Dragon, Karen E. (CDC/NIOSH/EID)

From:	Middendorf, Paul (CDC/NIOSH/OD)
Sent:	Monday, February 13, 2012 10:57 AM
To:	Susan Sidel; NIOSH Docket Office (CDC)
Cc:	WTC STAC (CDC)
Subject:	FW: Thomas Cahill/Aerosals for FTP
Attachments:	WTC aersols ACS 2003.ppt

For docket #248

Susan,
I'm sending this to the docket so we can keep track of it and the public will know what we're sharing. If there are problems with that, please let me know.

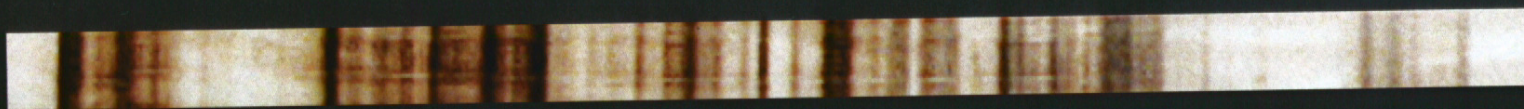
Paul

-----Original Message-----
From: SUSAN P SIDEL [
Sent: Monday, February 13, 2012 10:31 AM
To: Middendorf, Paul (CDC/NIOSH/OD)
Subject: Thomas Cahill/Aerosals for FTP

Hi Paul,

I'm following up on Virginia's suggestion. Attached are some additional materials. This powerpoint presentation was in the ACS book Elizabeth recommended

Very fine aerosols from the World Trade Center collapse piles: Anaerobic Incineration?



Thomas A. Cahill, Steven S. Cliff, Kevin D. Perry (U. Utah) , James Shackelford, Michael Meier, Michael Dunlap, Graham Bench, (LLNL), and Robert Leifer (DOE EML)

DELTA* (δ) Group
University of California, Davis

* Detection and Evaluation in Long-range Transport of Aerosols

Background

The collapse of the World Trade Center structures (South Tower, North Tower, and WTC 7) presented two very different types of air pollution events:

1. Initial fires and collapse-derived "dust storm"
2. Continuing emissions from the debris piles

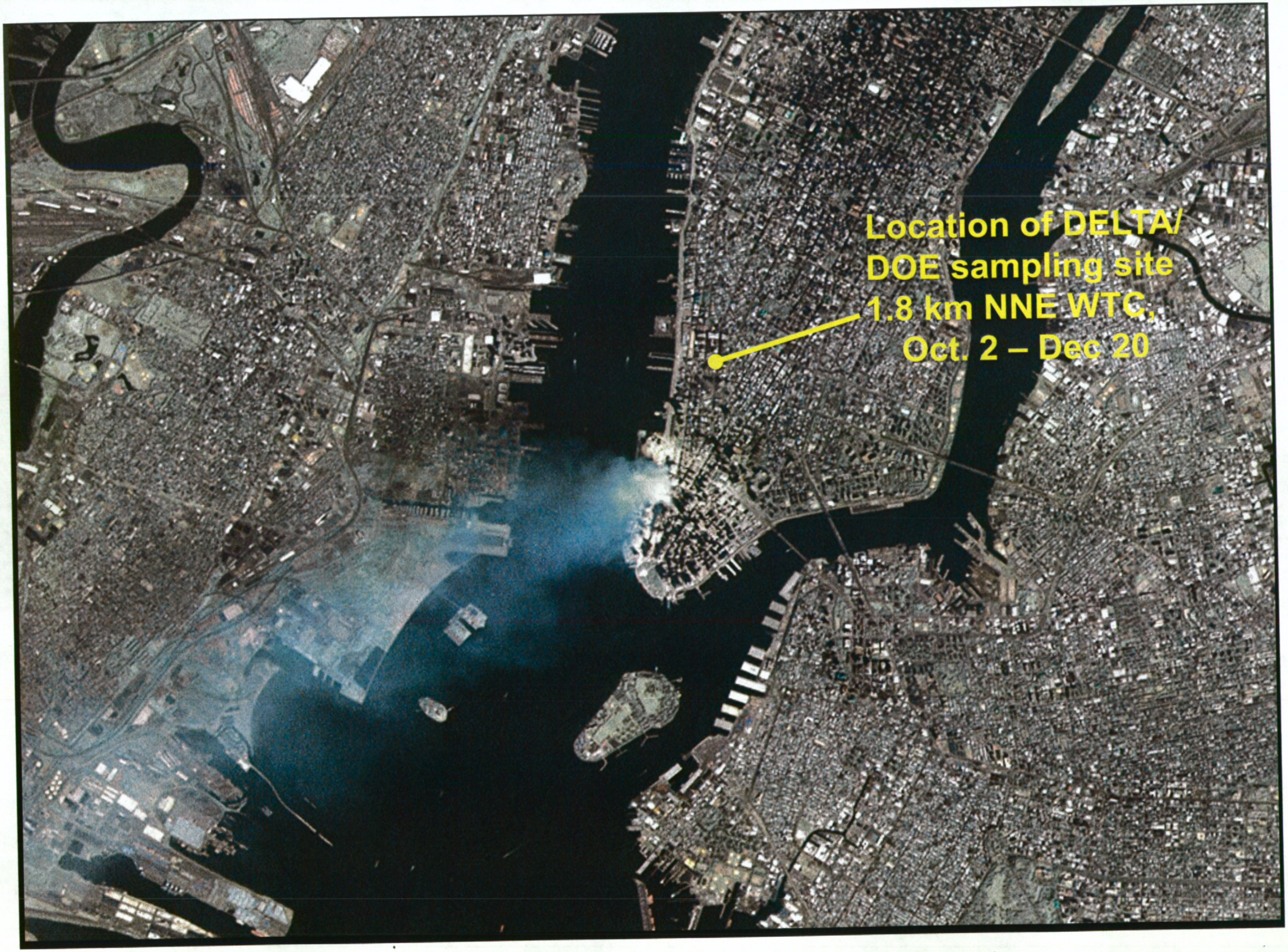
Both cases shared the unusual aspect of a massive ground level source of particulate matter in a highly populated area with potential health impacts.

New data to explain aerosols from the WTC collapse piles

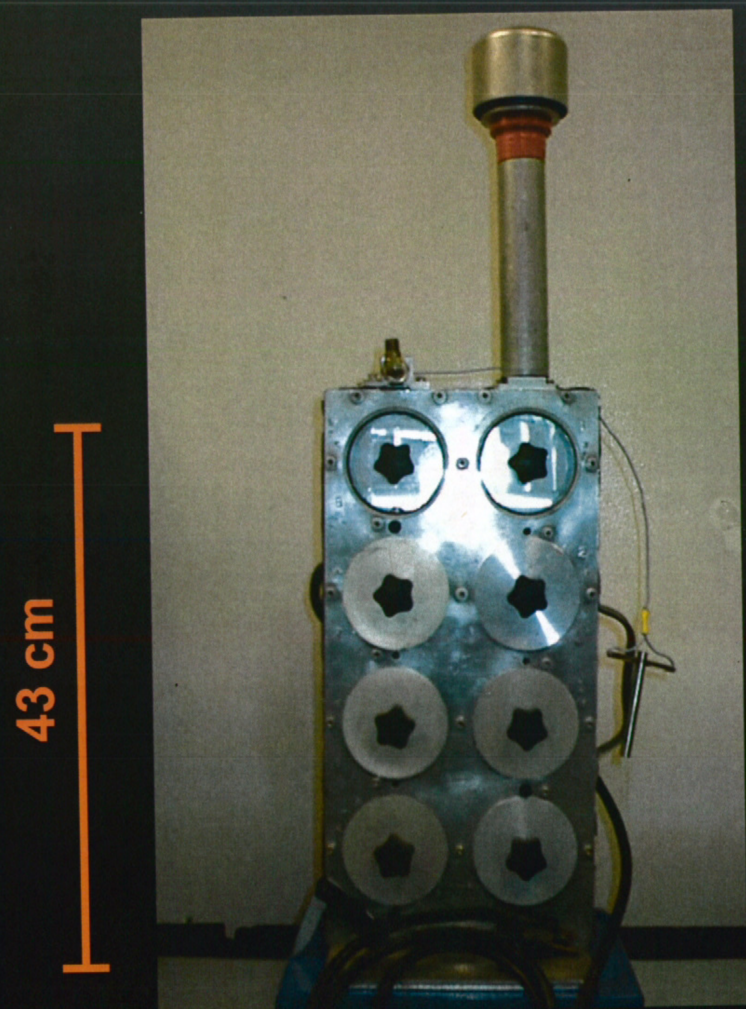
- Association of metals with prior data on municipal incinerators, especially those with chlorine-rich waste
- Correlation between coarse, metal coated aerosols with very fine aerosols
- New time and compositionally resolved data on fine and very fine aerosols
  - Indoor very fine aerosols near WTC, May, 2002
  - Outdoor very fine Eastern urban aerosols, August, 2002

In addition….

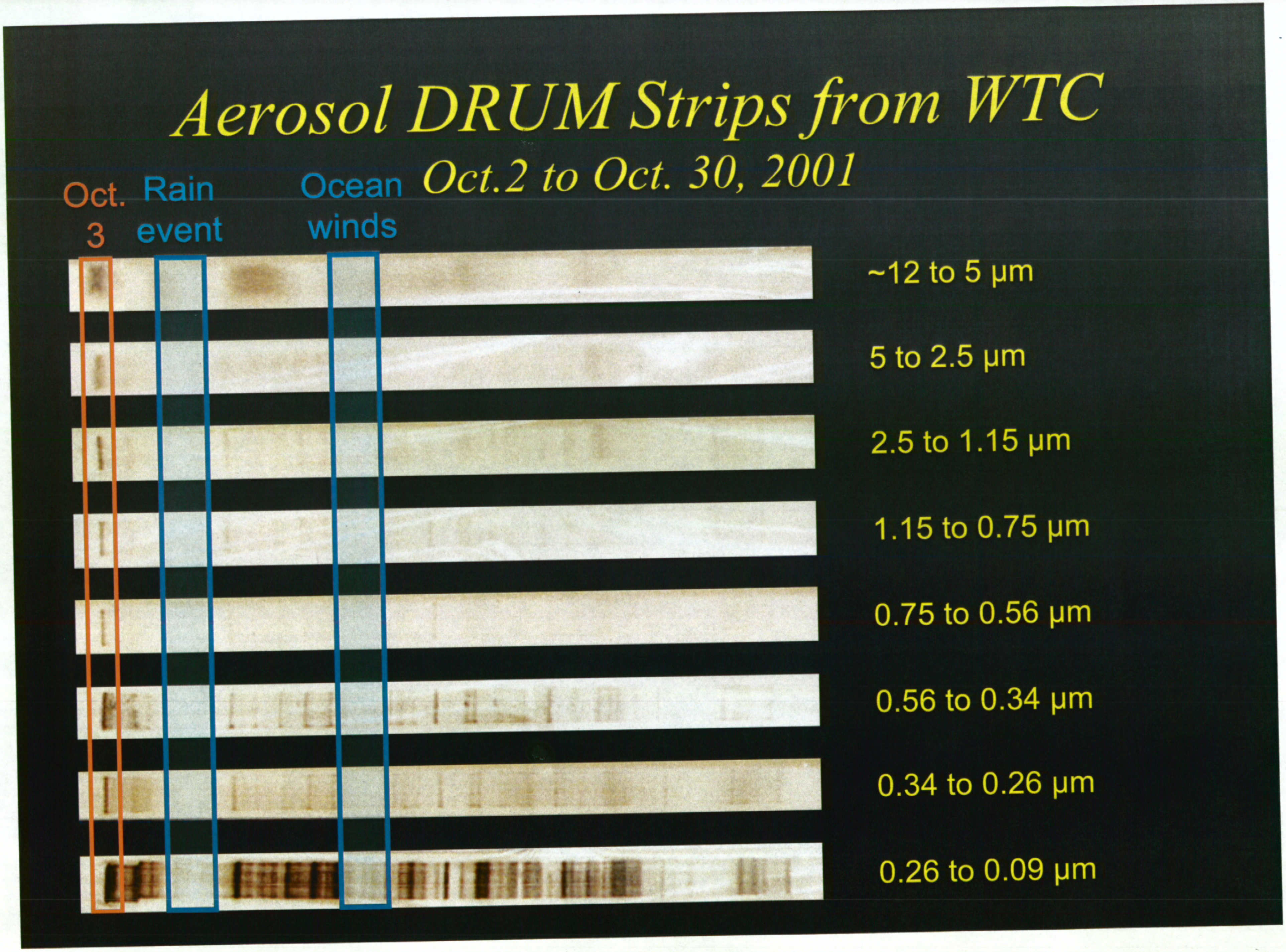
- Indoor aerosol data for Sept, 11, 2001 for 8 hr in a near-WTC office


Location of DELTA/
DOE sampling site
1.8 km NNE WTC,
Oct. 2 – Dec 20

DELTA Group slotted 8 DRUM Impactor



- 8 size ranges:
  - Inlet (~ 12) to 5.0 µm
  - 5.0 to 2.5 µm
  - 2.5 to 1.15 µm
  - 1.15 to 0.75 µm
  - 0.75 to 0.56 µm
  - 0.56 to 0.34 µm
  - 0.34 to 0.26 µm
  - 0.26 to 0.09 µm
- 10.4 l/min, critical orifice control, ¼ hp pump
- 6.5 x 168 mm Mylar strips
- For 42 day run, 4 mm/day, time resolution = 1 hr.
- Field portable
  - 10 kg, 43 × 22 × 13 cm



Aerosol DRUM Strips from WTC
Oct.2 to Oct. 30, 2001
Oct. 3
Rain event
Ocean winds
~12 to 5 µm
5 to 2.5 µm
2.5 to 1.15 µm
1.15 to 0.75 µm
0.75 to 0.56 µm
0.56 to 0.34 µm
0.34 to 0.26 µm
0.26 to 0.09 µm

DELTA Group Analytical Techniques

Beam based, 100-500 μm, non-destructive

- Soft beta ray mass (β mass)
- 320-820 nm optical attenuation, 10 nm steps
- Synchrotron X-ray fluorescence, polarized "white" beam 4 keV to 18 keV (S-XRF) – ALS LBNL
- Scanning Transmission Ion microscopy (STIM) – CAMS LLNL
- Proton Elastic Scattering Analysis (PESA) - LLNL
- Laser Desorption Ionization Time-of-Flight Mass Spectrometry (LDITOF/MS)
- Scanning Electron Microscopy (SEM)

Under what conditions and with what efficiency can the WTC plume impact the sampling site, 1.8 km NNE of the WTC and 50 m above ground level?

Wind direction:

- HYSPLIT trajectory wind from $202^\circ \pm 60^\circ$ (incl. dispersion)
- Weighting by cosine $\Delta\theta$

Plume lofting:

- Surface temperature of the WTC collapse site

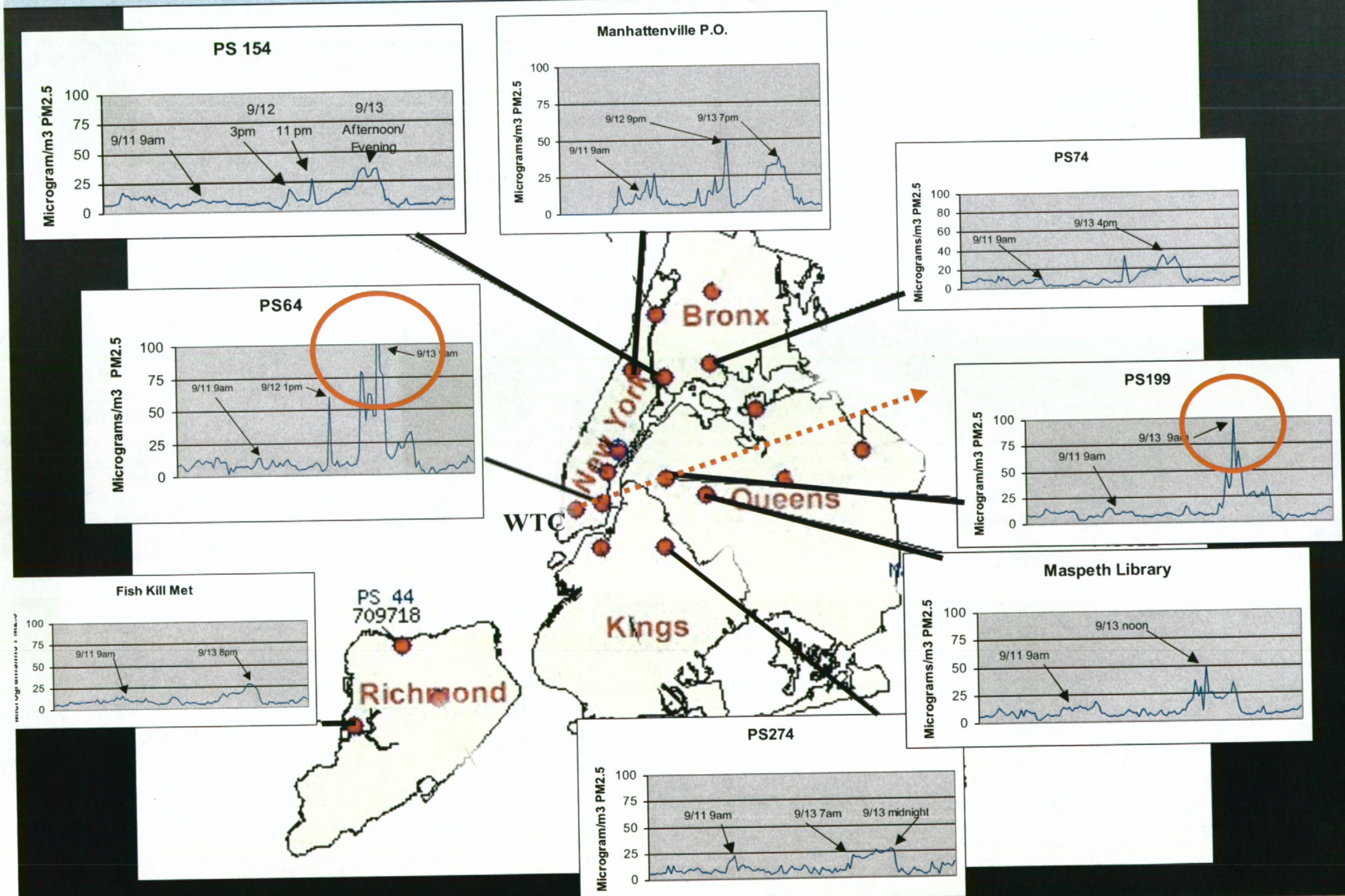
Vertical atmospheric stability:

- HYSPLIT isentropic trajectories subsiding and/or high vertical dispersion

Concentrations are modulated by:

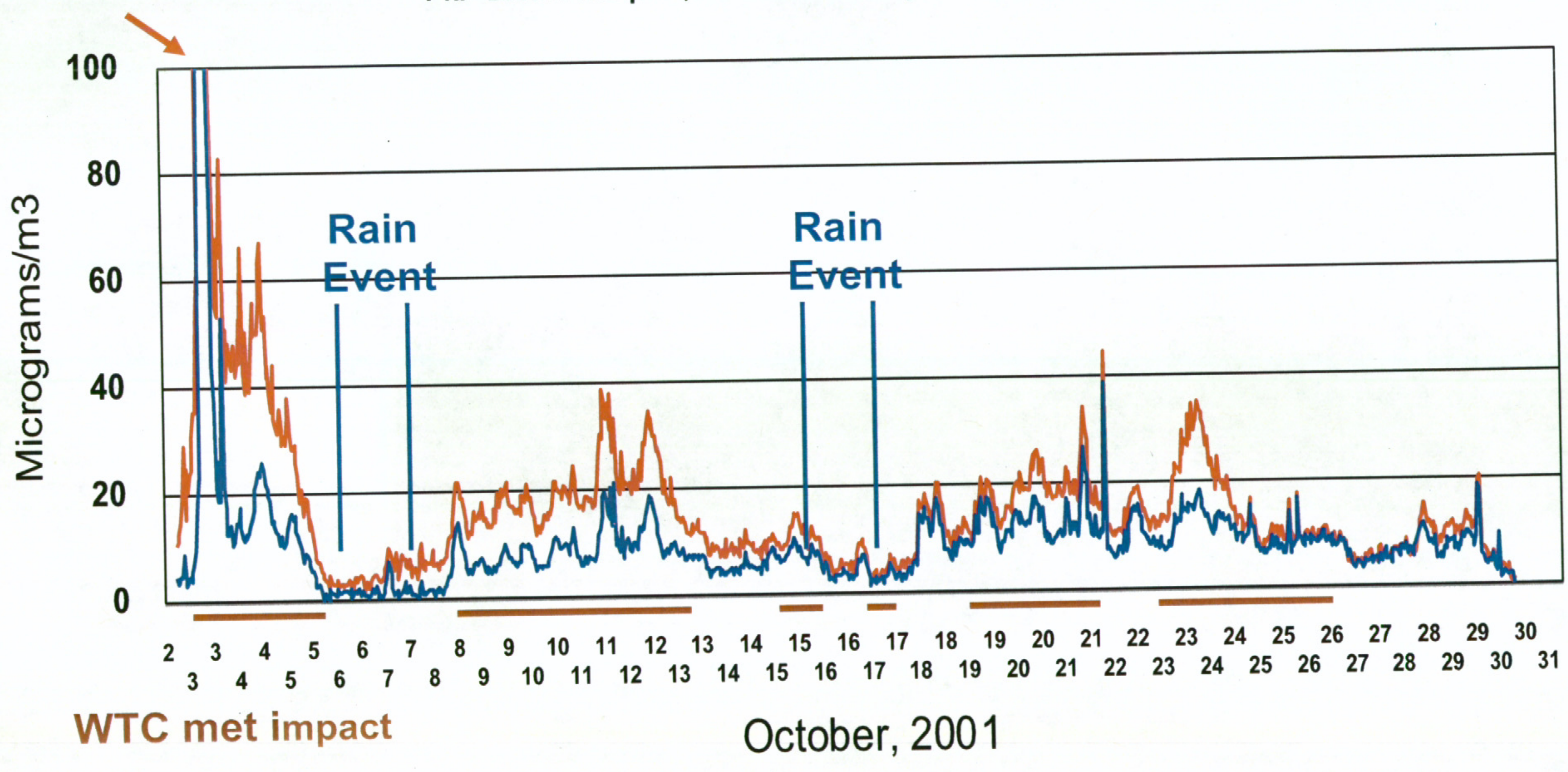
- Emission rates from the collapse piles
- Vertical and horizontal dispersion rates
- Wind speed - "Residence Time" 1/u (200m) weighting
- Rainfall and fogs - Estimates of wet and dry removal rates

PM2.5 Measurements in NYC - Week of Sept 10 2001



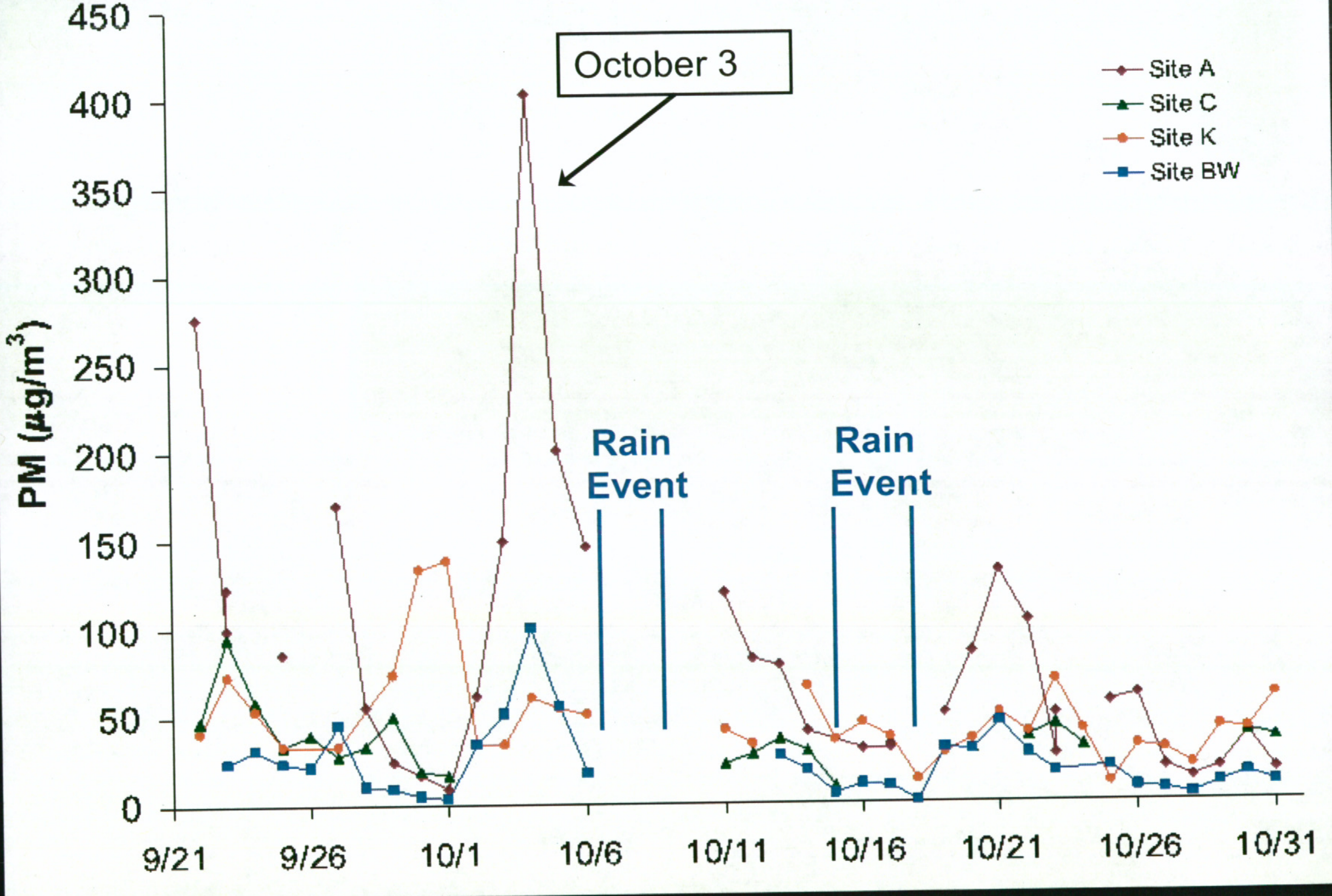
Coarse and Fine Aerosols in New York City

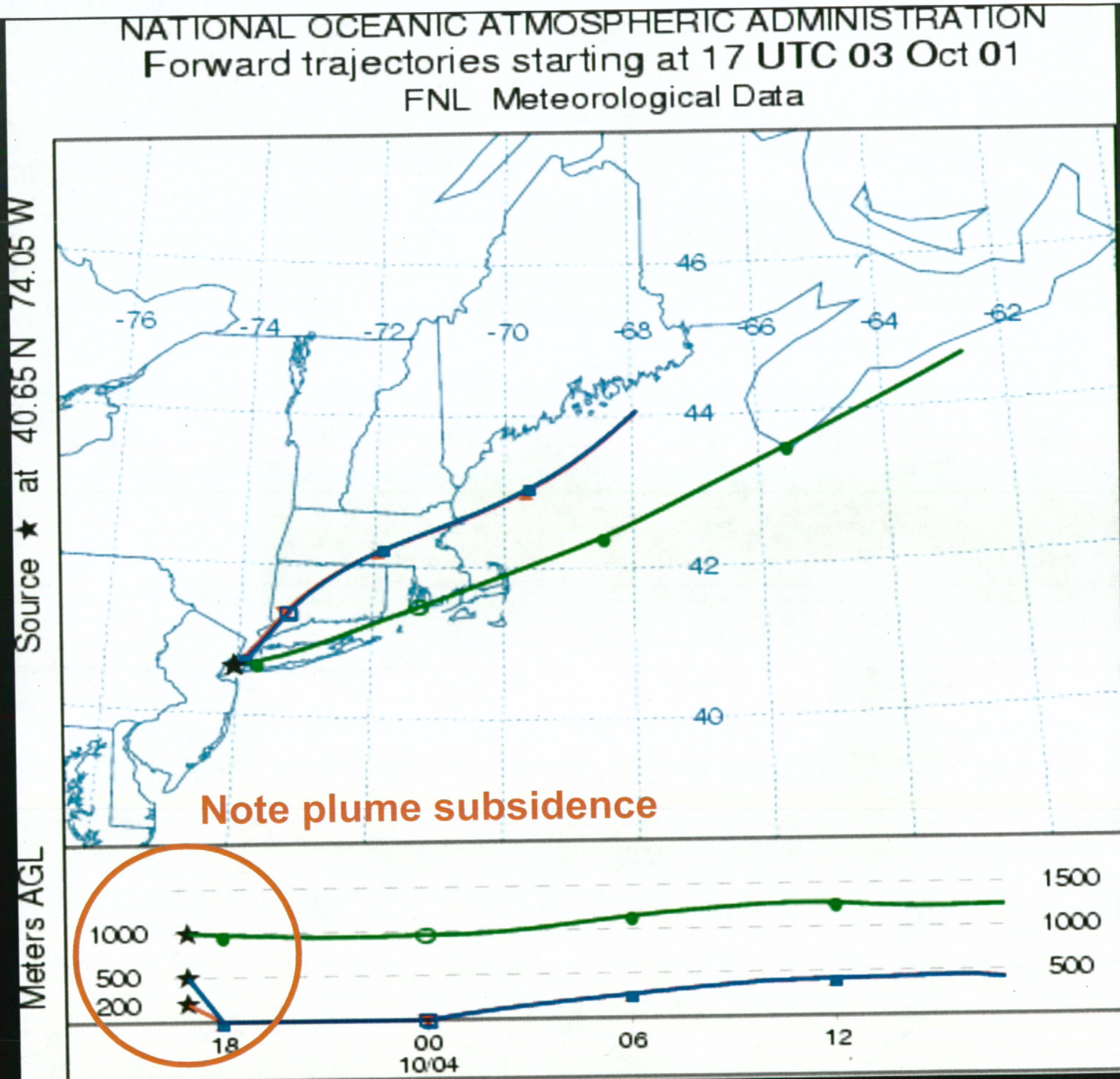
1 hr DRUM samples, LLNL STIM analysis, UC Davis DELTA Group



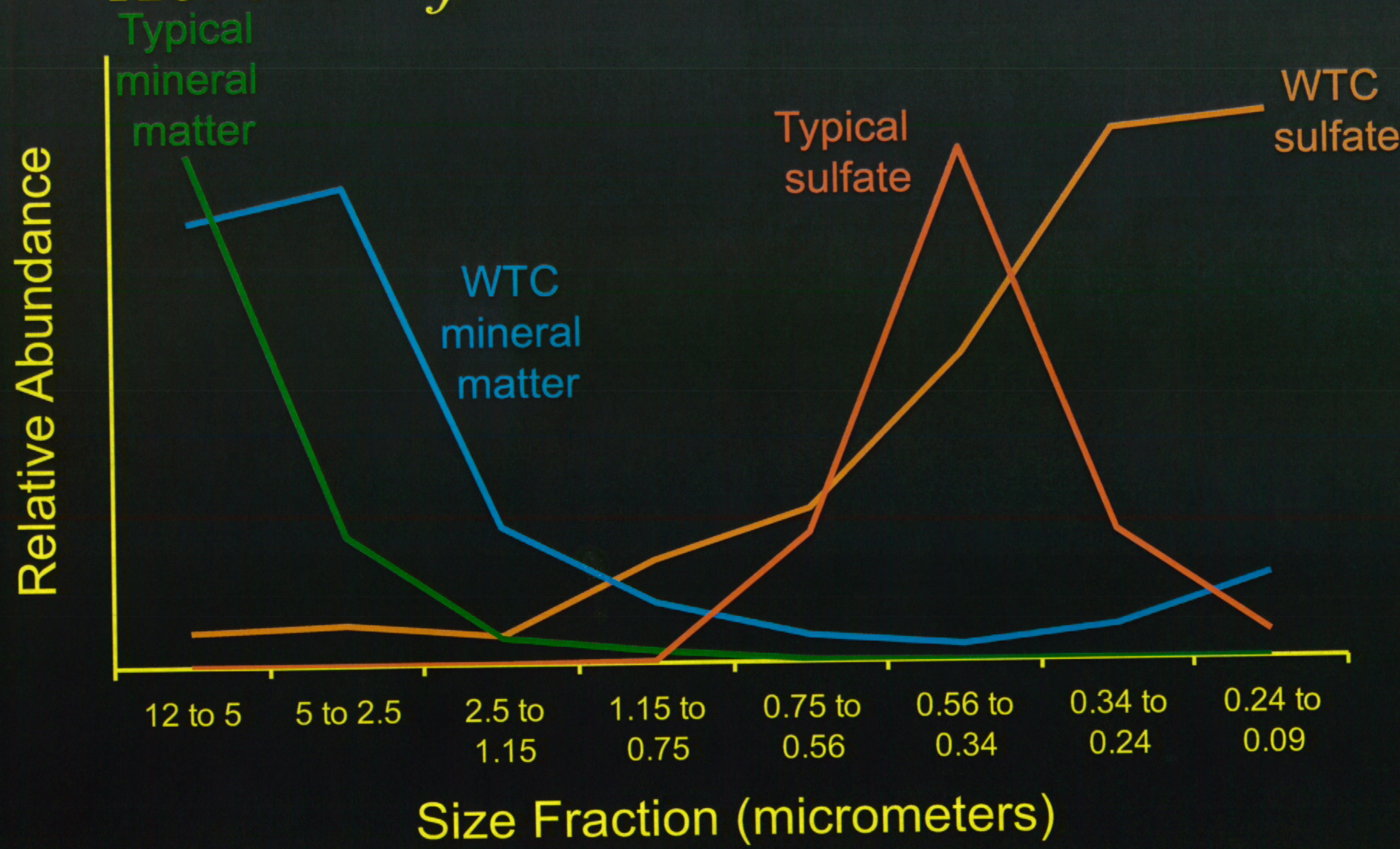
Note: PM10 is roughly PM12, no ultra-fines;
on 10/18,19: 10/26-30 PM10 = PM5.0
PM2.5 contains no ultra fines < 0.1 micons

EPA Analysis of PM_{10} Mass
24 hour data




NATIONAL OCEANIC ATMOSPHERIC ADMINISTRATION
Forward trajectories starting at 17 UTC 03 Oct 01
FNL Meteorological Data
Source ★ at 40.65 N 74.05 W
-76
-74
-72
-70
-68
-66
-64
-62
46
44
42
40
Note plume subsidence
Meters AGL
1000
500
200
1500
1000
500
18
00
10/04
06
12

Anomalous Size Distribution of Aerosols from the WTC, October 3



Why do we care about very fine ($0.26 > D_p > 0.09$ μm) aerosols?

⇒ EPA (AAAR, 10/2002) summarized 5 causal factors most likely to explain the statistically solid data connecting fine $PM_{2.5}$ aerosols and human health.

- → Biological aerosols (bacteria, molds, viruses…)
- → acidic aerosols
- → very fine/ultra fine (< 0.1 μm) insoluble aerosols
- → fine transition metals
- → high temperature organics

⇒ 4 of the 5 reached unprecedented ambient levels in the very fine aerosol plumes from the WTC collapse piles

On most days, the plumes lofted above NYC so that only those on or near the WTC site breathed these aerosols.

Why was the debris pile so hot, so long?

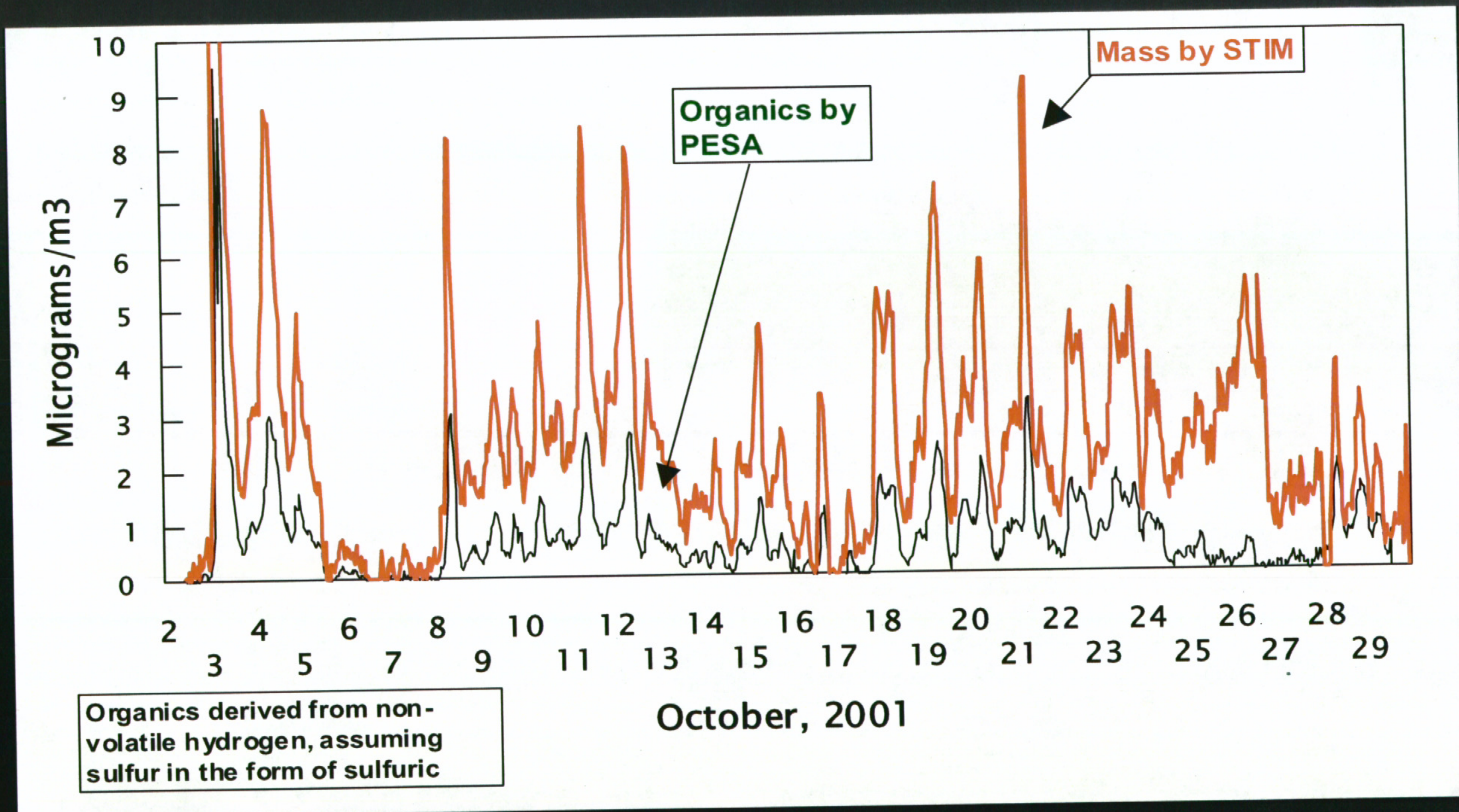
⇒Energy (est.) (in units of 10^{11} joules)

- → Kinetic energy of falling building 5 (+2.5°C)
- → Chemical energy of cars in garage 10
- → Chemical energy of diesel/Con Ed oil 150
  - Especially under WTC #7
- → Chemical energy of building combustibles 430
  - Perhaps 15% burned before the buildings collapsed

The surface and near sub-surface debris pile was hot enough to melt aluminum, make steel red hot, and burned until Dec. 19.

But this is still much cooler than typical sources of very fine particle metals such as power plants, smelters, and diesels.

Very fine mass by STIM and estimated total organic matter from PESA



Very fine aerosol plumes at Varick Street

⇒ 18 events with very fine ($0.26 > D_p > 0.09$ μm) aerosol mass > 3.0 μg/m³, > 10 x background, in 3 to 6 hr plumes

Criteria		# events
HYSPLIT wind in SSW quadrant		14 + 1 calm
Very fine organics	> 1.0 μg/m³,	16
2.5 to 5 μm cement dust	EF > 2.5	16
2.5 to 5 μm sulfate	> 0.3 μg/m³	15
Simultaneous ground based 3 hr hazes plumes at LaGuardia airport, Lv < 15 km		5 (+ 3 days Sept.)

5 events met all 5 criteria, 4 more met 4 of the 5 criteria – these 9 are labeled "highly probable events";

6 met 3 of the 5 criteria – labeled "WTC influence"

a total of 15 events over 20 days,

1 met only 2 of the criteria - uncertain source

2 met one of the criteria, but not SSW quadrant – labeled "non-WTC plumes

none of the criteria – labeled "background days" - a total of 6 days

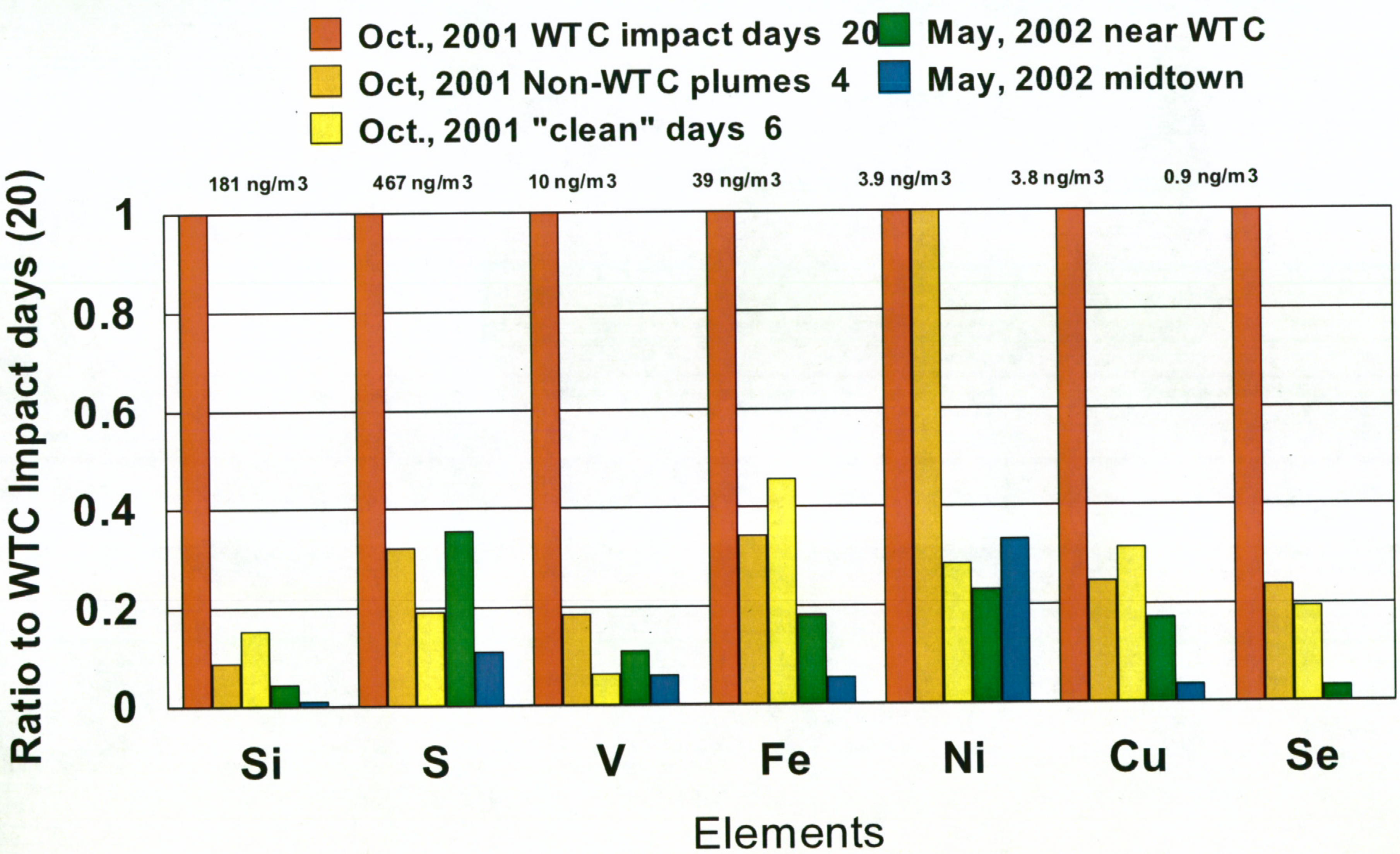
Concentration of Very Fine Aerosols

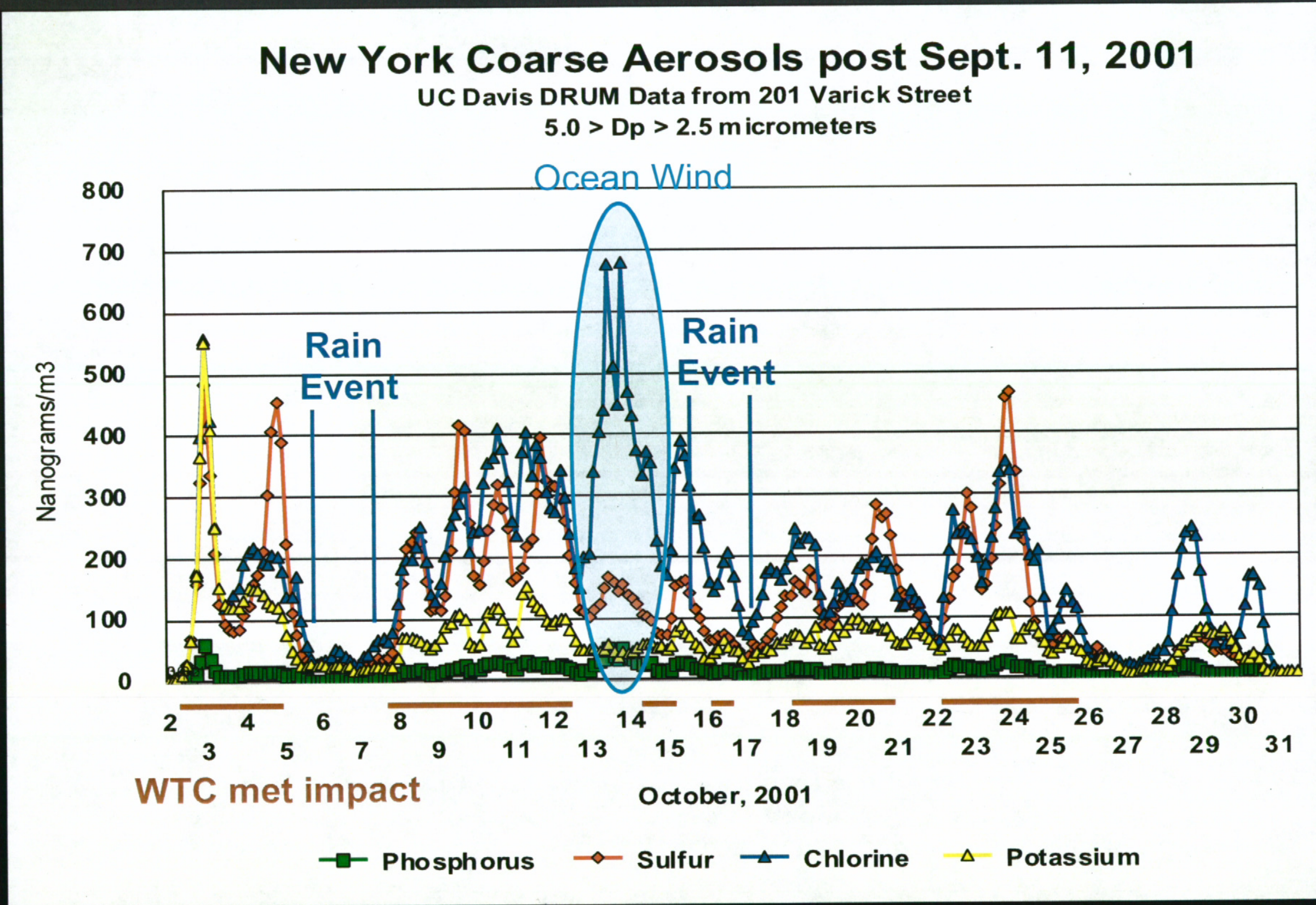
3 hr peak averages, Micrograms/m³ (ng/m³ - V, Ni)

Date	WTC impact	Mass	Org.	SiO_2	H_2SO_4	*V*	*Ni*
Oct. 7	No	0.5	0.04	0.02	0.1	*0.1*	*0.1*
Oct. 3	Yes	50.6	9.3	1.4	17.1	*115*	*22.7*
Oct. 4	Yes	9.3	3.2	2.6	3.7	*61*	*8.0*
Oct. 5	Yes	4.7	1.5	0.9	1.9	*3*	*1.3*
Oct.12	Yes	8.2	3.0	2.9	2.2	*24*	*7.1*
Oct.15	Yes	4.8	1.6	1.3	1.1	*3*	*17.3*
Oct.24	Yes	3.8	1.0	0.2	1.6	*5*	*6.7*
Oct.29	No	2.4	1.2	0.07	0.9	*2*	*1.6*
Kuwait	-	na	na	0.6	5.5	*na*	*5.0*
Beijing	-	na	na	1.1	6.7	*0.8*	*1.8*

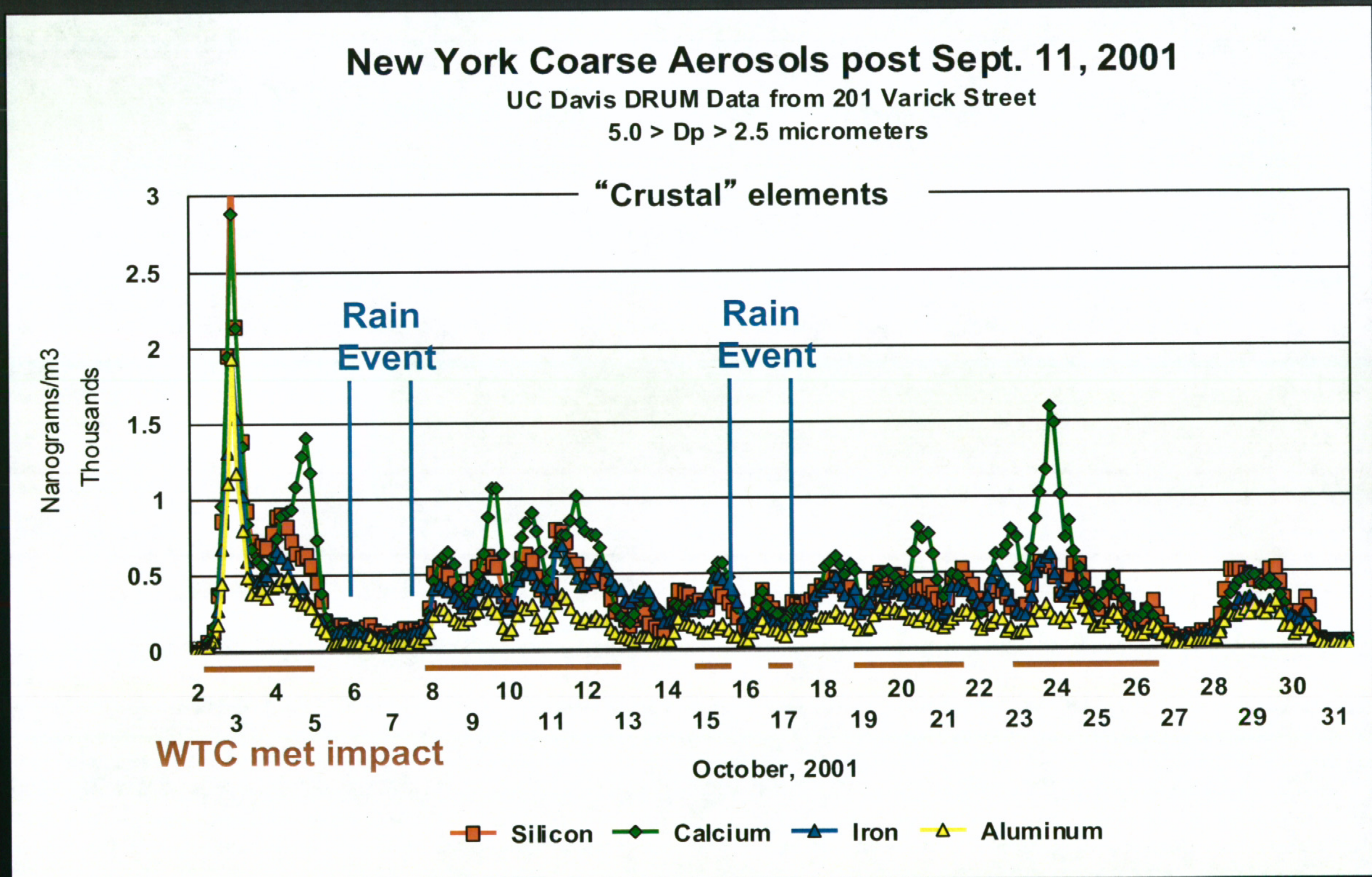
Comparison of October, 2001 to May, 2002

Very fine particles 0.26 > Dp > 0.09 microns





New York Coarse Aerosols post Sept. 11, 2001
UC Davis DRUM Data from 201 Varick Street
5.0 > Dp > 2.5 micrometers
Ocean Wind
Rain Event
Rain Event
Nanograms/m3
0
100
200
300
400
500
600
700
800
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
WTC met impact
October, 2001
Phosphorus
Sulfur
Chlorine
Potassium

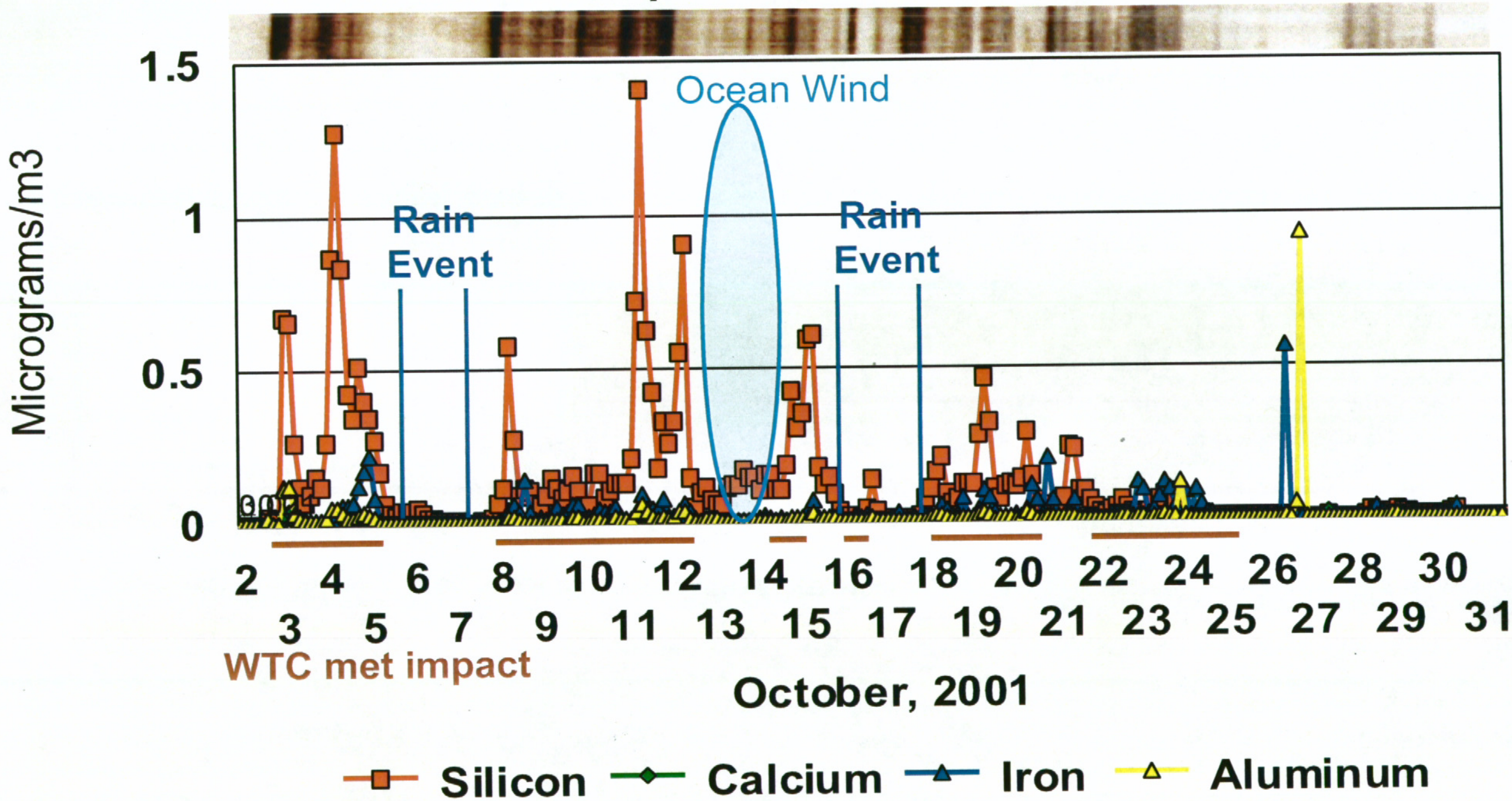


New York Coarse Aerosols post Sept. 11, 2001
UC Davis DRUM Data from 201 Varick Street
5.0 > Dp > 2.5 micrometers
"Crustal" elements
Nanograms/m3
Thousands
0
0.5
1
1.5
2
2.5
3
Rain Event
Rain Event
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
WTC met impact
October, 2001
Silicon
Calcium
Iron
Aluminum

New York very fine Aerosols post Sept. 11, 200

UC Davis DRUM Data from 1.8 km NNE

0.26 > Dp > 0.09 micrometers



Proposed explanation of very fine aerosols size and composition

- Problems:
  - We see very fine aerosols typical of combustion temperatures far higher than the WTC collapse piles
  - We see some elements abundantly and others hardly at all, despite similar abundances in the collapse dust
  - We see organic species in the very fine mode that would not survive high temperatures
- Explanation
  - The hot collapse piles are converting some species to gasses that can escape to the surface of the piles and then form aerosols, a process that yields very fine particles

Incineration with 10% chlorine	Boiling Point	Earth crustal	Bulk dust EPA	Bulk dust Lioy	Volatility Temp	Principal Species
Metal	°C	ppm	ppm	ppm	°C	
Chromium	2639	102	71.5	165	1594	CrO_2 , O_3
Beryllium	1280	2.8	1.75	3.2	1042	$Be(OH)_2$
Barium	1634	425	195	381	895	$BaCl_2$
Nickel	2834	84	15.5	43.5	686	$NiCl_2$
Antimony	697	0.2	na	na	653	Sb_2O_3
Silver	2190	0.004	4.9	2.3	620	AgCl
Selenium		0.05	< 0.96	na	315	SeO_2
Cadmium	761	0.15	3.8	7.2	211	Cd
Vanadium	3480	120	18.3	38.9	147	VCl_4
Thallium	1464	9.6	<0.96	1.4	136	TlOH
Osmium	4224	0.0015	na	na	40	OsO_4
Arsenic	814	1.8	< 0.96	2.6	32	As_2O_3
Mercury	353	0.085	0.37	nd	25	Hg
SiO_2	1725	9000	na	na	12	$SiCl_4$
Lead	1748	14	98	305	-12	$PbCl_4$

Predicted metal emissions from the WTC collapse piles

- Assumption: The molecular compounds will oxidize when these gasses reach the hot surface, which was capable of spontaneous surface fires until mid-December.

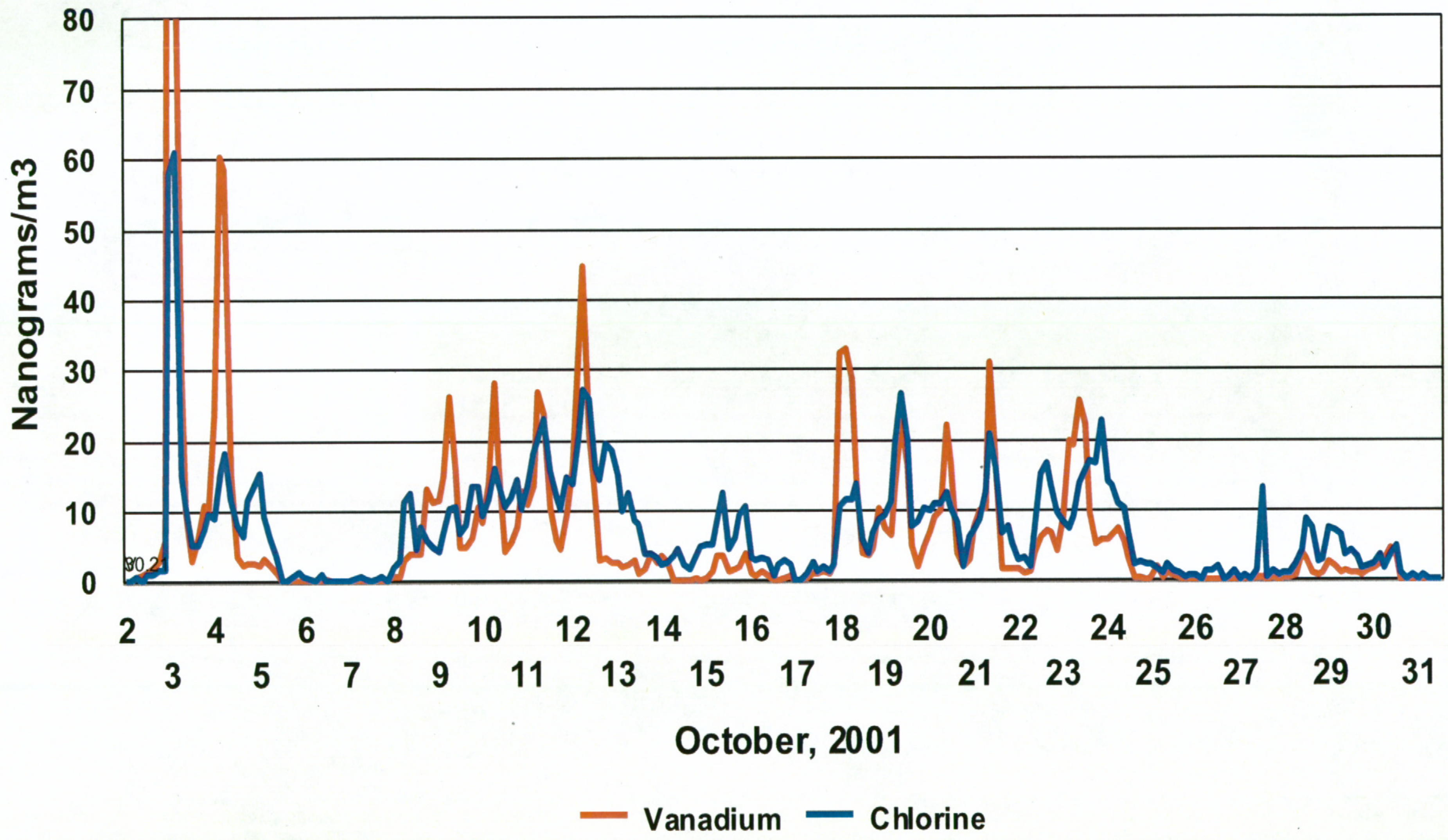
- There will then be fine metal aerosols, probably as oxides, richest in those elements with both high abundance and chlorine-depressed volatility temperatures –
  - **Silicon, vanadium, nickel, lead**

- There will then be an absence of fine metal aerosols with high volatility temperatures, even if their abundance is high –
  - **Chromium, barium**

Very fine mode aerosols in WTC plume and non-plume conditions

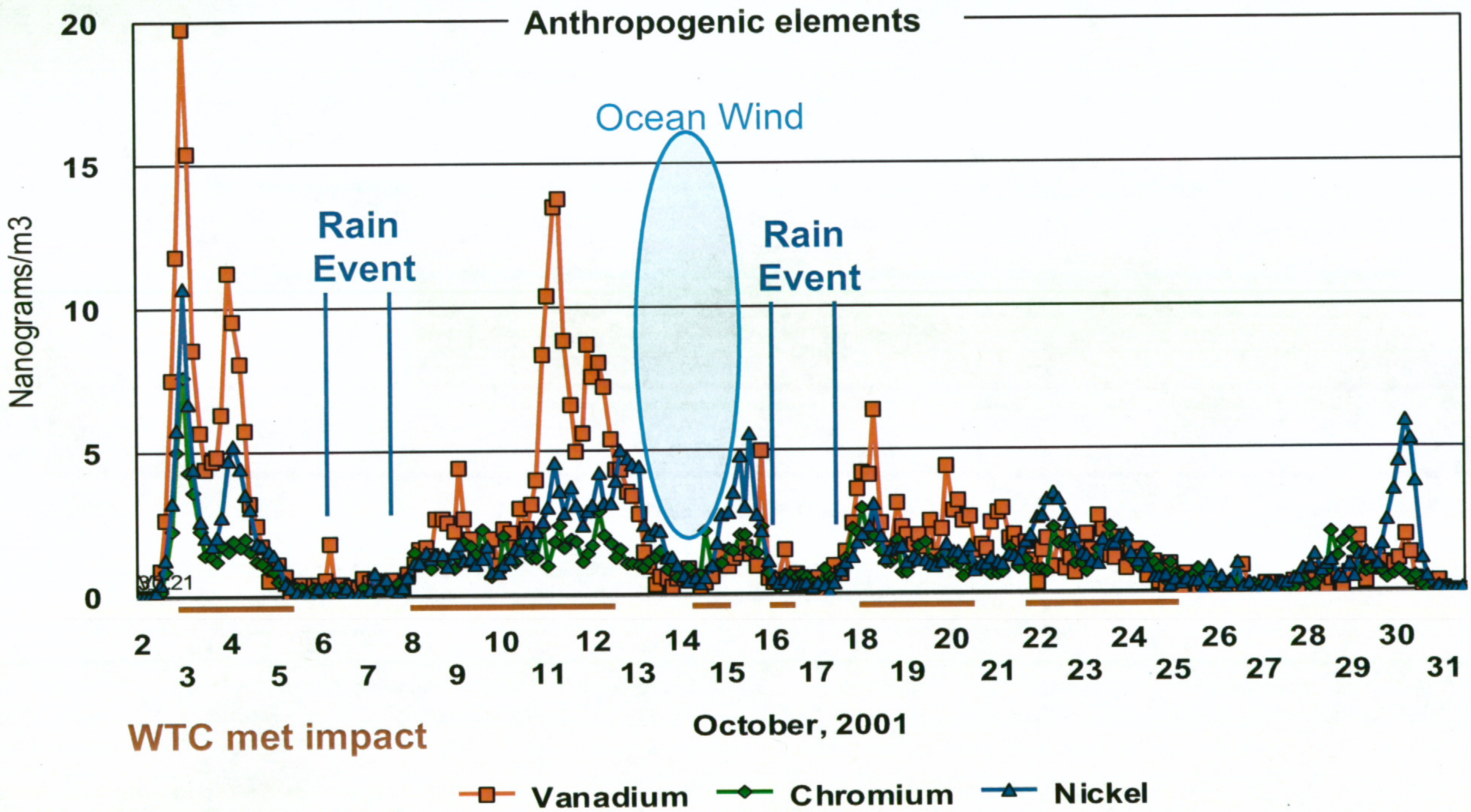
Very fine aerosols	October 7 background	October 3 WTC plume	Average Abundance WTC dust	Volatility Temperature 10% chlorine
0.26 - 0.09 µm	µg/m^3	µg/m^3		
Mass	0.53	50.7	na	na
Organics	0.04	9.3	na	na
Sulfur	0.04	5.6	na	na
	ng/m^3	ng/m^3	ppm	^{o}C
Silicon	11	698	abundant	12
Vanadium	0.1	114	30	147
Lead	<0.5	26	200	-12
Nickel	0.1	23	30	686
Chromium	<0.1	1.5	120	1594
Barium	< 0.1	< 0.5	290	895

Very fine aerosols 0.26 . Dp > 0.09 micrometers



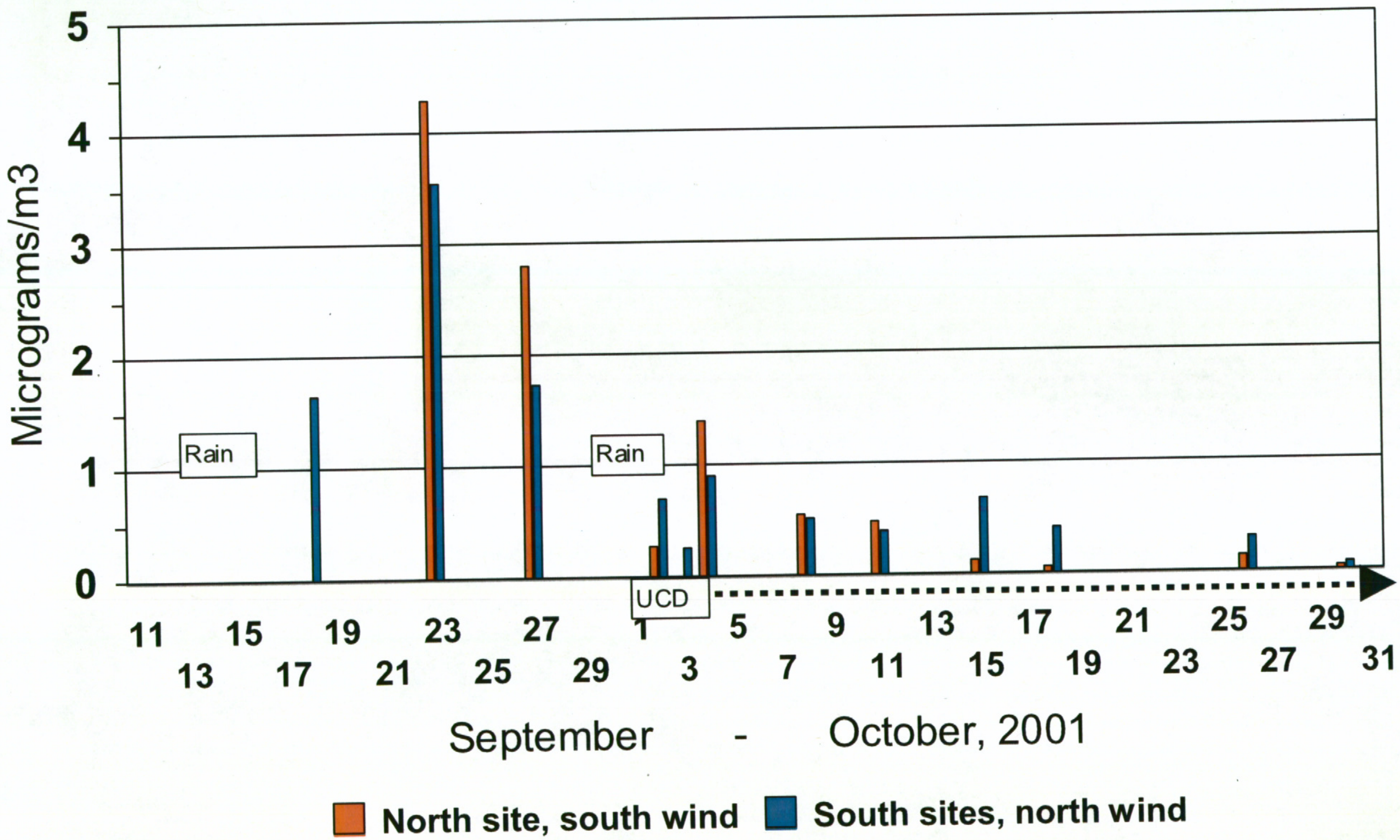
New York Aerosols post Sept. 11, 2001

UC Davis DRUM Data from 201 Varick Street



Lead in lower Manhattan near WTC

EPA 12 hr lead values



Conclusions – WTC Aerosols

(additions since September, 2002 in blue)

- There were heavy and continuing emissions of aerosols in narrow plumes of unusual size and composition from the WTC collapse site that on 9 to 15 occasions impacted 201 Varick St, 1.8 km NNE.
- Coarse particles were similar to the initial collapse aerosols (cement, dry wall, glass, ...) but had chemicals and soot from the ongoing combustion. Little asbestos was expected or observed.
- The presence of unprecedented (vis. Beijing, Kuwait) levels of very fine ($0.26 > D_p > 0.09$ μm) particles by mass and number in narrow plumes was more typical of an industrial source, specifically a chlorine rich municipal incinerator, than any normal ambient air situation. Upwind sources were a very minor contribution.
- The very fine silicon and sulfur and many of the coarse metals like vanadium decreased steadily during October. Very fine particles near the WTC site in May, 2002, were generally < 10% of the October, 2001 plume impact days at Varick Street. (except S, Ni)

For more details……..

- ⇒Lioy et al, Environmental Health Perspectives 110, #7 703-714 July, 2002 (3 bulk samples collected dry, 9/16, 9/17, exhaustive analyses)
- ⇒Cahill et al (in press, Aerosol Science & Technology (2003)
- ⇒EPA web site www.epa.gov/ response to 9/11, EPA ORD analysis and Power Point presentation
- ⇒NASA EOS Landsat Thematic Mapper , IKONOS satellite photos from Spaceimaging.com,
- ⇒ DELTA web site http://delta.ucdavis.edu, WTC data and the Fall, 2002 ACS Powerpoint presentation.

Acknowledgements

- We wish to thank all the people and groups that contributed time and resources for this unfunded project, especially LLNL (STIM/PESA grant) , ALS LBNL (S-XRF beam time), UCD DELTA Group staff, and DOE EML NYC.
- The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model (http://www.arl.noaa.gov/ready.html) and the READY web site used in this publication.
- We gratefully acknowledge the support of the American Lung Association for the May, 2002 study, and Prof. John Ondov for urban data examples.
- We wish to thank all the people who helped increase our understanding of the WTC problem, and in particular the very helpful analysis of Prof. Ian Kennedy (UCD Engineering) and Dr. William Wilson, (ORD, US EPA.
- Finally, we want to thank the organizers of this symposium and the support they provided for this program.

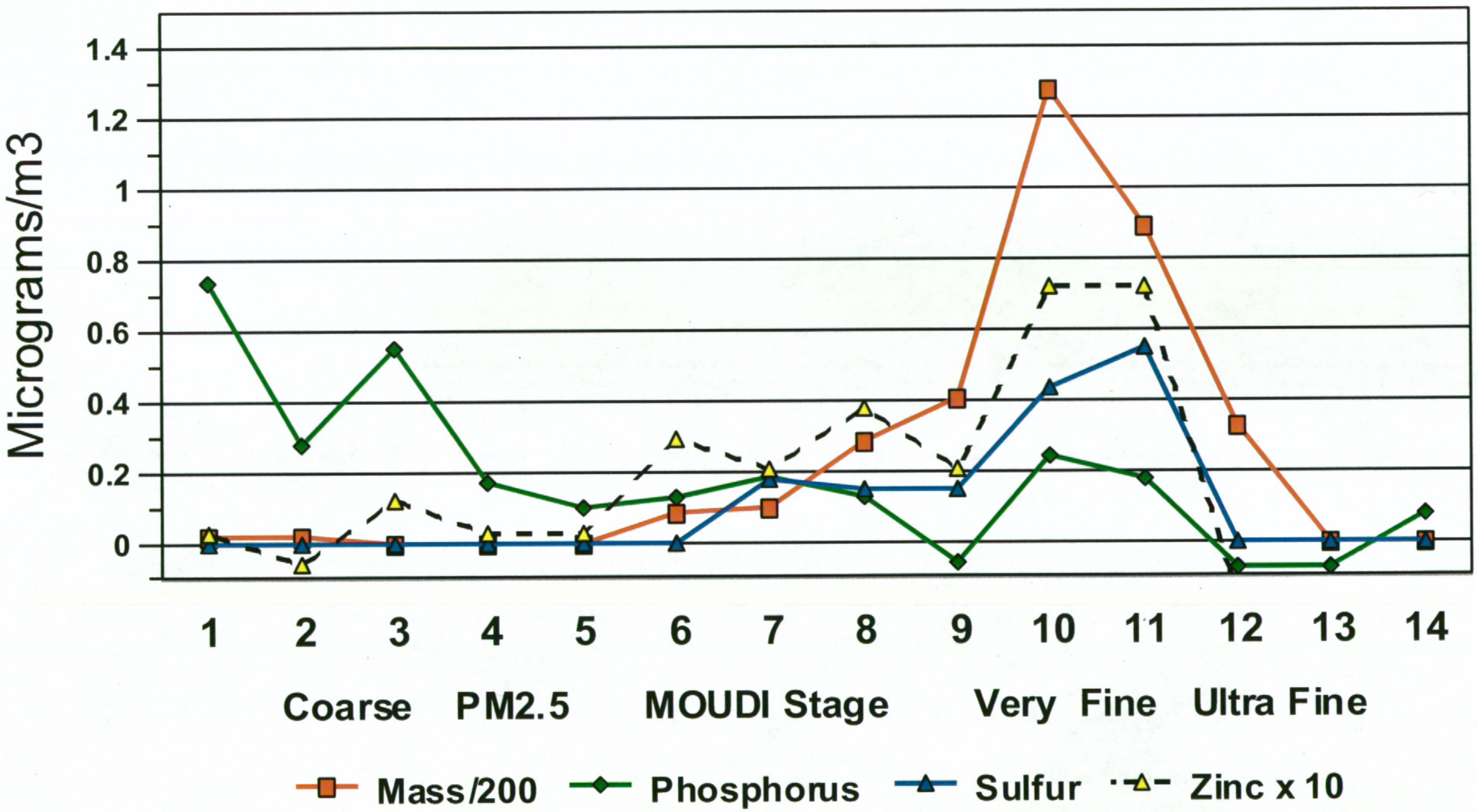
Other Aerosol Sources – October, 2001

- ⇒Regional Aerosols > 100 km
  - →Sulfates, organic matter
- ⇒New York/New Jersey Metropolitan 15 – 100 km
  - →Natural oceanic aerosols
  - →Heavy fuel oil
    - Power plants (all reportedly using natural gas)
    - Ships
  - →Other sources
- ⇒Local < 15 km
  - →Diesel generators and trucks, smoking cars
  - →New York industrial sources

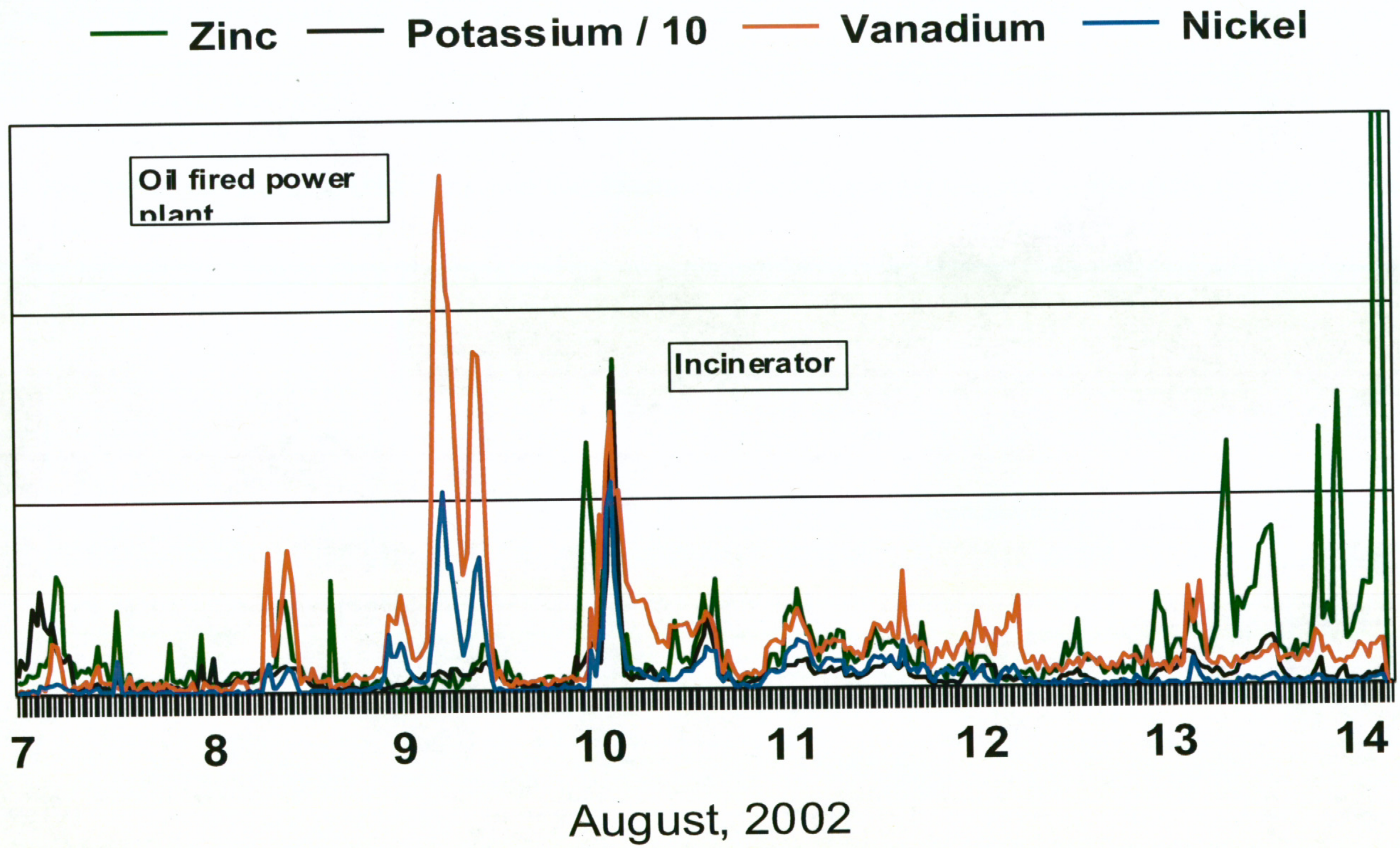
Elemental Analysis of Size Resolved Diesel Particles

C-12 Sample #4, CA fuel , Dilution :1

S-XRF Analysis, UC Davis; on Mylar, no grease



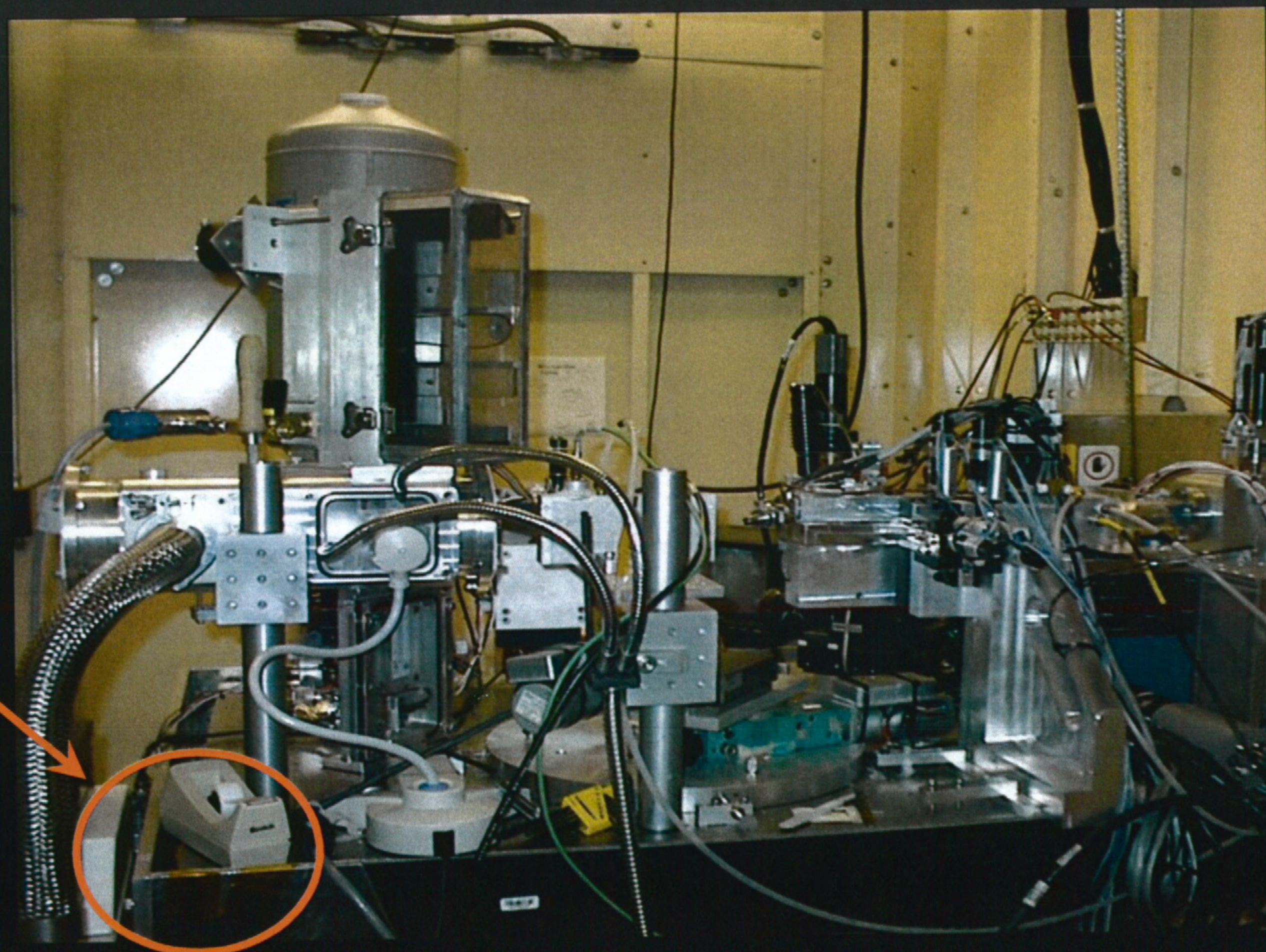
y fine (0.26 > Dp > 0.09 micron) aerosols at an eastern US city.
Typical source signatures, Summer, 2002




Aerosol DRUM Strips – coarse to very fine
New York City,
Oct 2 to 30, 2001
Beijing, P.R. China
March 20 to April 26, 2001
Coarse
~12 to 5 µm
5 to 2.5 µm
2.5 to 1.15 µm
1.15 to 0.75 µm
0.75 to 0.56 µm
0.56 to 0.34 µm
0.34 to 0.26 µm
Very fine
0.26 to 0.09 µm

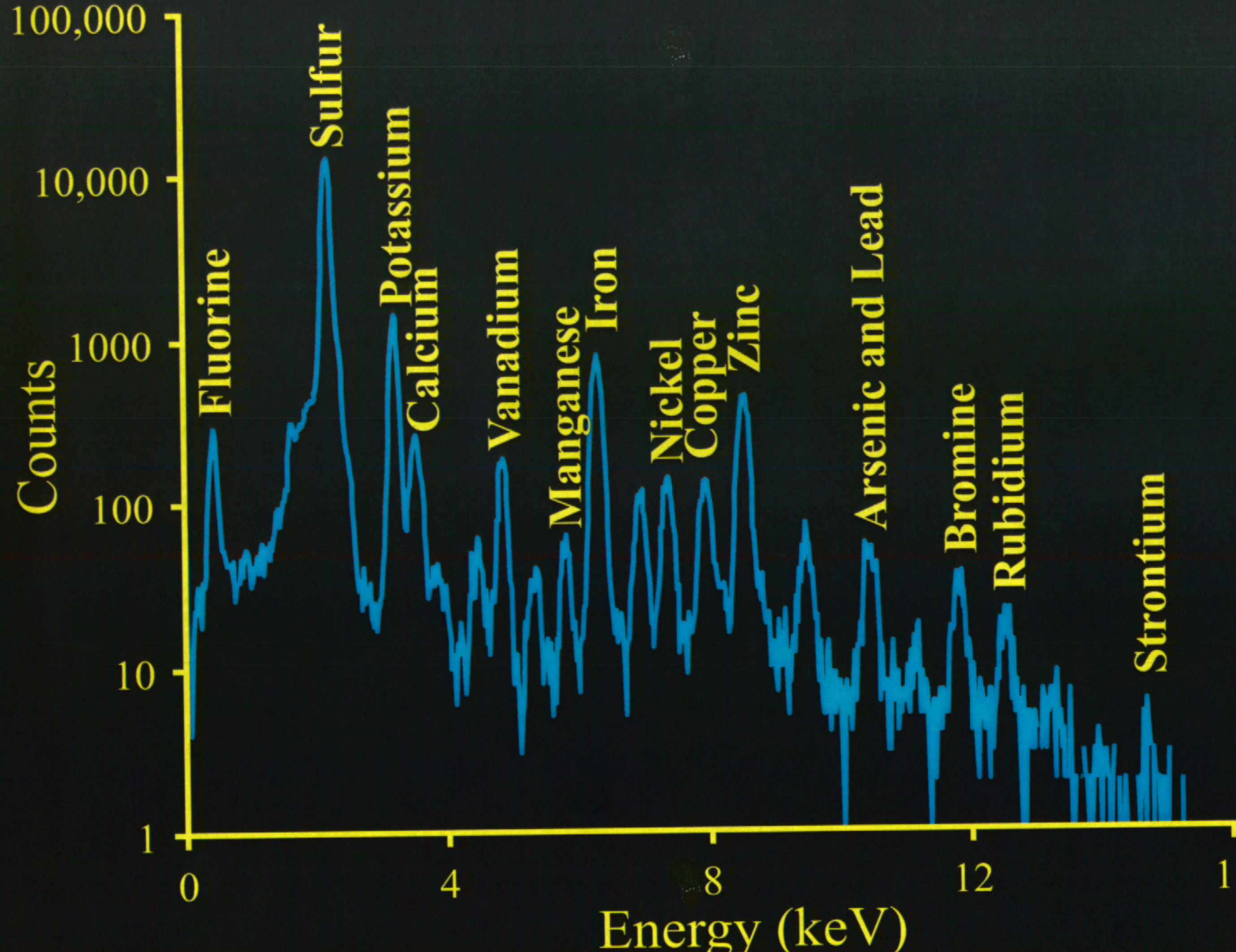
DELTA Group Synchrotron-XRF Facility at the LBNL Advanced Light Source

For scale?
(At least it's not duct tape.)



Typical S-XRF Spectrum

Raw data, Teflon substrate with no blank subtraction



	RTI XRF	IMPROVE	S-XRF
Na	150	100	14
Si	6	23	3
S	4	20	3
V	1	6	0.1
Ni	0.9	0.9	0.2
As	1.7	0.5	0.1
Sr	2.3	1.3	0.3
Cd	7.6	NA	NA
Ba	84	NA	1.0
Pb	4	2	0.6

MDL values (ng/cm^2)

Analysis of coarse aerosols

$D_p > 2.5\mu m$

- Large amounts of coarse aerosol mass was seen during the October 3 3 hr plume (220 $\mu g/m^3$) and smaller amounts later in the month
- Composition was crustal with enhanced calcium (vis cement dust) during times of WTC transport, with pH from 11.0 to 12.1 (USGS, 9/2001)
- Particles were visibly coated with soot
- Numerous non-crustal elements had high enrichment factors showing anthropogenic sources
- Many of these non-crustal elements decreased later in October

But one can argue against this hypothesis

- No convincing local meteorology – street canyon effects, etc,
- Not similar to dust from the immediate collapse (Lioy et al, 2002)
- No prior size/time/compositionally resolved data from NYC for comparison purposes
- No data on emission factors at source
- Strange elemental ratios with no clear sources

Were the aerosols observed at Varick Street from the WTC collapse piles?

- High levels of very fine $< 0.26\ \mu m$ mass, H, and S in short duration (circa 3 hr) plumes
  - Short atmospheric lifetimes, therefore local
- Peaks seen on winds from the Southwest
  - Subsiding isentropic trajectories, so ground impact
- Relatively fine 5.0 to 2.5 μm cement dust with anomalous elements (sulfur, metals,,,)
- On 5 occasions, simultaneous haze plumes at La Guardia

Proposed Answers

⇒Indoor fine particles?

→Either the very fine particles (such as silica) never penetrated the three buildings we tested (most probable) or they were effectively cleaned up (possible).

⇒October 3, 4, and 5?

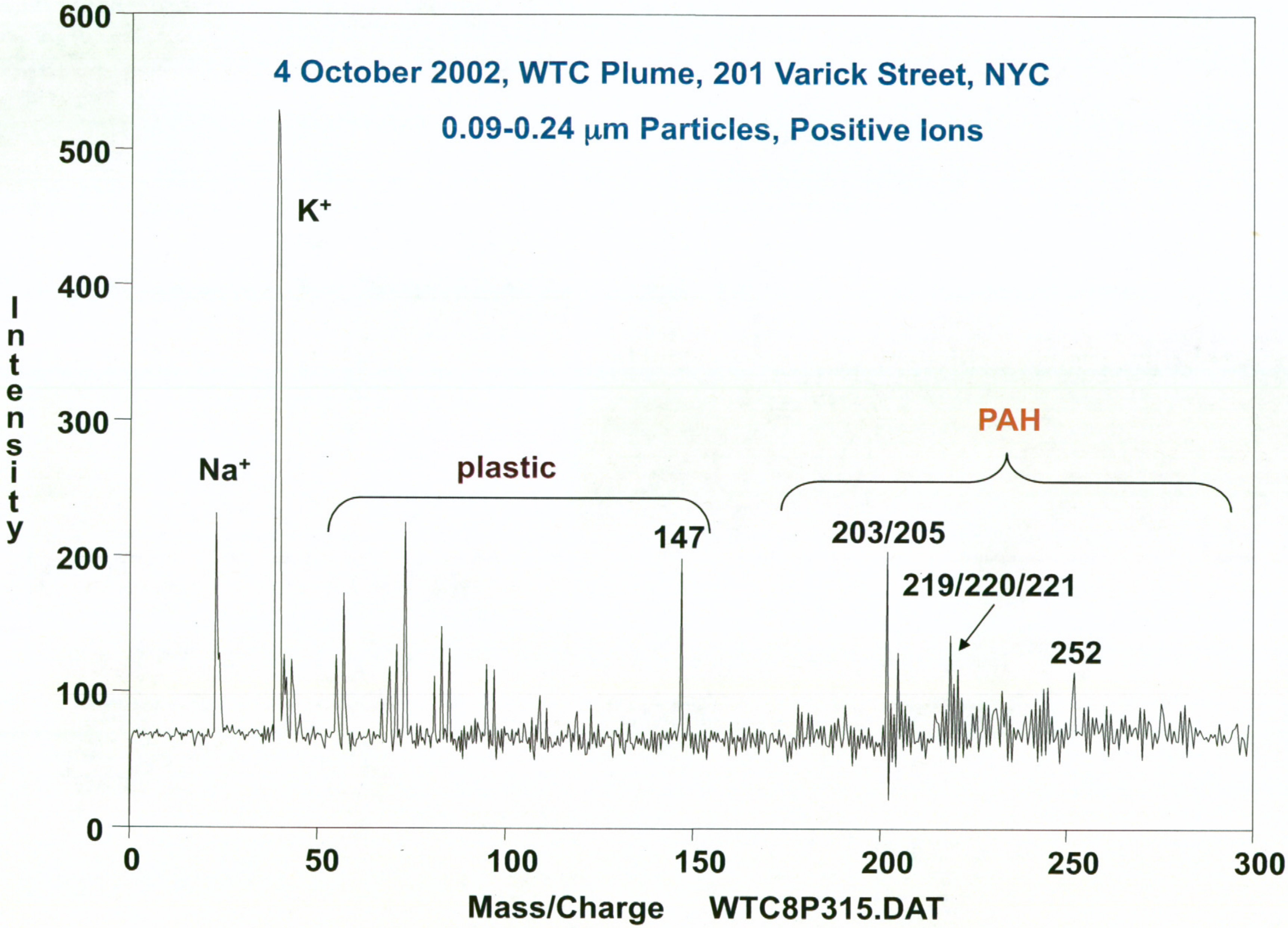
→These days were high because unusual meteorology (plus a cooling WTC debris pile) drove the plume down to 50 m (and below).

Under what conditions and with what efficiency can the WTC plume impact the sampling site, 1.8 km NNE of the WTC and 50 m above ground level?

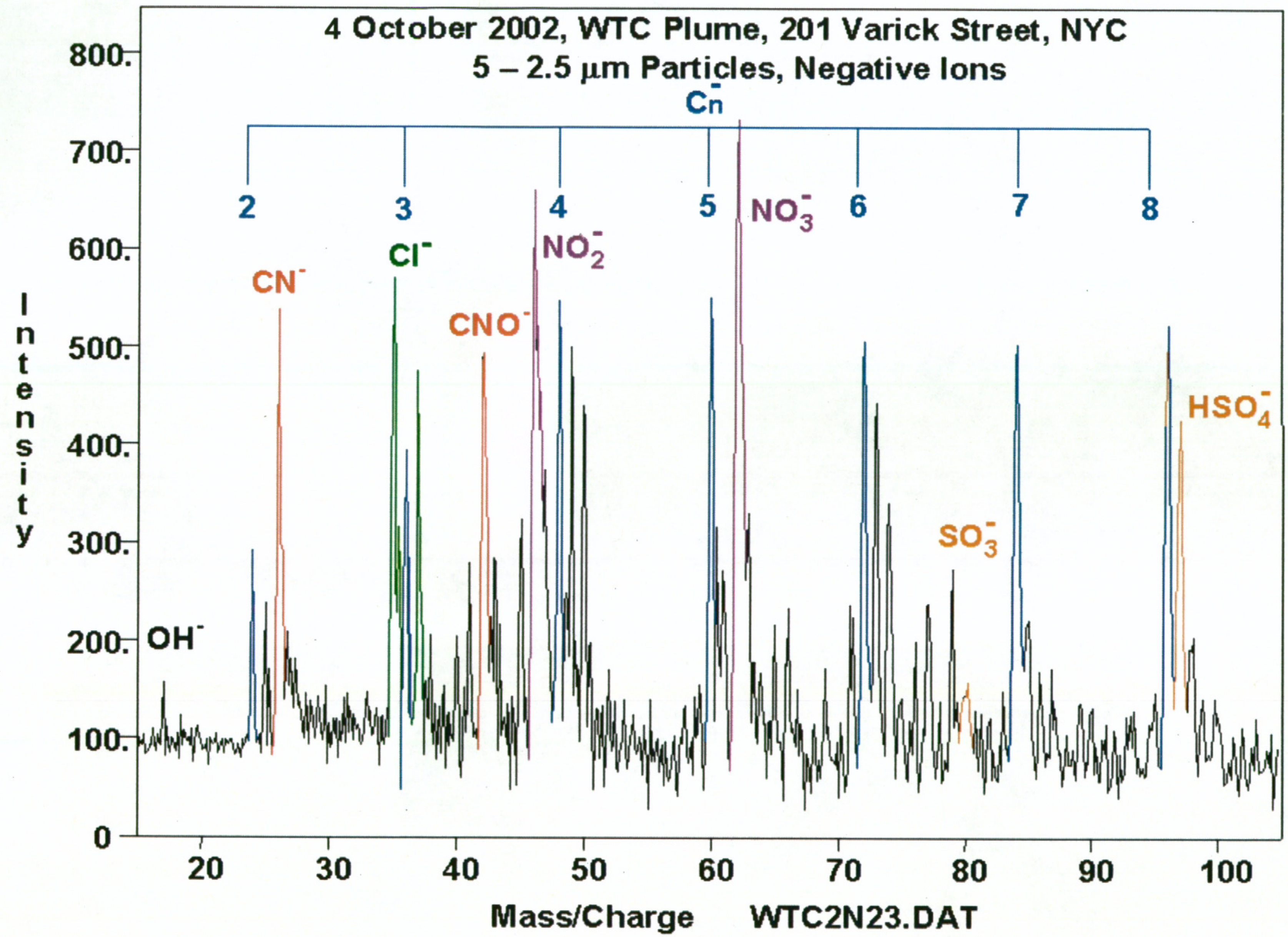
- Wind direction:
  - HYSPLIT trajectory wind from SW
- Plume lofting:
  - Surface temperature of the WTC collapse site
- Wind speed:
  - "Residence Time" 1/u (200m) weighting
- Vertical atmospheric stability:
  - HYSPLIT isentropic trajectories subsiding
- Removal - settling, diffusion, rainfall and fogs:
  - Estimates of wet and dry removal rates

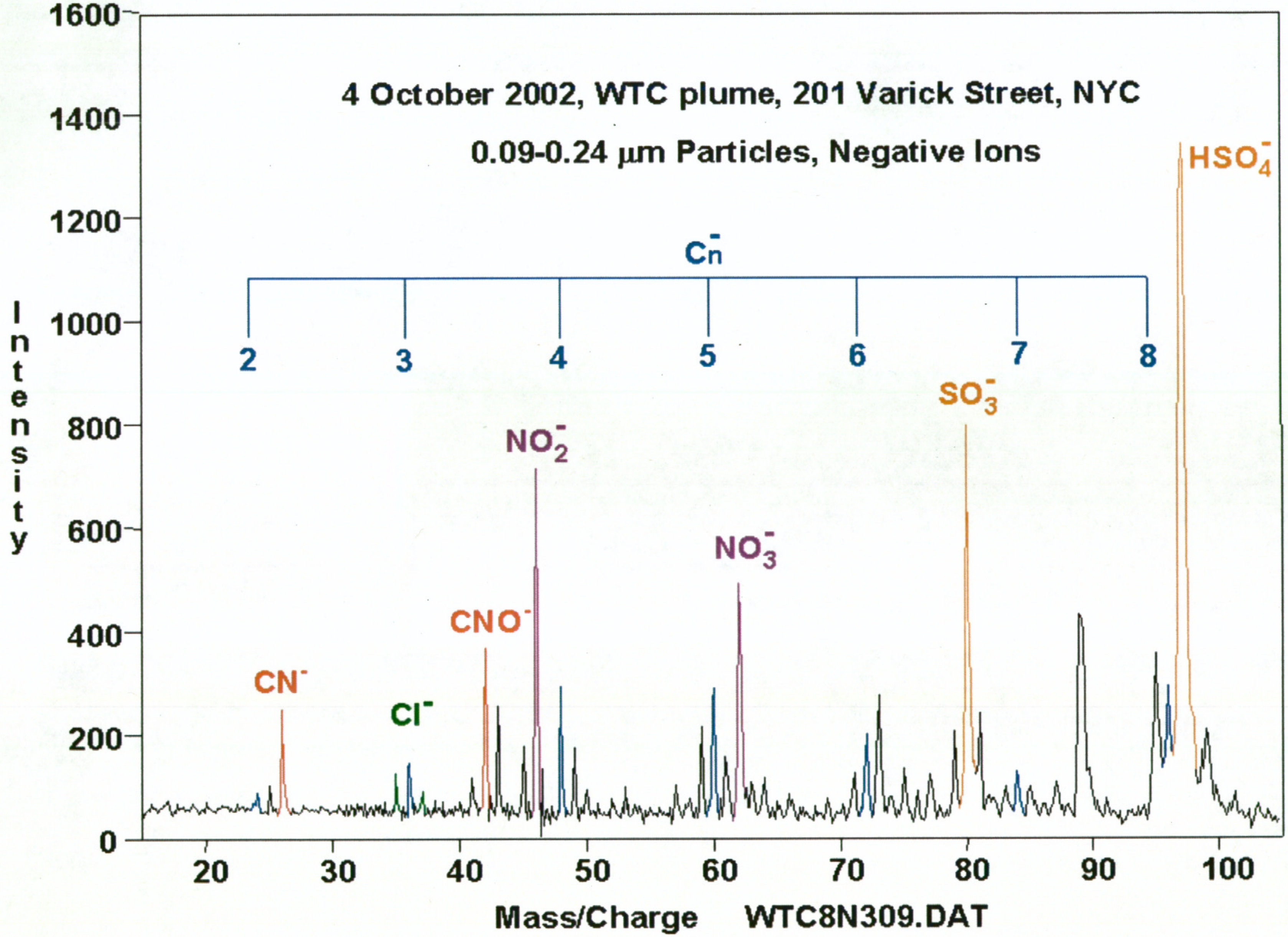
Outstanding Questions - WTC Aerosols

- What are the health impacts of these aerosols?
- Do the very fine particles linger indoors?
- Why was October 3 so impacted?
- What is the source of the S/V/Ni "fuel oil" combustion signature?
- What is the morphology of the metal and soot-coated coarse particles?
- What are the sources and impacts of the organic matter?

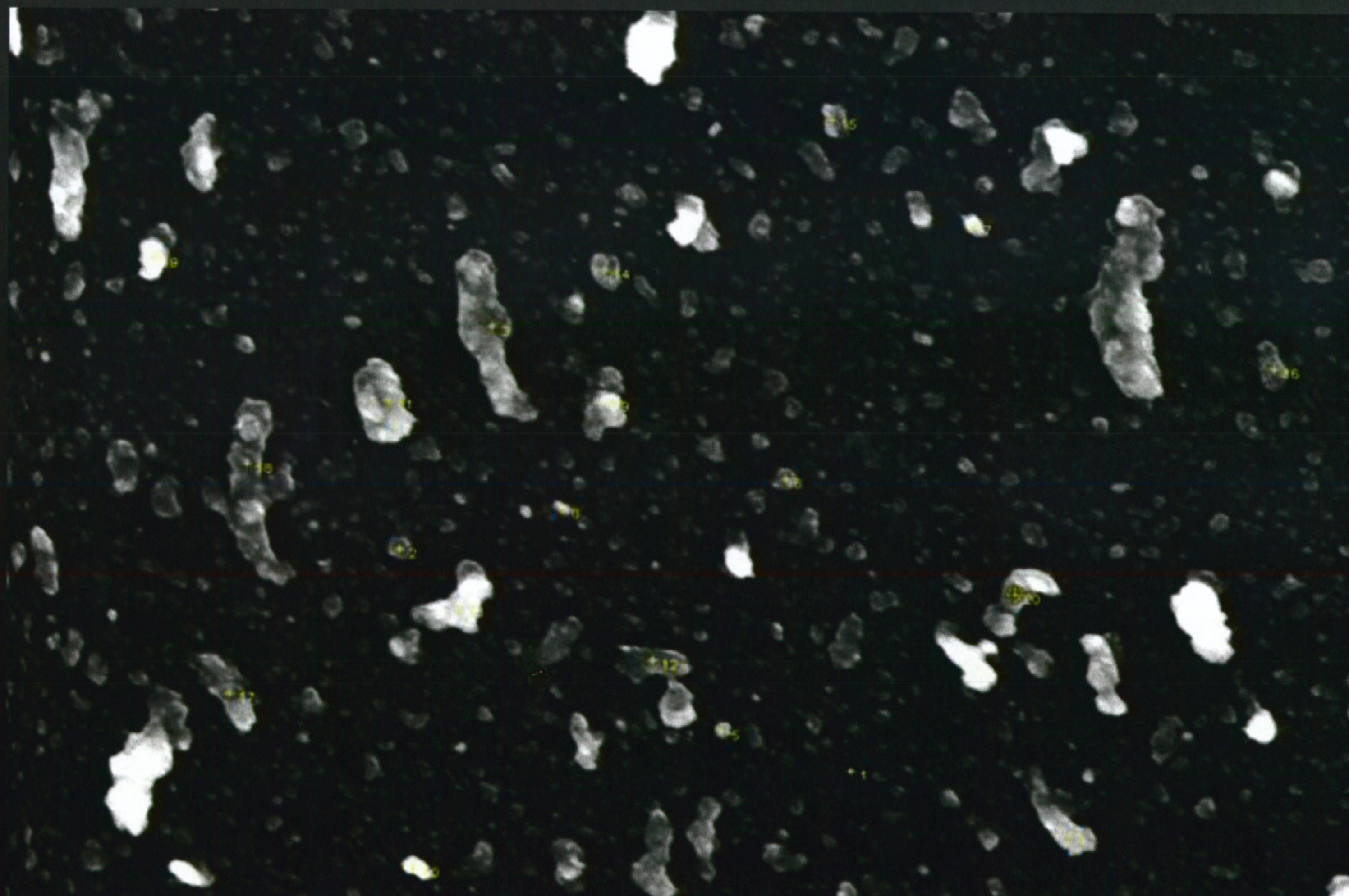


4 October 2002, WTC Plume, 201 Varick Street, NYC
0.09-0.24 μm Particles, Positive Ions
Intensity
600
500
400
300
200
100
0
K+
Na+
plastic
147
PAH
203/205
219/220/221
252
0
50
100
150
200
250
300
Mass/Charge
WTC8P315.DAT


4 October 2002, WTC Plume, 201 Varick Street, NYC
5 – 2.5 µm Particles, Negative Ions
C_n^-
2
3
4
5
6
7
8
OH$^-$
CN$^-$
Cl$^-$
CNO$^-$
NO_2^-
NO_3^-
SO_3^-
HSO_4^-
Intensity
0
100.
200.
300.
400.
500.
600.
700.
800.
20
30
40
50
60
70
80
90
100
Mass/Charge
WTC2N23.DAT


4 October 2002, WTC plume, 201 Varick Street, NYC
0.09-0.24 µm Particles, Negative Ions
Intensity
0
200
400
600
800
1000
1200
1400
1600
20
30
40
50
60
70
80
90
100
Mass/Charge
WTC8N309.DAT
C_n^-
2
3
4
5
6
7
8
CN^-
Cl^-
CNO^-
NO_2^-
NO_3^-
SO_3^-
HSO_4^-

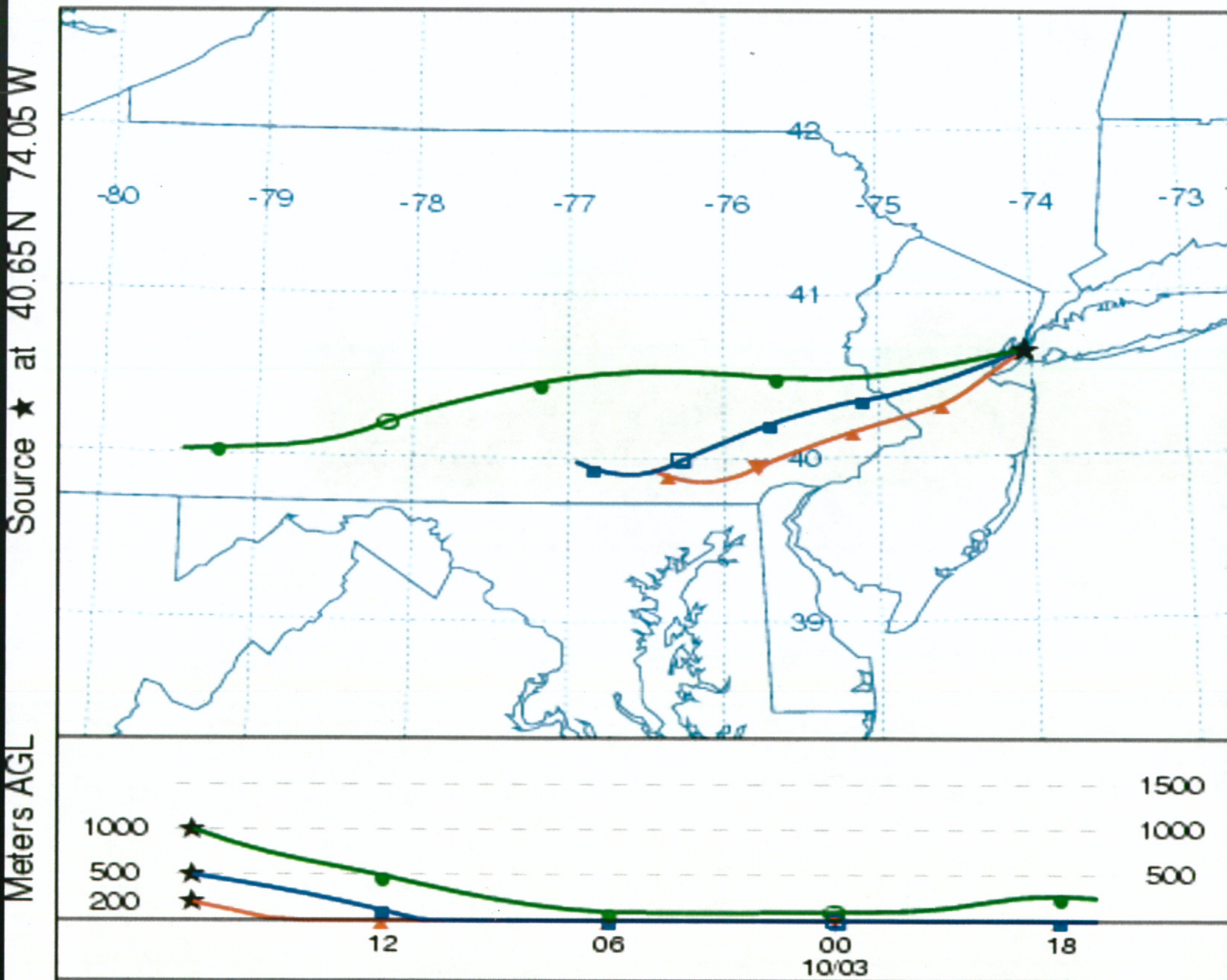
Very fine Particles 0.26 to 0.09 μm, Oct. 3



NATIONAL OCEANIC ATMOSPHERIC ADMINISTRATION

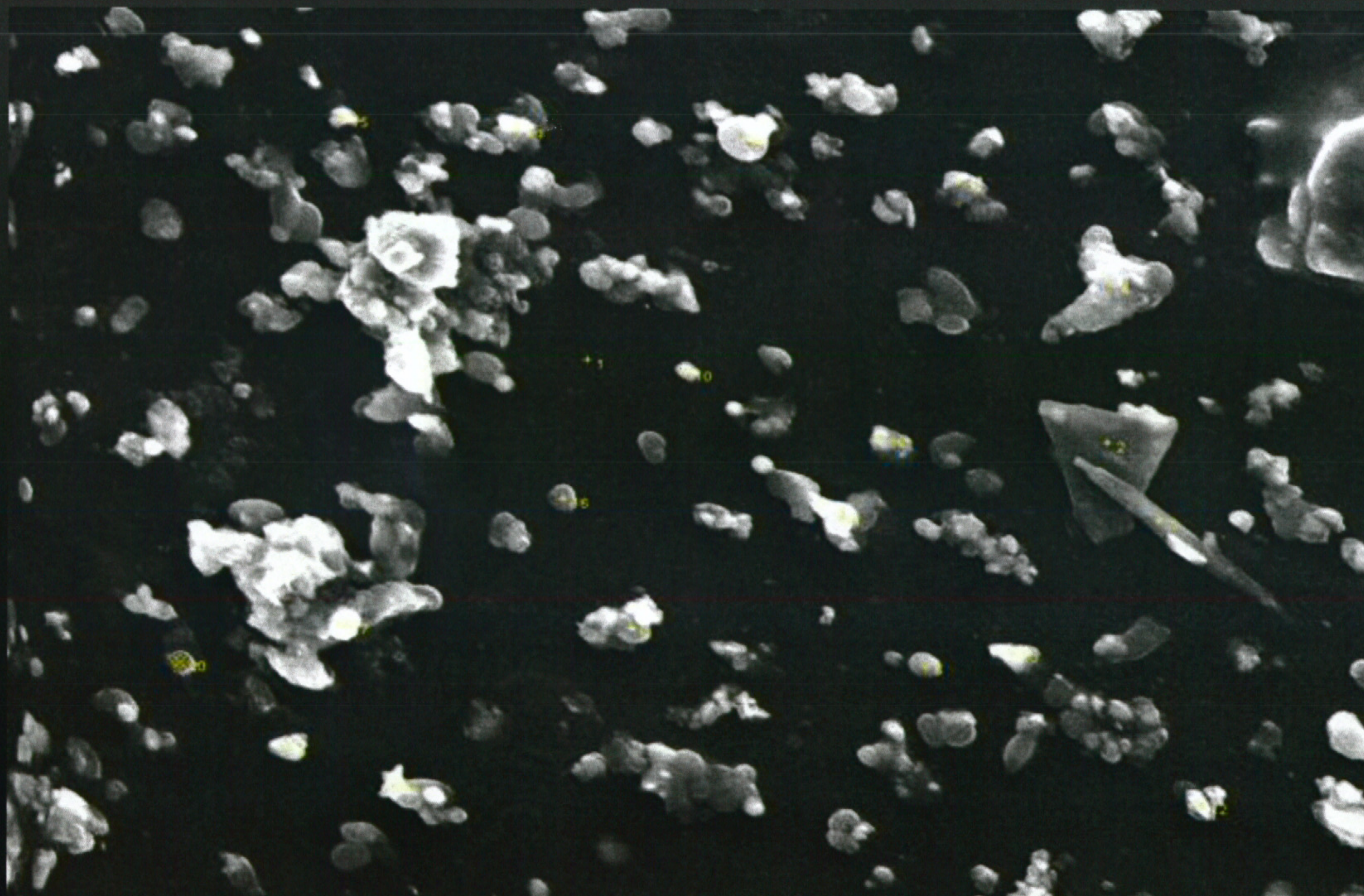
Backward trajectories ending at 17 UTC 03 Oct 01

FNL Meteorological Data



October 3 Sites - Sampling	Sources/ Sinks	Distance to WTC site (km)	$PM_{2.5}$ Mass (24 hr) ($\mu g/m^3$)	$PM_{2.5}$ Mass DRUM – time resolved, ($\mu g/m^3$)
Fresh Kills S.I.		- 21.	22.3 (EPA)	
	842 MW PP S.I., (gas)			
PS 44 Staten Is.		- 17.	27.6 (EPA)	
Battery Park		- 0.9	30.6 (EPA)	
	WTC Site plus diesels	≡ 0.0		
MBCC NNW		+ 0.7	37.8 (EPA)	
DOE EML NNE		+ 1.8	48.2 (DRUM)	
(site at 50 m)				135 in 3 hr plume
				25.3 12 hr non- plume
PS 64 NE		+ 2.7	36.0 (EPA)	

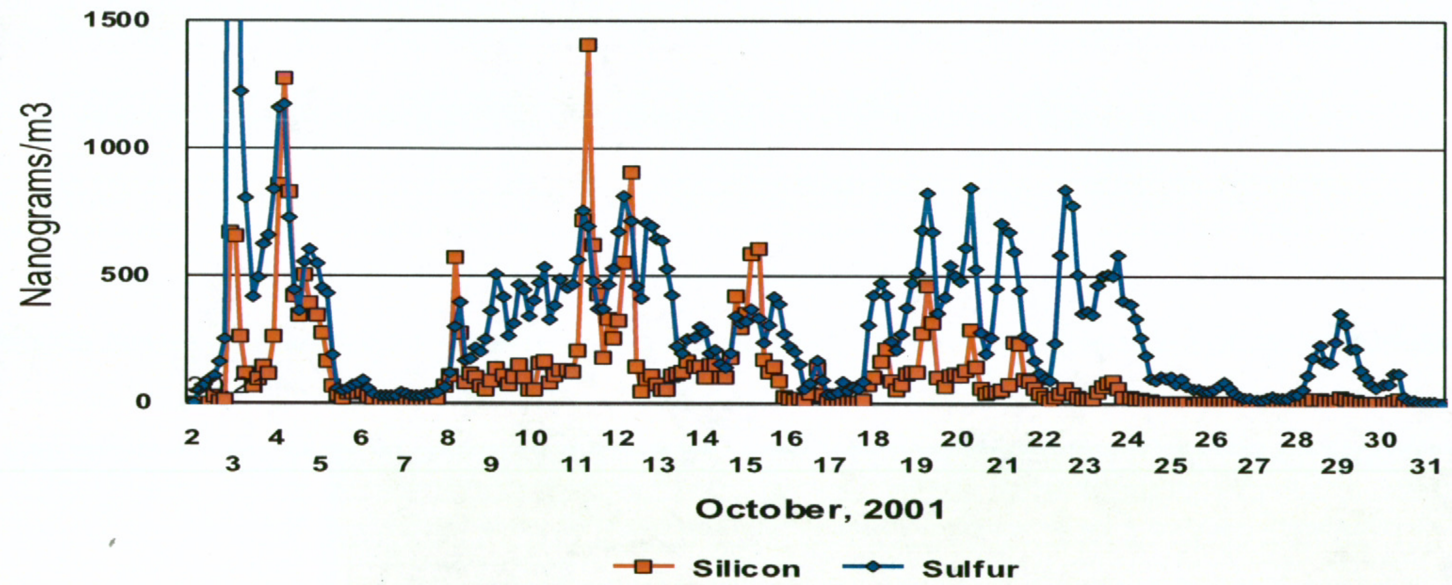
Coarse particles ~ 12 to 5 μm, Oct. 3

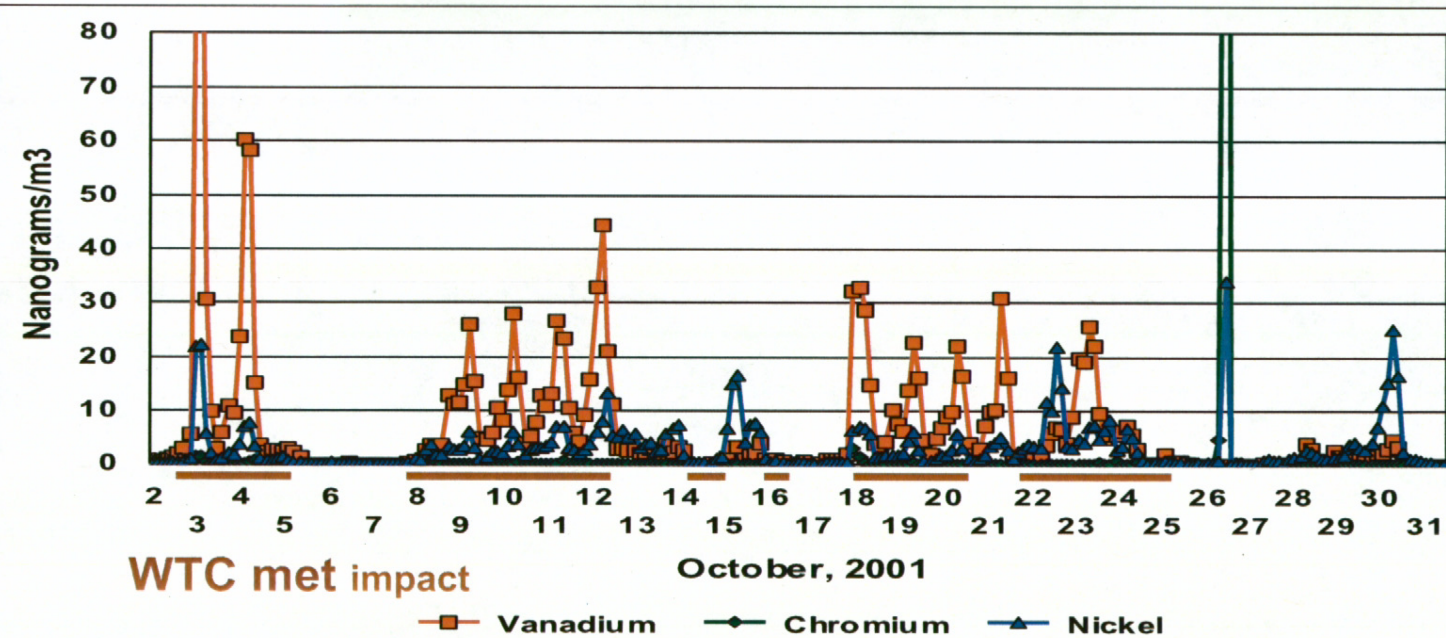


New York Very Fine Aerosols post Sept. 11, 2001

UC Davis DRUM Data from 1.8 km NNE

0.26 > Dp > 0.09 micrometers





Incineration with 10% chlorine	Boiling Point	Earth crustal	Bulk dust EPA 2003	Bulk dust Lioy 2002	Volatility Temp	Principal Species
Metal	°C	ppm	ppm	ppm	°C	
Chromium	2639	102	71.5	165	1594	CrO_2, O_3
Beryllium	1280	2.8	1.75	3.2	1042	$Be(OH)_2$
Barium	1634	425	195	381	895	$BaCl_2$
Antimony	697	0.2	na	na	653	Sb_2O_3
Selenium		0.05	< 0.96	na	315	SeO_2
Cadmium	761	0.15	3.8	7.2	211	Cd
Osmium	4224	0.0015	na	na	40	OsO_4
Arsenic	814	1.8	< 0.96	2.6	32	As_2O_3
Mercury	353	0.085	0.37	nd	25	Hg
Vanadium	3480	120	18.3	38.9	147	VCl_4
Nickel	2834	84	15.5	43.5	686	$NiCl_2$
Silver	2190	0.004	4.9	2.3	620	AgCl
Thallium	1464	9.6	<0.96	1.4	136	TlOH
Lead	1748	14	98	305	-12	$PbCl_4$
SiO_2	1725	280,000	na	na	12	$SiCl_4$