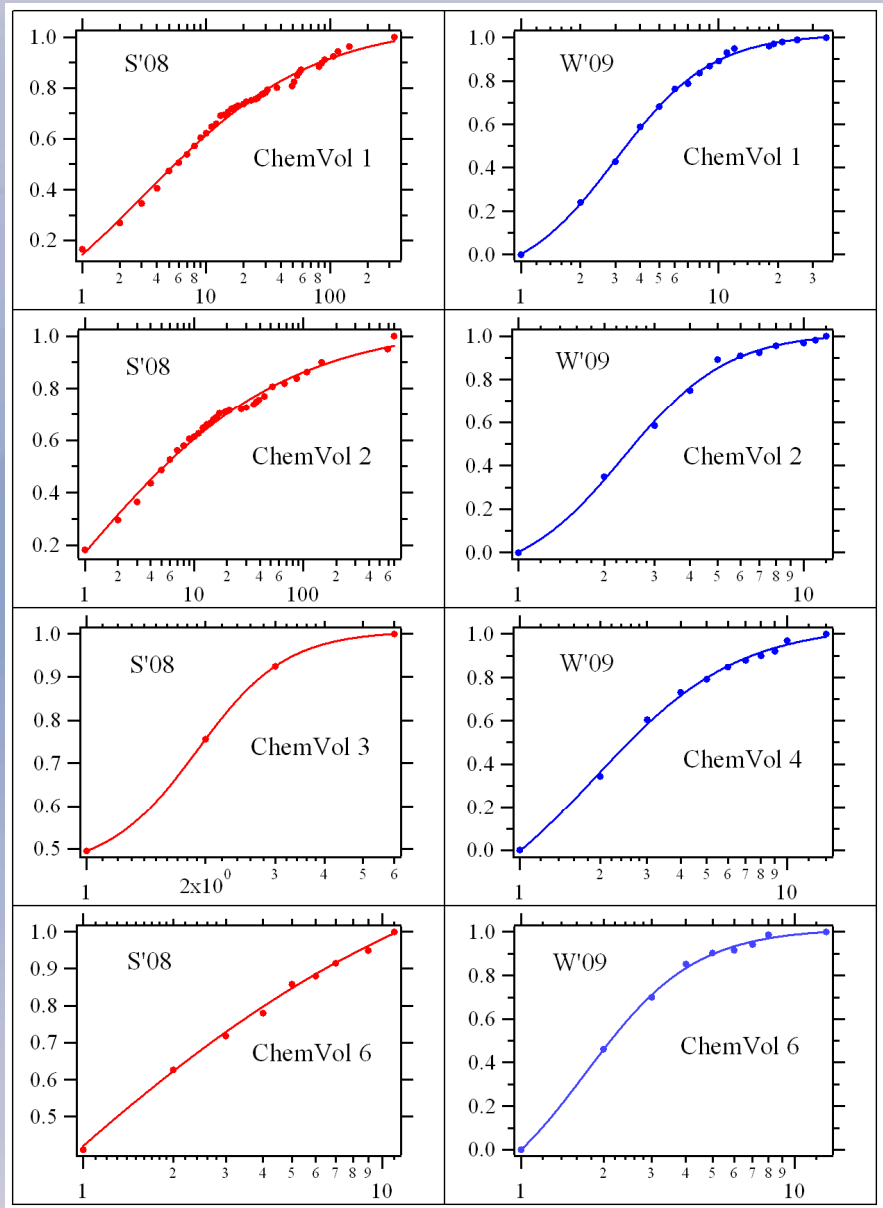
Fidelity – Dot Product Matrices

Summer 2008 Experiment							
Pre-study	**ChemVol Sampling (average dot product ± 1 standard deviation)**						
Class	EC	K	CAN	EC/OC	Na/K	K/C	Ca/C
EC	**0.93 ± 0.06**	0.23 ± 0.06	0.26 ± 0.08	0.27 ± 0.08	0.27 ± 0.1	0.4 ± 0.1	0.32 ± 0.06
K	0.2 ± 0.1	**0.93 ± 0.04**	0.2 ± 0.1	0.273 ± 0.09	0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
CAN	0.26 ± 0.09	0.25 ± 0.09	**0.92 ± 0.05**	0.234 ± 0.09	0.3 ± 0.2	0.3 ± 0.1	0.3 ± 0.2
EC/OC	0.4 ± 0.2	0.31 ± 0.06	0.32 ± 0.08	**0.90 ± 0.04**	0.33 ± 0.08	0.6 ± 0.1	0.28 ± 0.06
Na/K	0.30 ± 0.08	0.26 ± 0.05	0.31 ± 0.06	0.25 ± 0.08	**0.96 ± 0.03**	0.4 ± 0.1	0.42 ± 0.04
K/C	0.4 ± 0.1	0.27 ± 0.07	0.3 ± 0.1	0.42 ± 0.08	0.3 ± 0.1	**0.95 ± 0.03**	0.27 ± 0.08
Ca/C	0.3 ± 0.1	0.29 ± 0.06	0.34 ± 0.06	0.24 ± 0.07	0.5 ± 0.1	0.35 ± 0.09	**0.93 ± 0.04**
ChemVol	1	2	3	4	5	6	7
1	**0.86 ± 0.06**	0.5 ± 0.2	0.3 ± 0.1	0.52 ± 0.09	0.4 ± 0.2	0.39 ± 0.07	0.4 ± 0.1
2	0.3 ± 0.1	**0.83 ± 0.05**	0.2 ± 0.1	0.56 ± 0.07	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.1
3	0.44 ± 0.08	0.6 ± 0.1	**0.88 ± 0.06**	0.47 ± 0.09	0.72 ± 0.09	0.46 ± 0.06	0.6 ± 0.1
4	0.4 ± 0.1	0.6 ± 0.2	0.4 ± 0.1	**0.78 ± 0.08**	0.5 ± 0.2	0.3 ± 0.1	0.4 ± 0.1
5	0.42 ± 0.09	0.6 ± 0.1	0.59 ± 0.06	0.65 ± 0.09	**0.83 ± 0.06**	0.44 ± 0.08	0.6 ± 0.1
6	0.4 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.5 ± 0.1	0.3 ± 0.1	**0.80 ± 0.08**	0.4 ± 0.1
7	0.38 ± 0.09	0.5 ± 0.2	0.3 ± 0.2	0.4 ± 0.1	0.4 ± 0.2	0.3 ± 0.1	**0.73 ± 0.08**

Fidelity – Dot Product Matrices

Winter 2009 Experiment						
Pre-study	**ChemVol Sampling (average ± 1 standard deviation)**					
Class	MsC	CAN	EC	MCAN	PMP	Carbon
MsC	**0.98 ± 0.01**	0.43 ± 0.05	0.61 ± 0.04	0.54 ± 0.03	0.12 ± 0.03	0.19 ± 0.05
CAN	0.43 ± 0.05	**0.98 ± 0.02**	0.5 ± 0.1	0.52 ± 0.07	0.13 ± 0.03	0.17 ± 0.05
EC	0.61 ± 0.04	0.38 ± 0.05	**0.98 ± 0.02**	0.52 ± 0.03	0.12 ± 0.04	0.17 ± 0.08
MCAN	0.54 ± 0.03	0.4 ± 0.1	0.60 ± 0.09	**0.98 ± 0.02**	0.21 ± 0.06	0.4 ± 0.2
PMP	0.12 ± 0.03	0.1 ± 0.1	0.35 ± 0.07	0.31 ± 0.07	**0.98 ± 0.02**	0.5 ± 0.2
Carbon	0.19 ± 0.05	0.43 ± 0.06	0.59 ± 0.04	0.52 ± 0.03	0.11 ± 0.02	**0.99 ± 0.01**
ChemVol	1	2	3	4	5	6
1	**0.93 ± 0.03**	0.7 ± 0.2	0.5 ± 0.1	0.7 ± 0.2	0.5 ± 0.1	0.71 ± 0.08
2	0.6 ± 0.1	**0.93 ± 0.03**	0.4 ± 0.1	0.5 ± 0.2	0.47 ± 0.07	0.5 ± 0.1
3	0.6 ± 0.2	0.6 ± 0.2	**0.93 ± 0.03**	0.5 ± 0.2	0.4 ± 0.1	0.6 ± 0.1
4	0.66 ± 0.09	0.5 ± 0.1	0.44 ± 0.09	**0.94 ± 0.03**	0.46 ± 0.06	0.4 ± 0.1
5	0.6 ± 0.1	0.7 ± 0.2	0.5 ± 0.1	0.6 ± 0.2	**0.93 ± 0.03**	0.5 ± 0.1
6	0.72 ± 0.08	0.5 ± 0.2	0.5 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	**0.93 ± 0.04**

Heterogeneity and Temporal Stability



Thanks to

- **Keith Bein for building the instrument, developing the algorithm and basically doing all the interesting stuff**
- **Yongjing Zhao for helping to run everything and keep the single particle mass spectrometer operating**
- **You for staying awake**
- **CARB and EPRI for financial and moral support**

Questions?