Department of Toxic Substances Control

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Arnold Schwarzenegger
Governor

April 21, 2009

County of Los Angeles Department of Public Health
Environmental Health Director
5050 Commerce Drive
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County of Los Angeles Department of Public Health
Director and Health Officer
313 N. Figueroa Street, Room 806
Los Angeles, California 90012

The Honorable Board of Supervisors
County of Los Angeles
383 Kenneth Hahn Hall of Administration
500 West Temple Street
Los Angeles, California 90012

Dear Directors/Supervisors,

During the course of an on-going investigation, the Department of Toxic Substances Control (DTSC) worked with the University of California at Davis based Delta Group to obtain samples of coarse particulate matter generated by a Terminal Island automobile/appliance shredder, SA Recycling LLC, located at 901 New Dock Street, Terminal Island, CA 90731.

On April 8, 2009, DTSC received a report entitled "Deposition of coarse toxic particles in Wilmington, CA for the Department of Toxic Substances Control (DTSC)" from the Delta Group. A copy of the report and the supplemental are enclosed.

DTSC is in the process of evaluating the findings presented in the report, especially those addressing hazardous waste disposals and the potential for adverse health effects. We will report back to you when our evaluation is complete.

If you have any questions or concerns regarding this matter, please feel free to contact me at (916) 445-3941.

Sincerely,

ORIGINAL SIGNED BY:

Gale Filter
Deputy Director
Enforcement and Emergency Response Program

Enclosures

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DELTA GROUP, WALKER HALL ROOM 105
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From: Thomas A. Cahill
Professor of Physics (recalled) and Atmospheric Sciences (Emeritus), and
Head, DELTA Group

Summary of lead concentration data from:

Final Report
April 4, 2009

Deposition of coarse toxic particles in Wilmington, CA for the Department of Toxic Substances Control (DTSC)

Thomas A. Cahill, Professor of Physics (Recalled), Atmospheric Science and Head, Delta Group, David Barnes, Ph.D., Project Manager, UC Davis DELTA Group, and Kristen Smeltzer, DTSC

Executive Summary:

Elemental and mass values from the UC Davis DELTA Group 8 DRUM impactor, with DTSC personnel, support, and execution, have delivered unambiguous tracers of the impact of the Terminal Island auto/appliance shredder on Wilmington. These tracers overlap known hours of shredder operation and transport on south winds, and are confirmed by evidence of upwind aerosols from the harbor, including natural sea salt and the vanadium/nickel/sulfur pollution of ocean going ships using bunker oil as fuel.

The data indicate the presence of many metals measured at the Wilmington Fire Station 49, including lead, that occur in coarse particles that will readily settle onto the ground. The concentrations routinely exceed the DTSC limit of 1,000 ppm for all of the 3 size modes of particles larger than 1 μm particle diameter. (One example shown below)

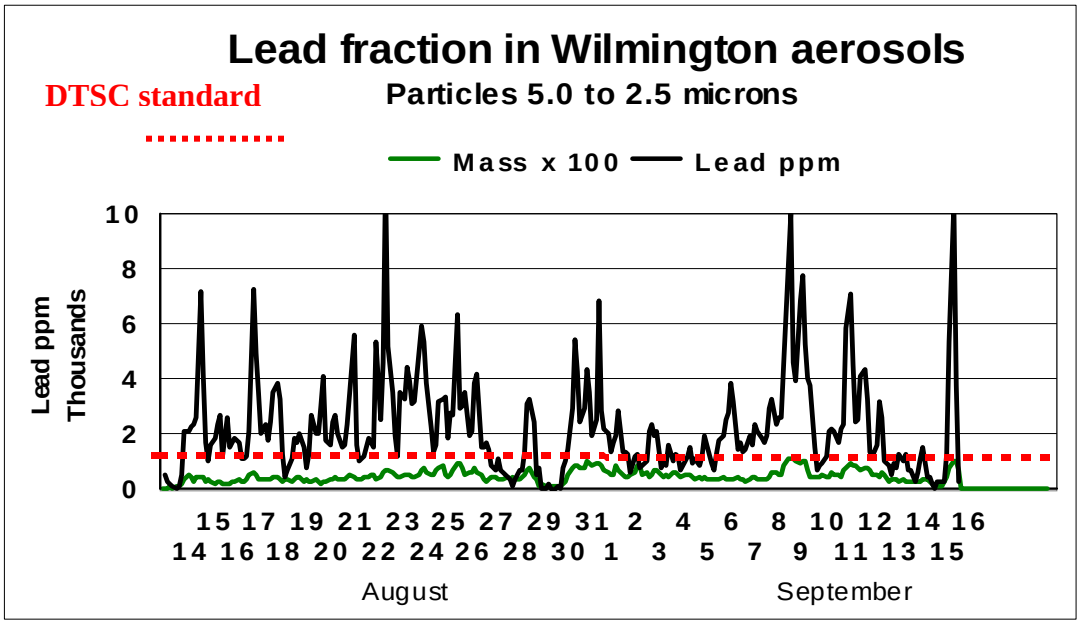

Figure 25 DRUM mass and elemental data – 5.0 to 2.5 μm lead (ppm)

At the request of DTSC, I have further analyzed the lead data to identify concentrations under several categories as measured at Fire Station 49, Wilmington, CA:

A. Over the entire period, August 14 – September 15, 2008

1. All particles in the air less than 10 μm diameter ("PM_{10}") 1,359 ppm
2. Particles between 10 and 2.5 μm ("Coarse") 2,369 ppm
3. Particles less than 2.5 μm ("Fine") 371 ppm
4. Those particles in the coarsest mode most likely to settle 2,185 ppm
5. Those particles in all modes weighted by ability to settle 2,186 ppm

B. 15 episodes in which meteorology predicted transport from Terminal Island to Fire Station 49 would occur and multiple shredder aerosol signatures were present.

6. All particles in the air less than 10 μm diameter ("PM_{10}") 3,316 ppm
7. Particles between 10 and 2.5 μm ("Coarse") 4,225 ppm
8. Particles less than 2.5 μm ("Fine") 1,384 ppm
9. Those particles in the coarsest mode most likely to settle 3,883 ppm
10. Those particles in all modes weighted by ability to settle 3,882 ppm

The settling calculations are based on Seinfeld and Pandis (1997).

Final Report
April 4, 2009

Deposition of coarse toxic particles in Wilmington, CA for the Department of Toxic Substances Control (DTSC)

Thomas A. Cahill, Professor of Physics (Recalled), Atmospheric Science and Head, Delta Group, David Barnes, Ph.D., Project Manager, UC Davis DELTA Group, and Kristen Smeltzer, DTSC

4/9/2009

Executive Summary:

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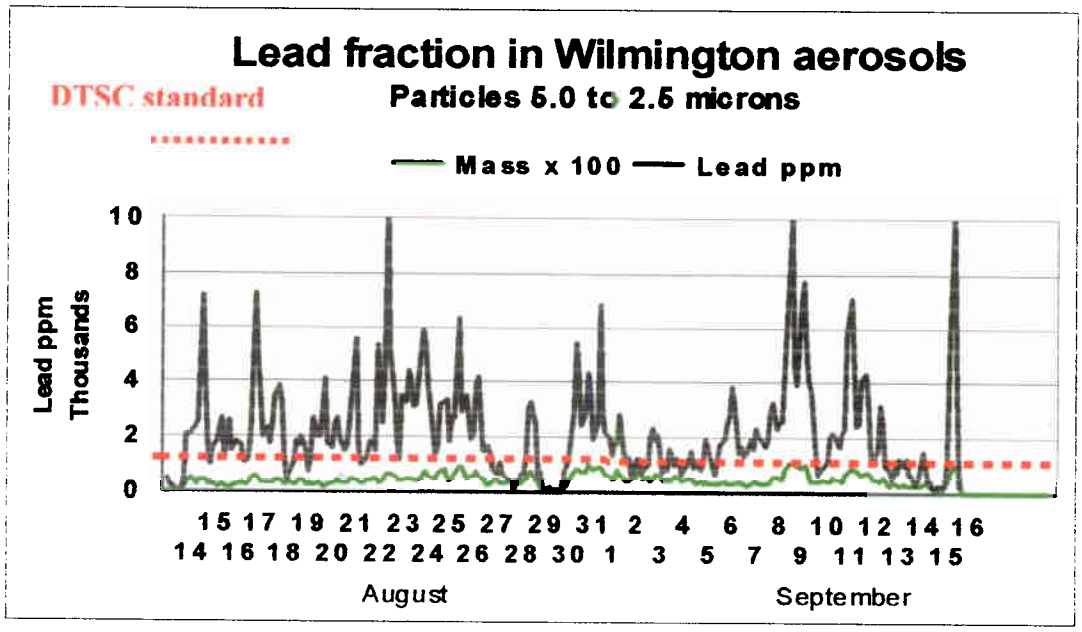
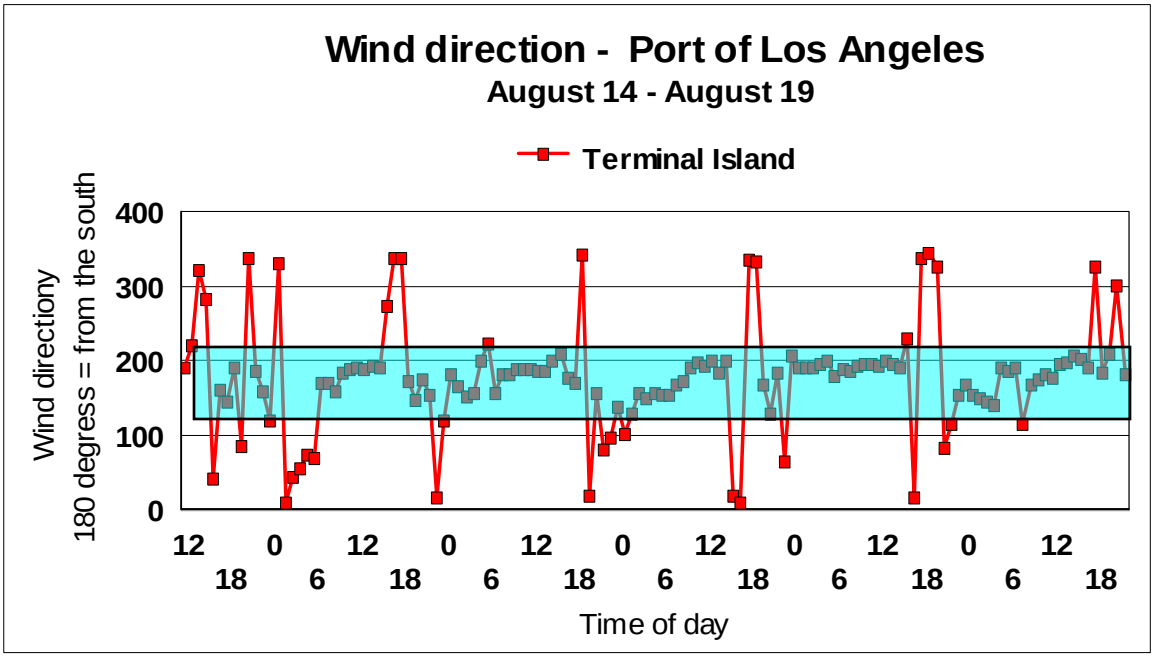
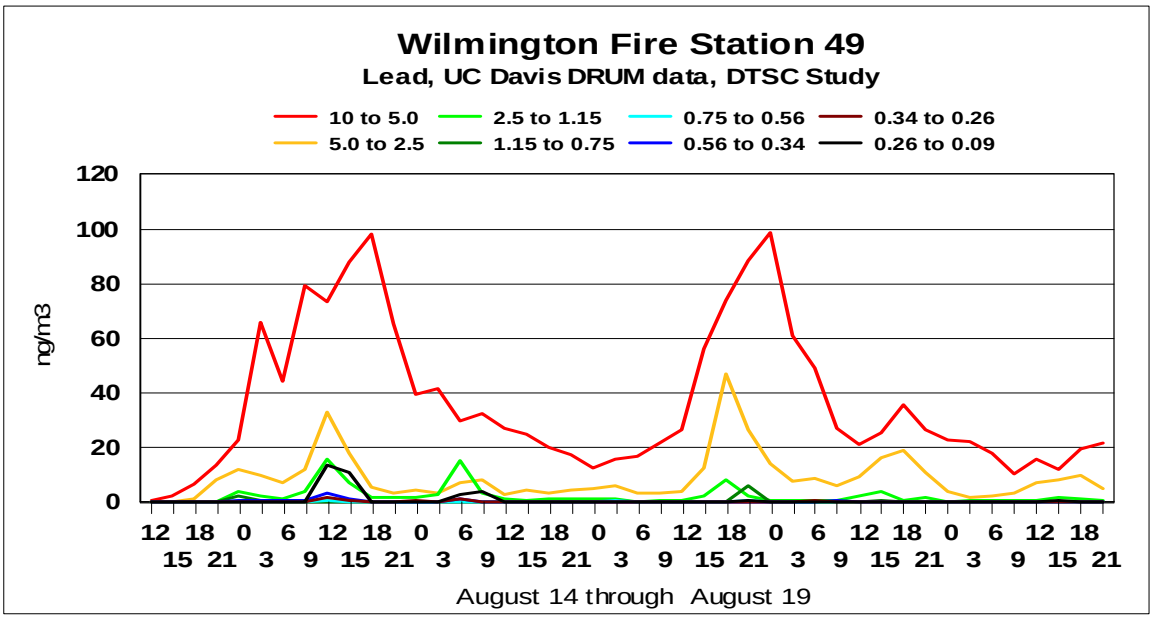


Figure 25 DRUM mass and elemental data – 5.0 to 2.5 μm lead (ppm)

In addition to the coarse toxic elements, the very fine elements from the shredder, especially very fine iron, are themselves in concentrations and particle sizes that are capable of causing health impacts to lungs.

With the availability of local wind data from the LA Port network, it is possible to examine meteorological transport and toxic elements in Wilmington on a 3 hr by 3 hr basis. The daytime wind direction is routinely from the shredder to Fire Station 49, shown below. The aqua range is ± 45 ^{o} around the 160 ^{o} wind trajectory to Wilmington.





The high lead values, as well as iron and other elements, peak when the wind is blowing from the shredder to Wilmington. There also appears to be extensive lead and iron pollution, in the coarsest mode only, of the entire area around the sampling site that may represent prior shredder impacts.

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Introduction to the summer, 2008 Wilmington study

The Wilmington Fire Station 49, located at 400 Yacht Street, Berth 194, Wilmington, CA 90744 lies almost directly downwind of the Terminal Island shredder, located at 901 New Dock Street, San Pedro, CA 90731, during daytime, while night winds come in from the northwest.

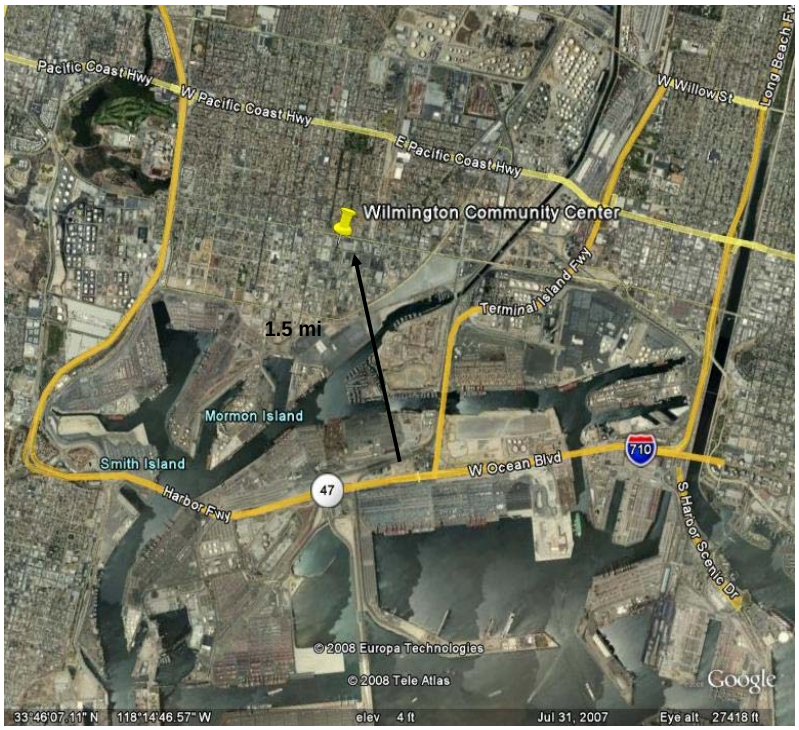


Figure 1 Satellite photo of the study area. Along daytime wind direction, shredder to sampling site to Wilmington Community Center is only 1.5 miles.

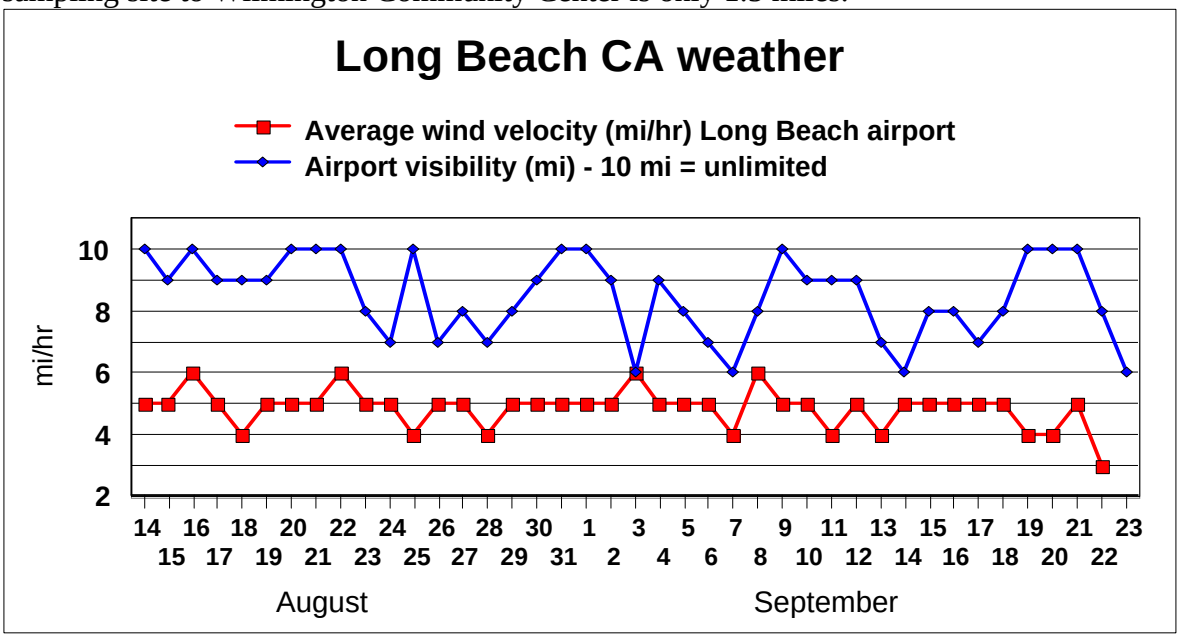


Figure 2 Regional meteorology from the Long Beach airport

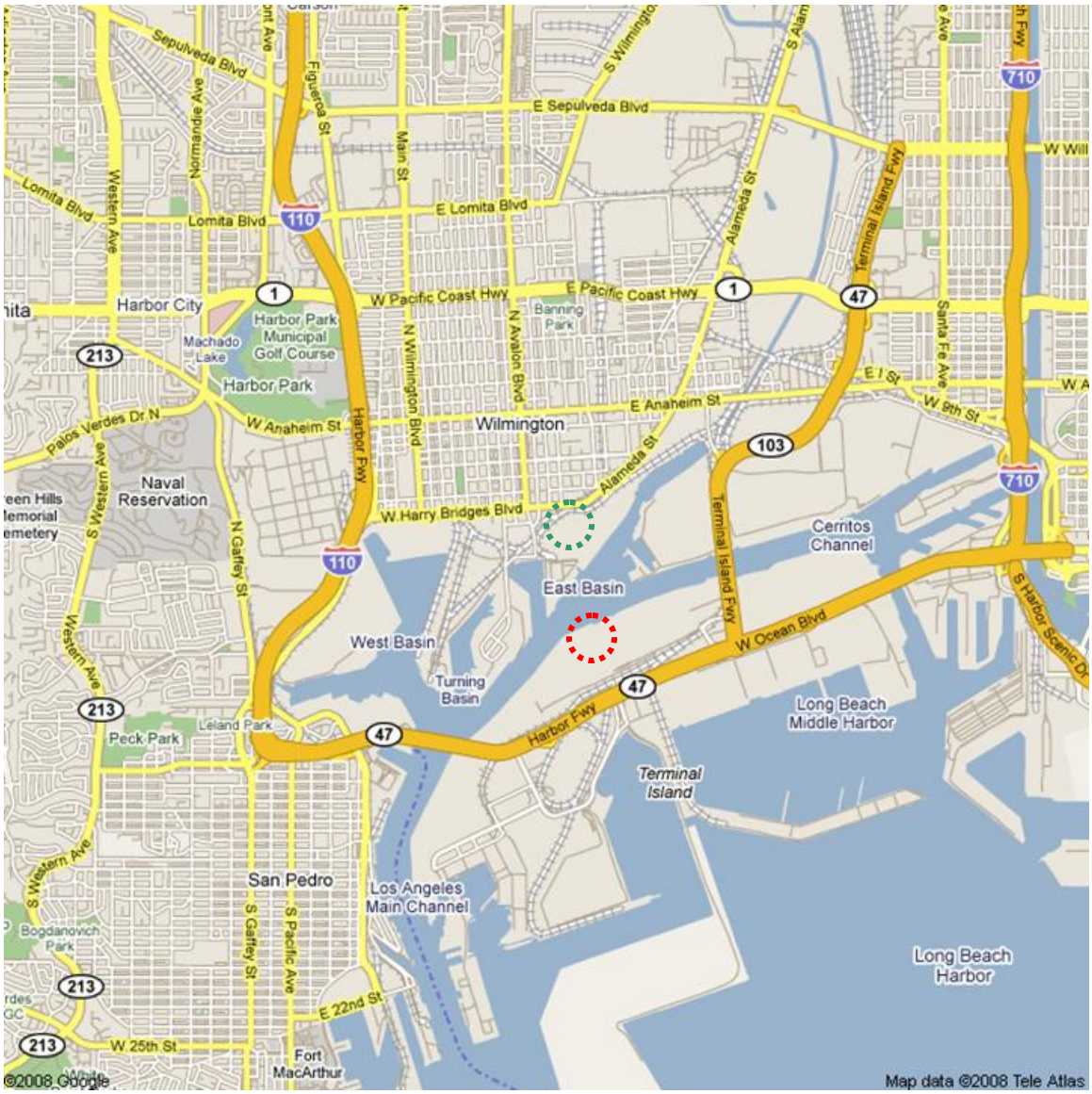


Figure 3 Street map of the study area. The approximate location of the shredder (red circle) and sampling site (green circle) are shown.

The overlap of the winds, with a typical 7 AM to 7 PM trajectory from the south in daytime, and Northwest at night, provides an overlap with shredder operations, which are typically 5 AM to circa 1 PM, then an evening shift. Thus, most of the day shift will impact the sampler, but the evening shift will not. Thus, the data we obtain is only a small fraction (about ¼) of the shredder emissions at this distance. Note that the nighttime wind direction may impact the city of Long Beach.

Local meteorology

The availability of metrological data from the Port of Los Angeles station network allows us to better identify local wind strength and direction.

Figure 4 Local meteorology from the Port of Los Angeles network.

Two sites were chosen for our analysis, the Terminal Island (TI) Source Dominated site and the Wilmington Community Center (SP) site. The aerosol sampling site at Fire Station 49 is almost exactly half way between these two sites, and thus falls on the wind trajectory. The shredder itself lies slightly to the east, and has a wind trajectory direction of roughly 160°, or from the SSE, to the sampling site and Wilmington Community Center.

The wind speed and direction for both sites are shown below in Figures 5 and 6

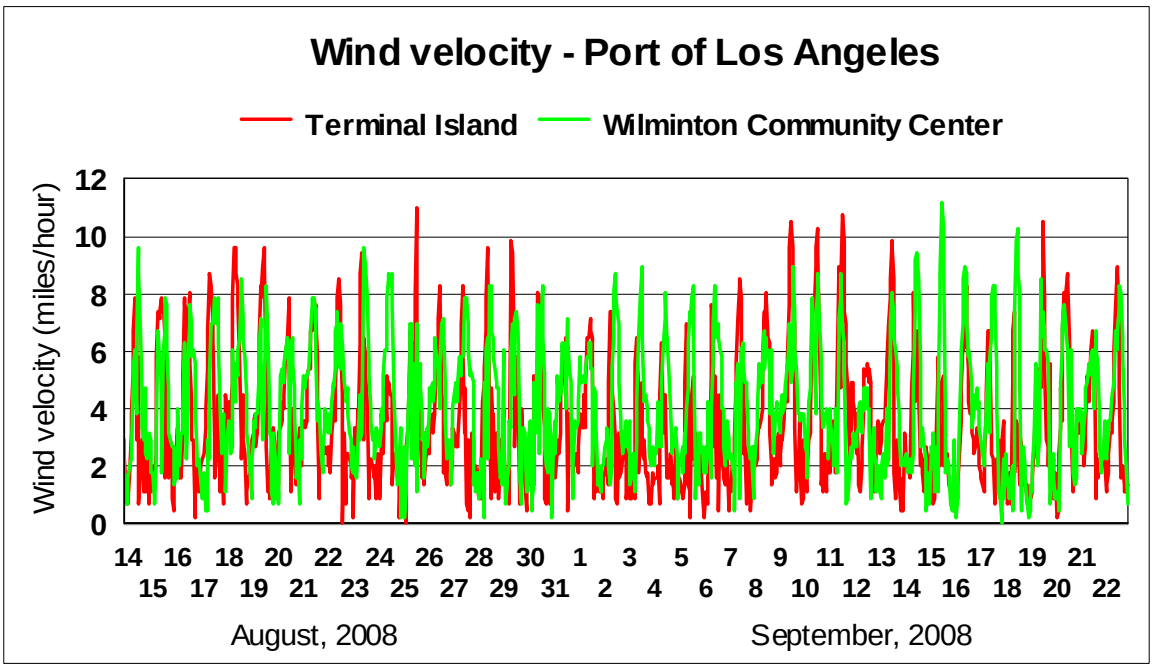


Figure 5 Wind speed for the TI and SP meteorological stations

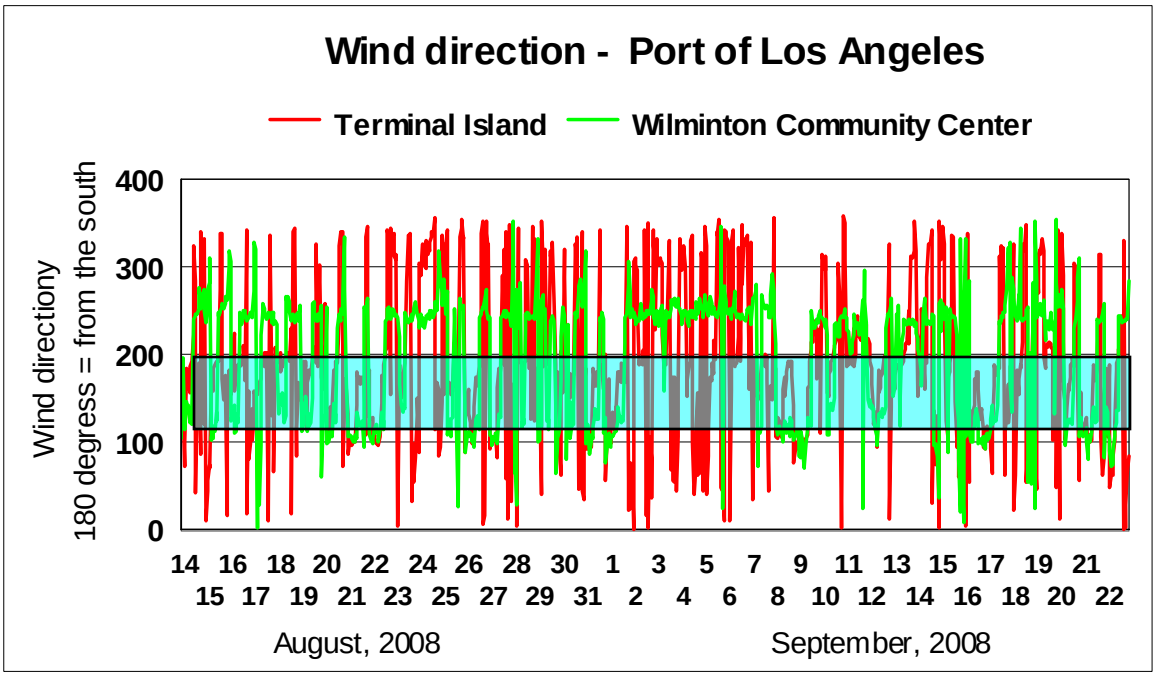


Figure 6 Wind direction from the TI and SP meteorological station. The aqua region is ± 45 ^{o} around the mean 160 ^{o} direction of wind from shredder to Fire Station 49.

Then samples collected are gauged and examined optically to detect any anomalies in the sample collection. A review spreadsheet is prepared for every operation (see below).

DRUM strip mounting guide				STAFF	TA Cahill	Rot rate	4.0	mm/dy	DTSC=	CA Department of
8 drum samplers				DATE:	10/10/08	DRUM #	8D-16			Toxic Subst. Control
Study	Site	Start	Intermediate		Intermediate		Intermediate		Stop	**Comments**
DTSC	**Wilm**		**Power out**		**Central blank**		**Other**			
Date	**8/14/08**				Sept 4	Sept 4			9/23/08	
Hour	**12:50 PM**								09:25 AM	vac pump on, the prog start
Lat/Long										measured beta at 4 mm start
Elevation										
Flow	**10.0 nom**								**39.85**	**days duration**
Stage 8	mm (pr)	10.0			86.9	92.9		159.4	**159.43**	**mm wo start, stop 4 mm**
0.26 to 0.09	mm (dr)	10.0			68.0	74.0		140.0		strong diurnal banding
	mm (mt)									4 mm gap before final line
7	mm (pr)	10.0			86.9	92.9		159.4		110-115; 120 - 125 verl black
0.34 to 0.26	mm (dr)	10.0			68.0	74.0		140.0		strong diurnal banding
	mm (mt)									4 mm gap before final line
6	mm (pr)	10.0			86.9	92.9		159.4		less color 113, 124 black
0.56 to 0.34	mm (dr)	10.0			68.0	74.0		140.0		4 mm gap before final line
	mm (mt)									black at 47
5	mm (pr)	10.0			86.9	92.9		159.4		
0.75 to 0.56	mm (dr)	10.0			68.0	74.0		140.0		4 mm gap before final line
	mm (mt)									black at 47
4	mm (pr)	10.0			86.9	92.9		159.4		
1.15 to 0.75	mm (dr)	10.0			68.0	72.0		140.0		4 mm gap before final line
	mm (mt)									black at 46
3	mm (pr)	10.0			86.9	92.9		159.4		
2.5 to 1.15	mm (dr)	10.0			68	75		142.5		4 mm gap before final line
	mm (mt)									black at 42
2	mm (pr)	10.0			86.9	92.9		159.4		l
5.0 to 2.5	mm (dr)	10.0			67	74		141		4 mm gap before final line
	mm (mt)									black at 46
1	mm (pr)	10.0			86.9	92.9		159.4		lots of mass
10.0 to 5.0	mm (dr)	10.0			68	74		141		4 mm gap before final line

Table 1 Characteristics of the collected DRUM samples

The samples are then photographed with a Canon EOS 8.2 Mpx camera with Macro lens in a fixed frame and under a bright white fluorescent light. A color pallet and a black to white gray scale are included in each picture, as is a frame identification title. Each sample is photographed twice, once against a black background which emphasizes scattering particles like soil and sea salt, once against a white background which emphasizes wood smoke and soot.

The frames and the standards are then removed in Photoshop 7.0, without any corrections for color or brightness.

Results – Optics

The pictures from the Wilmington sample collection are shown below. The 6 mm timing marker and clean background zone about ½ way through are shown. The rusty color in the larger size modes is unusual. The end peak is the DRUM stop mark.

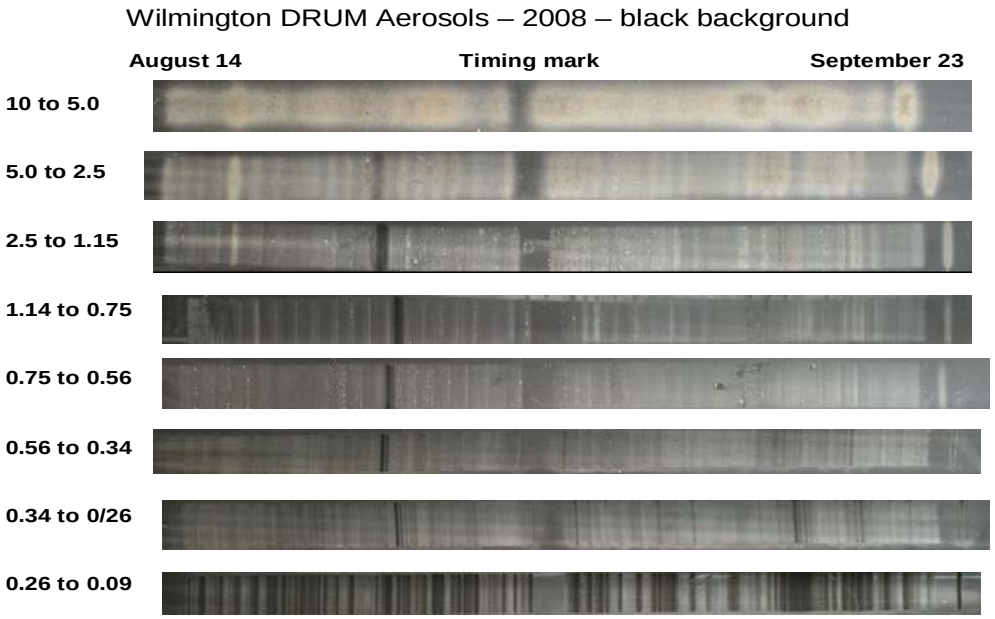


Figure 7 Wilmington DRUM aerosols – black background

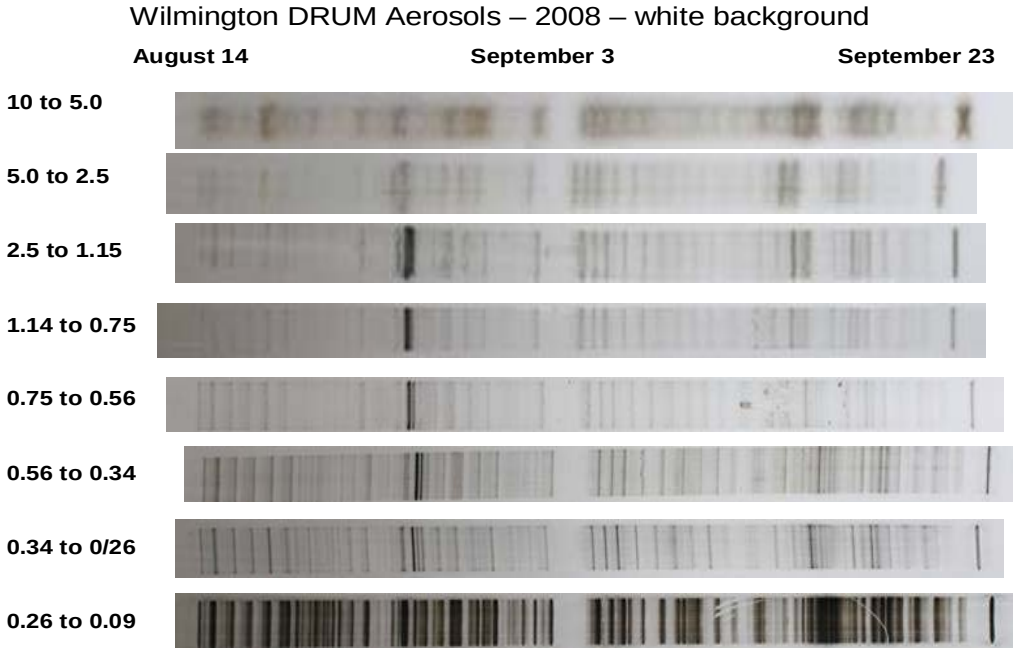


Figure 8 Wilmington DRUM aerosols – white background. Clear region near the middle is a timing/blank marker

Results – mass

Below we show the mass of particles, from the coarsest to the finest particle sizes. These data allow calculation of ground deposition.

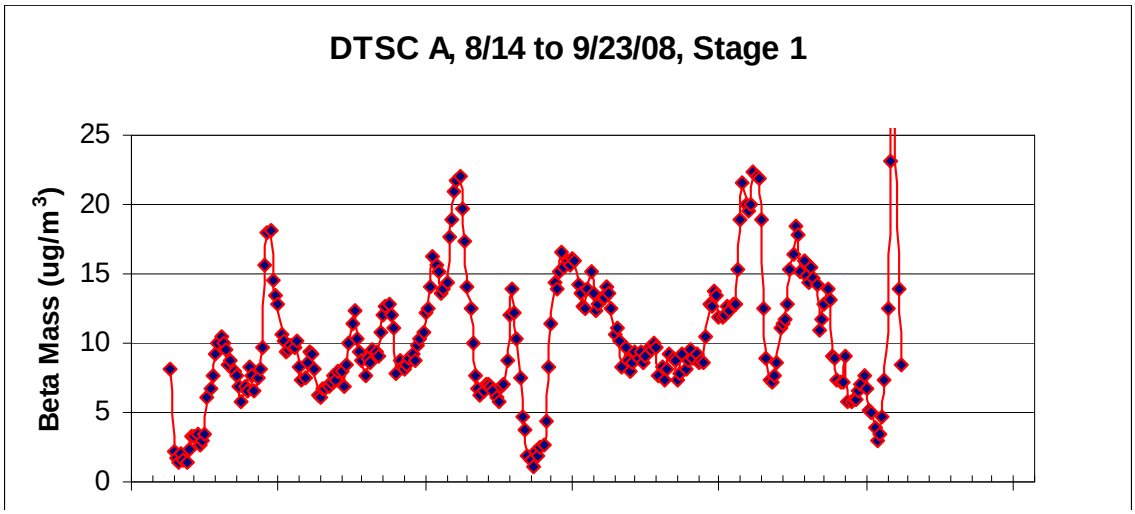


Figure 9 a – Stage 1, 10 to 5.0 µm diameter

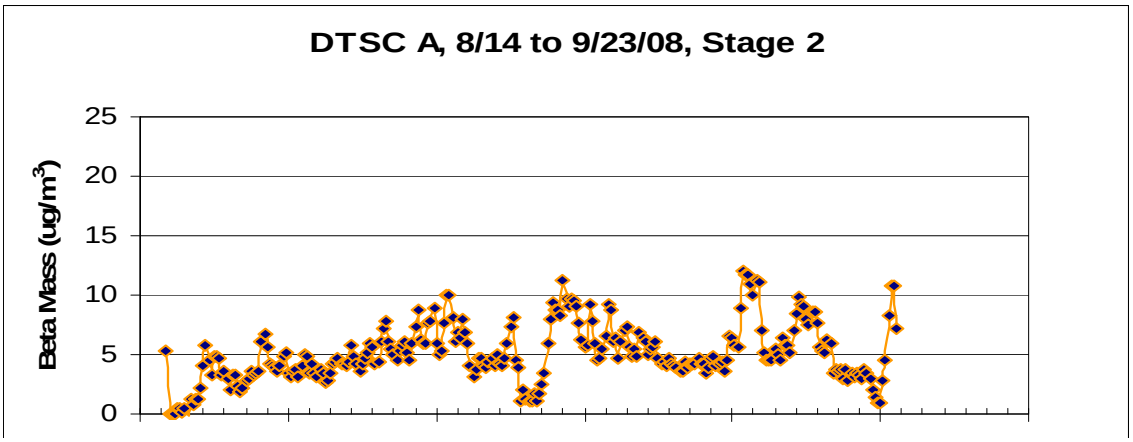


Figure 9 b – Stage 2, 5.0 to 2.5 µm diameter

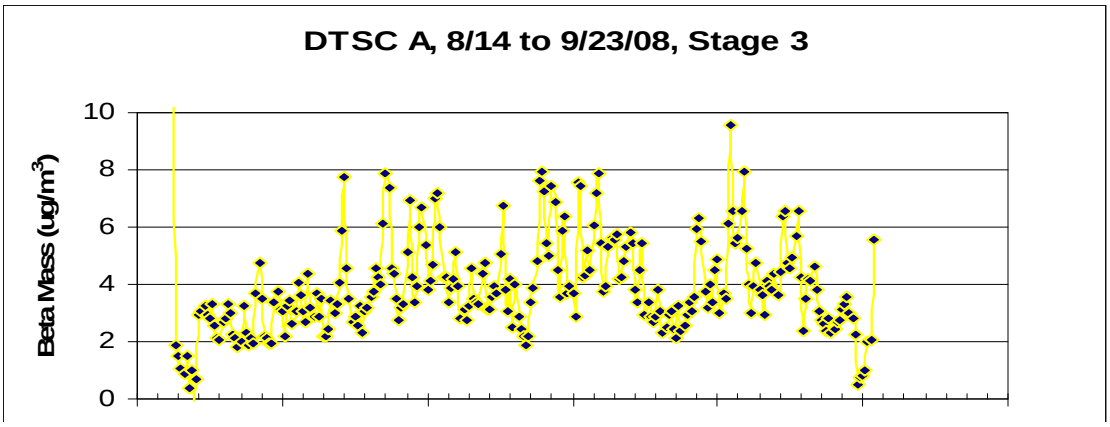


Figure 9 c – Stage 3, 2.5 to 1.15 µm diameter

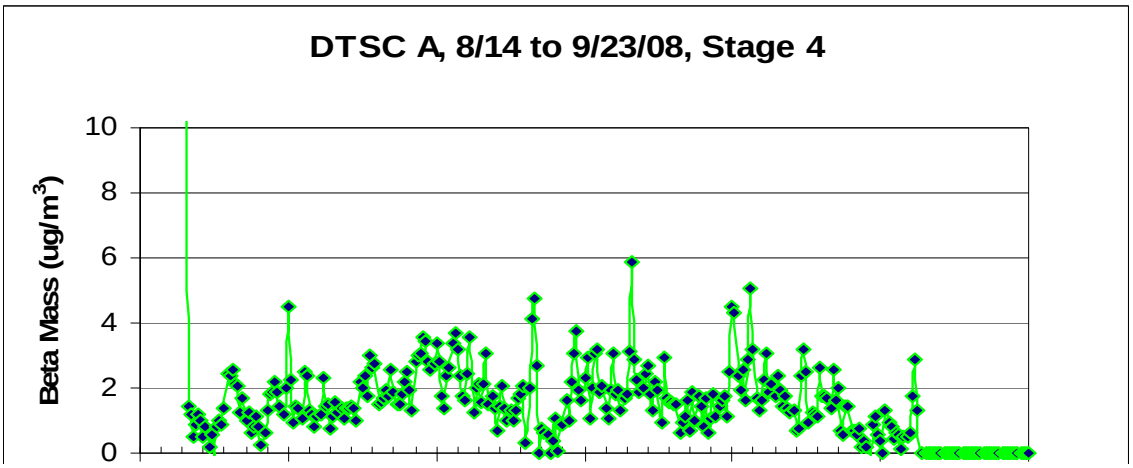


Figure 9 d – Stage 4, 1.15 to 0.75 µm diameter

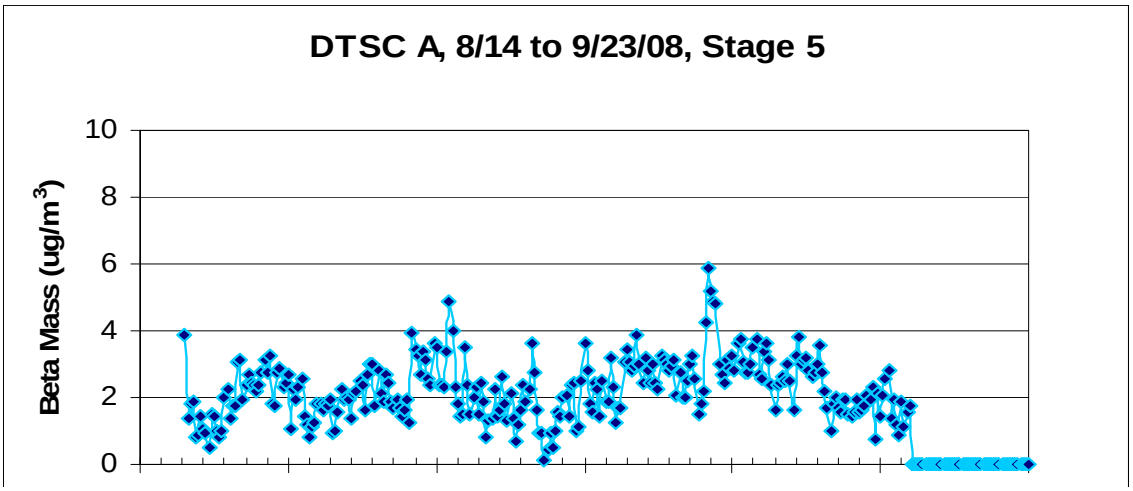


Figure 9 e – Stage 5, 0.75 to 0.56 µm diameter

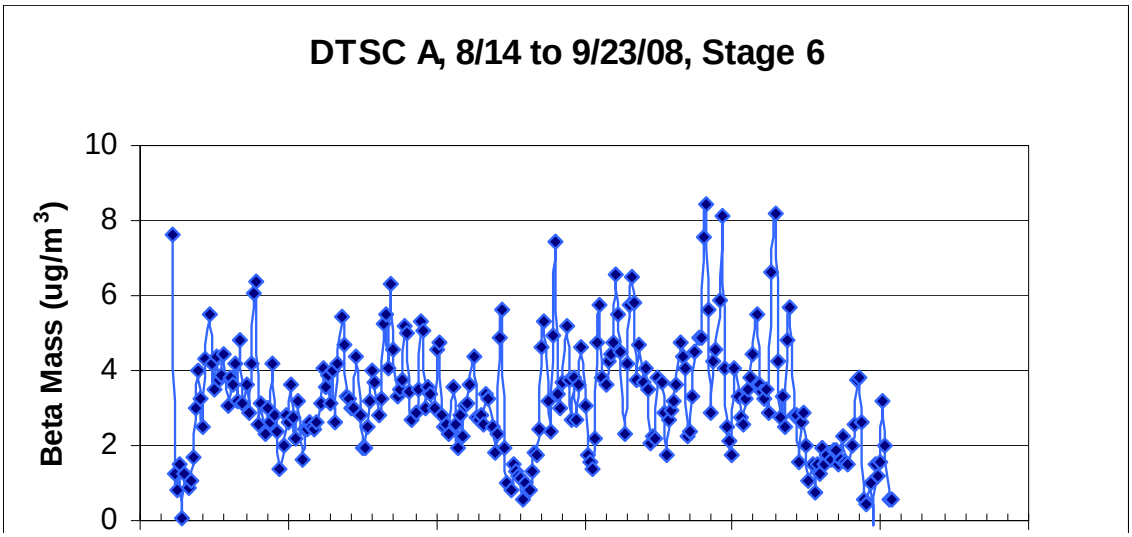


Figure 9 f – Stage 6, 0.56 to 0.34 µm diameter

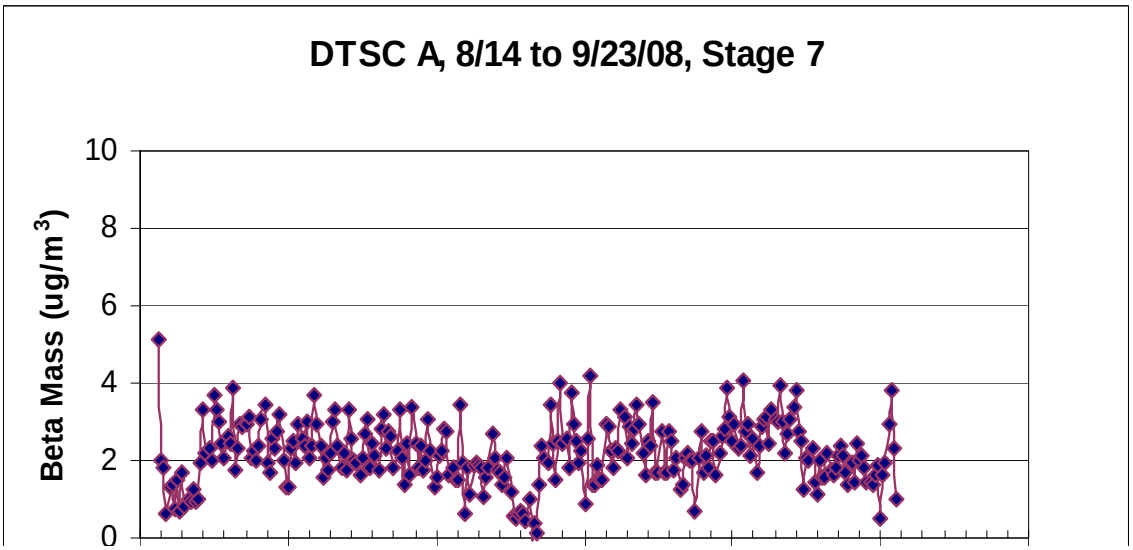


Figure 9 g – Stage 7, 0.34 to 0.26 μm diameter

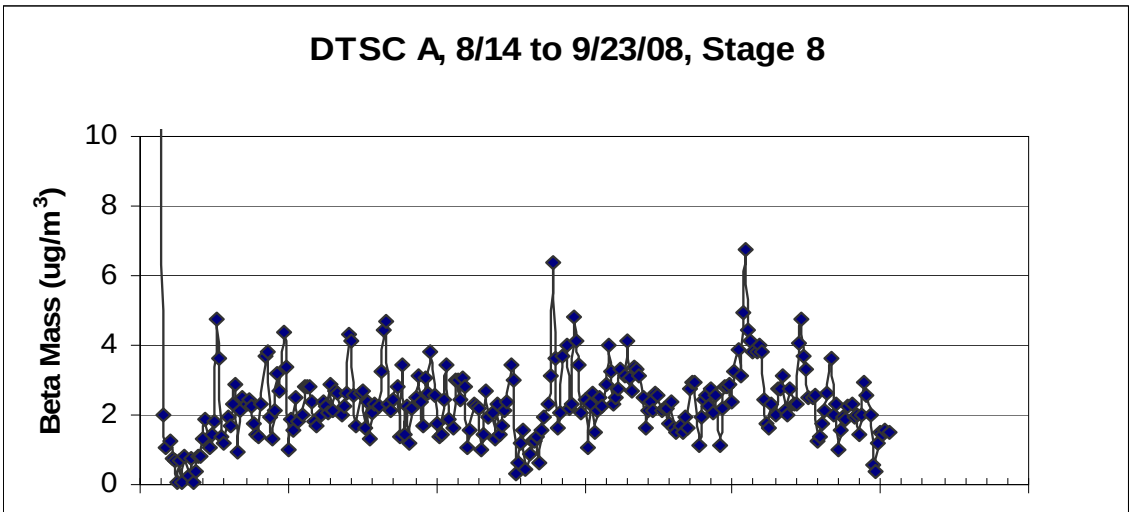


Figure 9 h – Stage 8, 0.26 to 0.09 μm diameter

Figure 9 a, b, c, d, e, f, g, h – Mass versus time for then DRUM sampler as a function of particle size.

These mass data are essential in calculating the fractional mass values for toxic elements.

Results - S-XRF elemental data

1. Long term size/compositional data

The samples were then analyzed on the UC Davis DELTA Group beam line 10.3.1 of the Advanced Light Source, Lawrence Berkeley NL, in January 2009. The sensitivity and quality assurance of the S-XRF are shown in Appendix A.

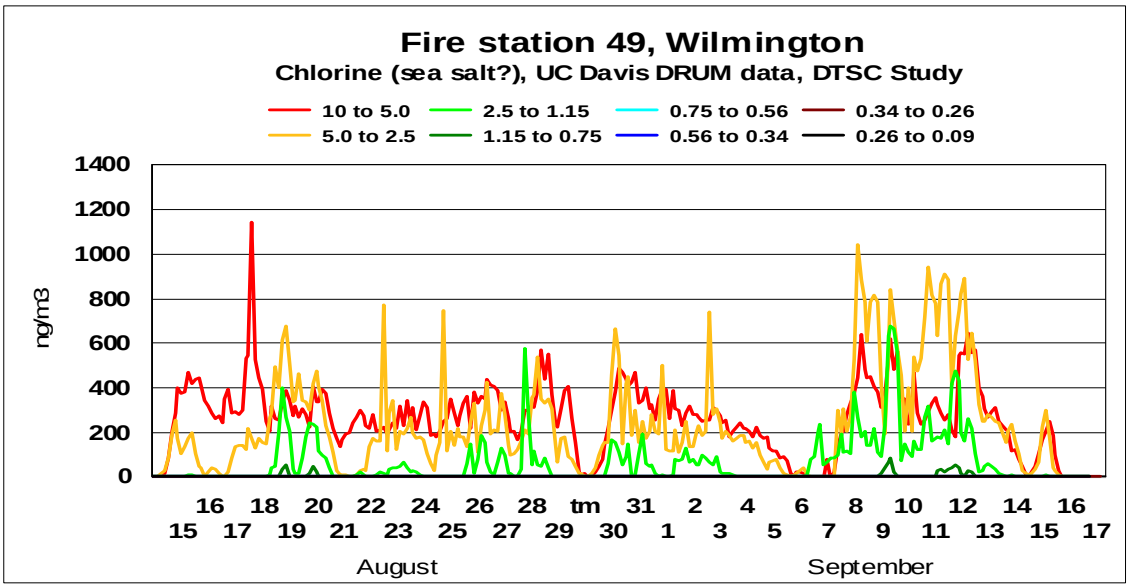


Figure 10 DRUM elemental data – chlorine (sea salt?)

The first element considered is chlorine, which in coarse particles is like sea salt. There appear to be other sources operating however, in the finer modes. The second element we consider is iron.

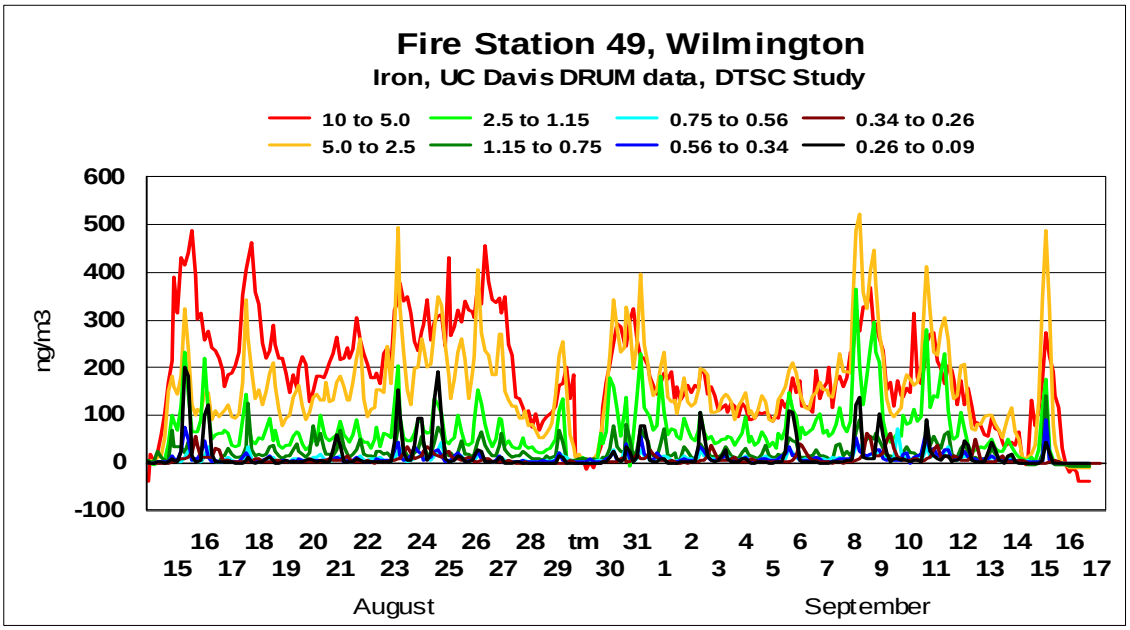


Figure 11 DRUM elemental data – iron

The key point here is that coarse iron normally comes from soil, but there is almost no open soil upwind of the Wilmington Fire Station 49. The iron signature simply should not be there.

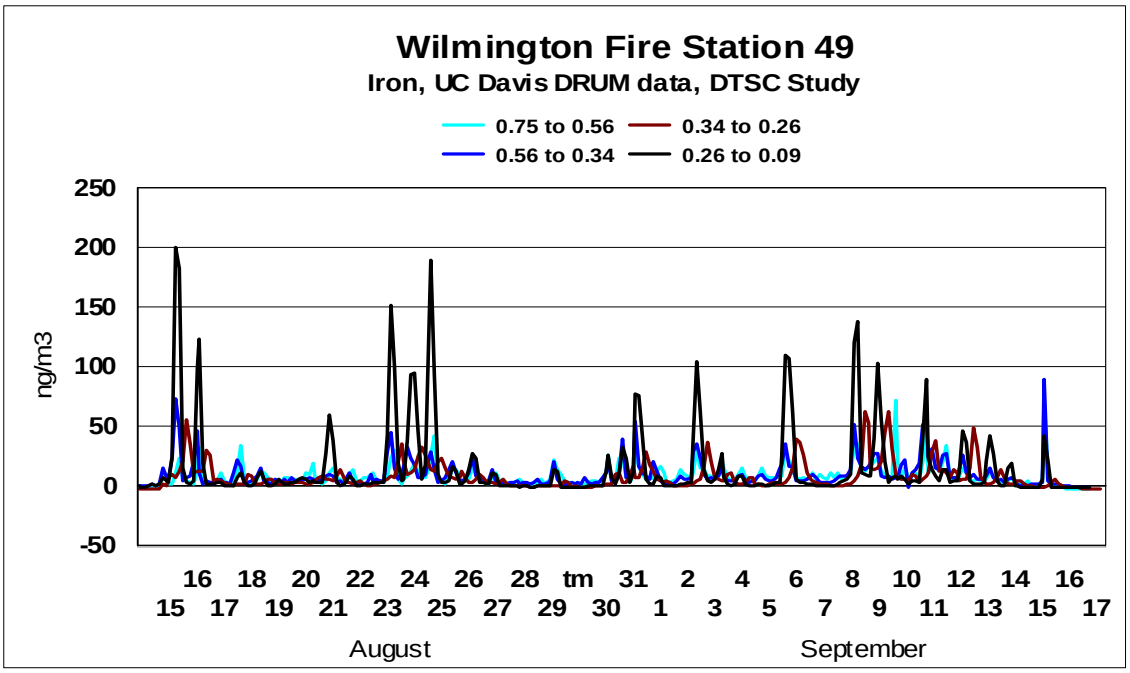


Figure 12 DRUM elemental data – fine modes of iron

Iron is a major component of soil, but exists almost entirely in particles above 1 µm in diameter. Thus, the sharp spikes in very fine iron are most unusual, and illustrate a vehicular or industrial source. This is also shown by the size distribution (below) showing that calcium in soil goes to low values in very fine sizes while iron remains elevated.

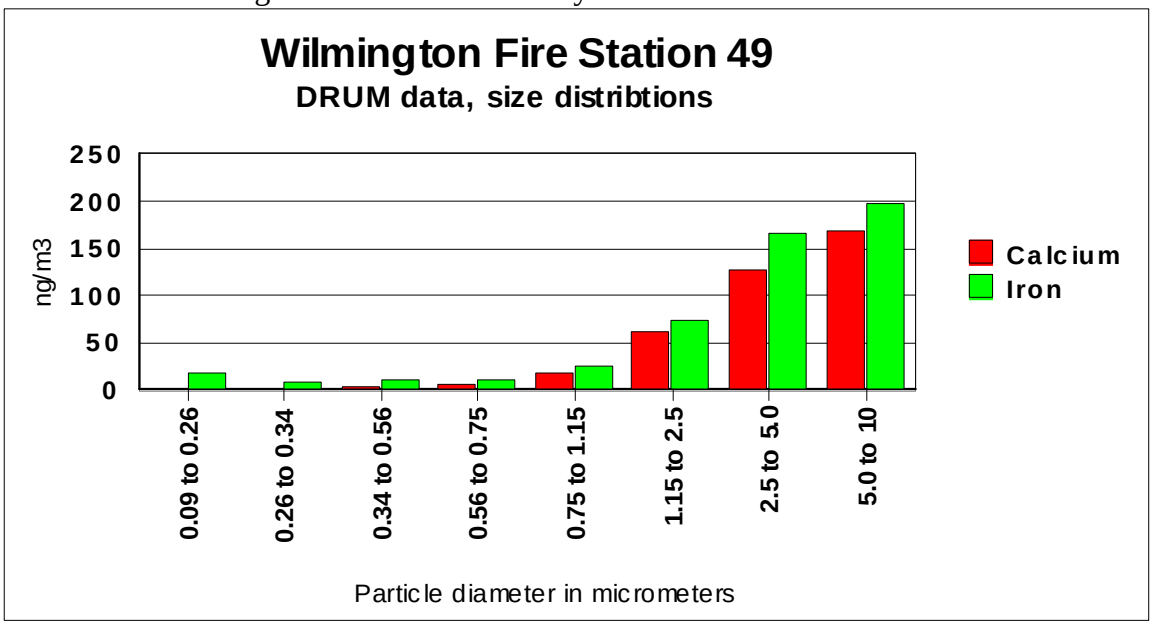


Figure 13 DRUM elemental data – size of iron and calcium

The sulfur shows an unusual coarse mode, the chlorine is sea salt.

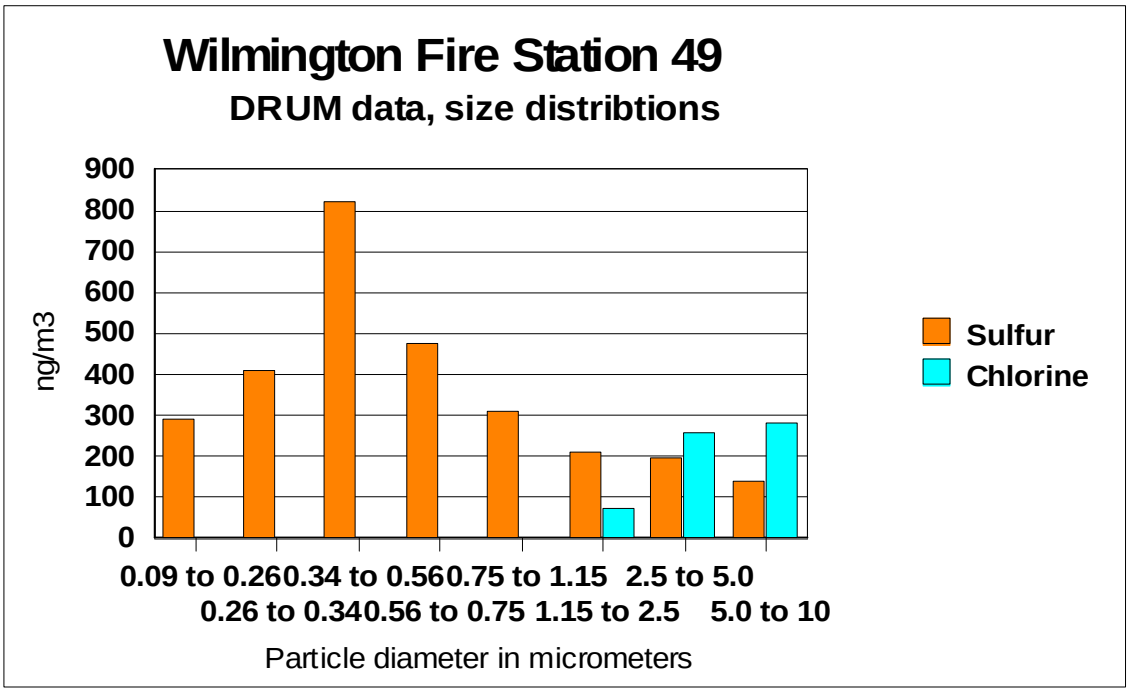


Figure 14 DRUM elemental data – size of sulfur and chlorine

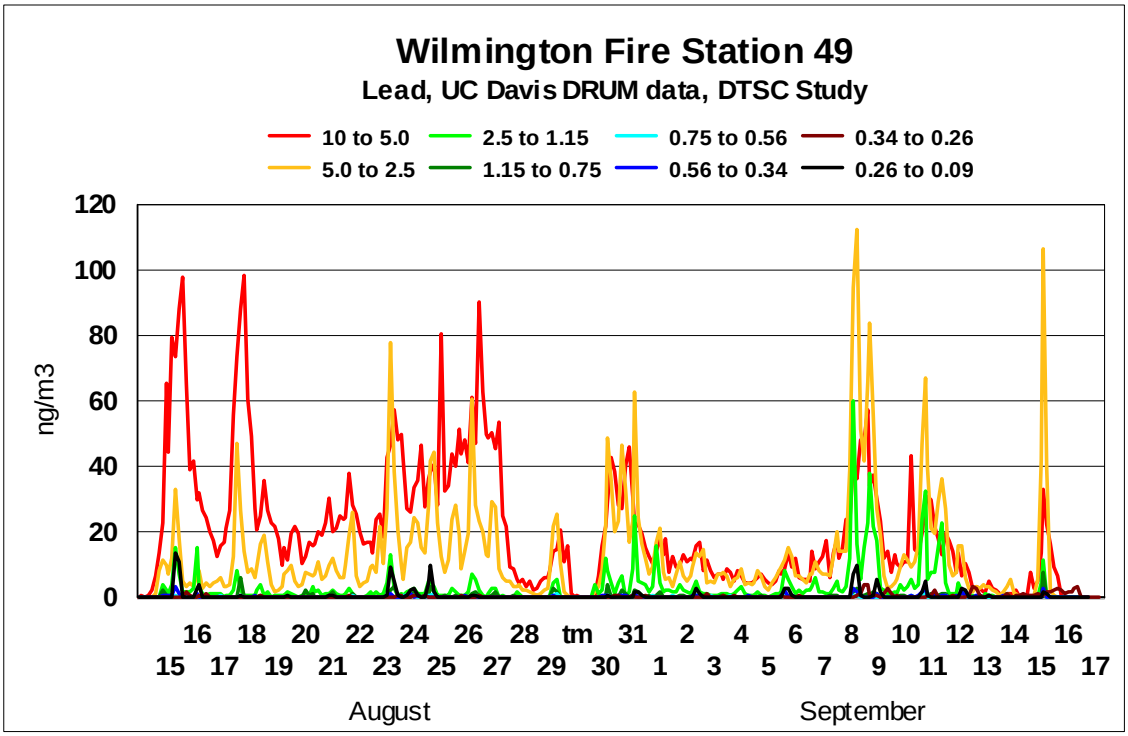


Figure 15 DRUM elemental data – lead

Lead is mostly in a coarse mode, and thus will readily settle to the ground.

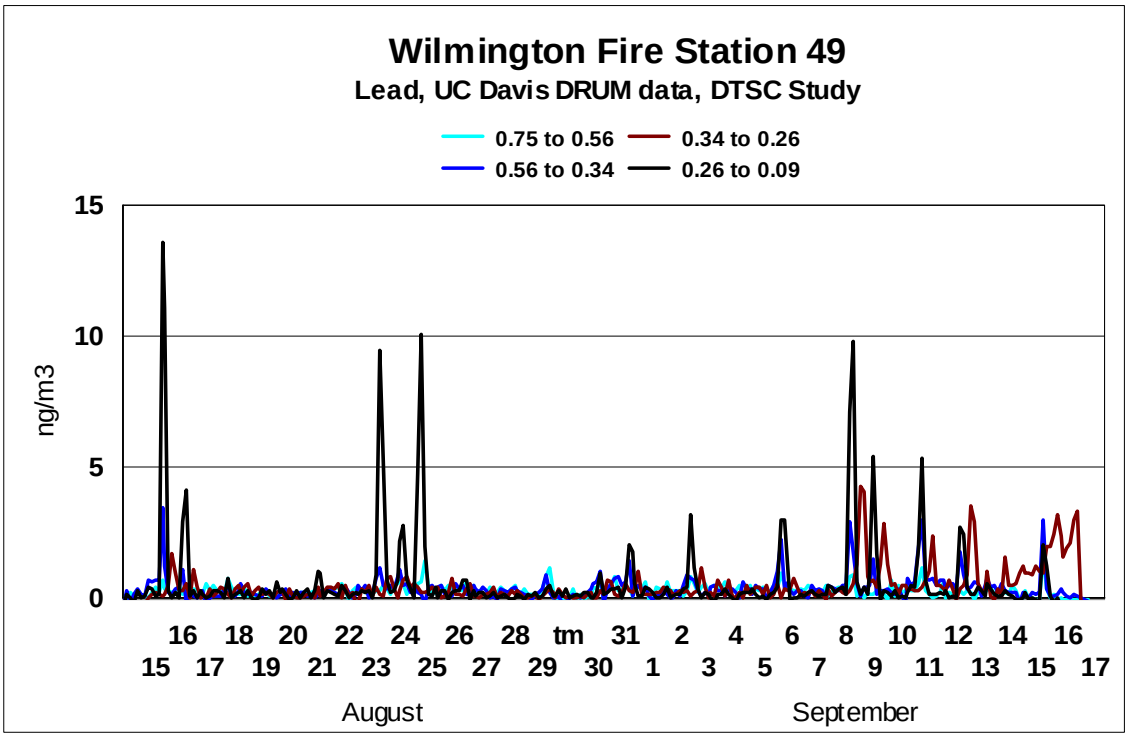


Figure 16 DRUM elemental data – fine modes of lead

The fine mode lead has unknown sources, but its concentrations are far below CA lead standards based on the lead in gas era.

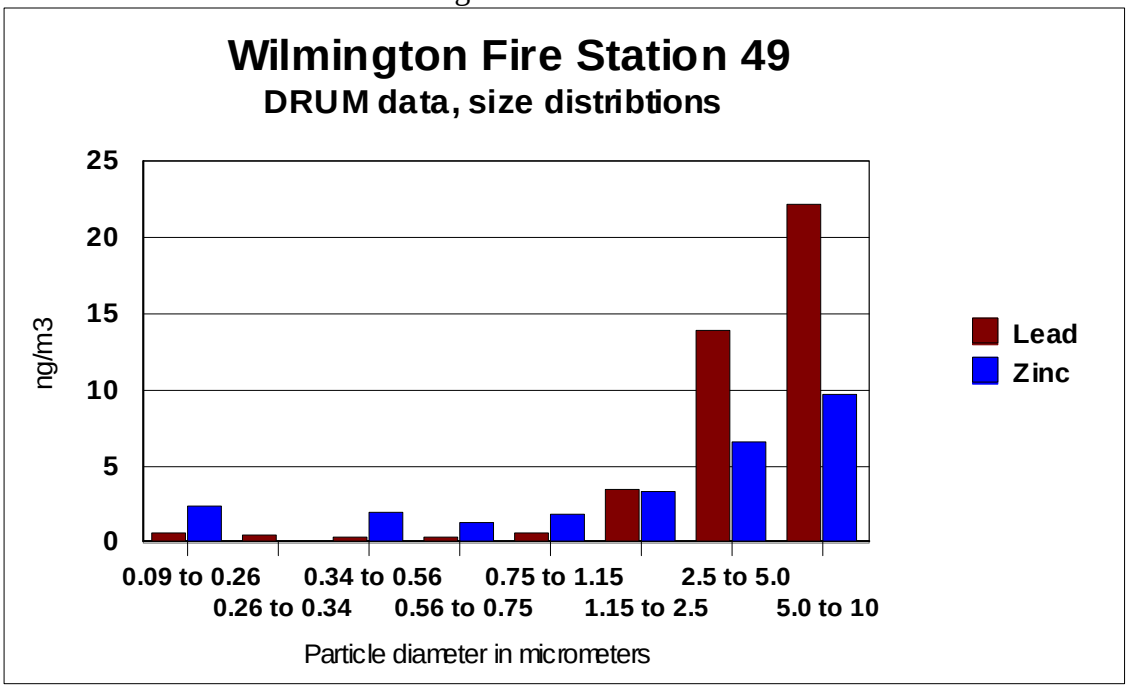


Figure 17 DRUM elemental data – size of lead and zinc

We now examine a set of three elements in some detail, sulfur, vanadium, and nickel. Each shows highly correlated patterns on the daytime winds that blow across the shredder to the Wilmington sampling site.

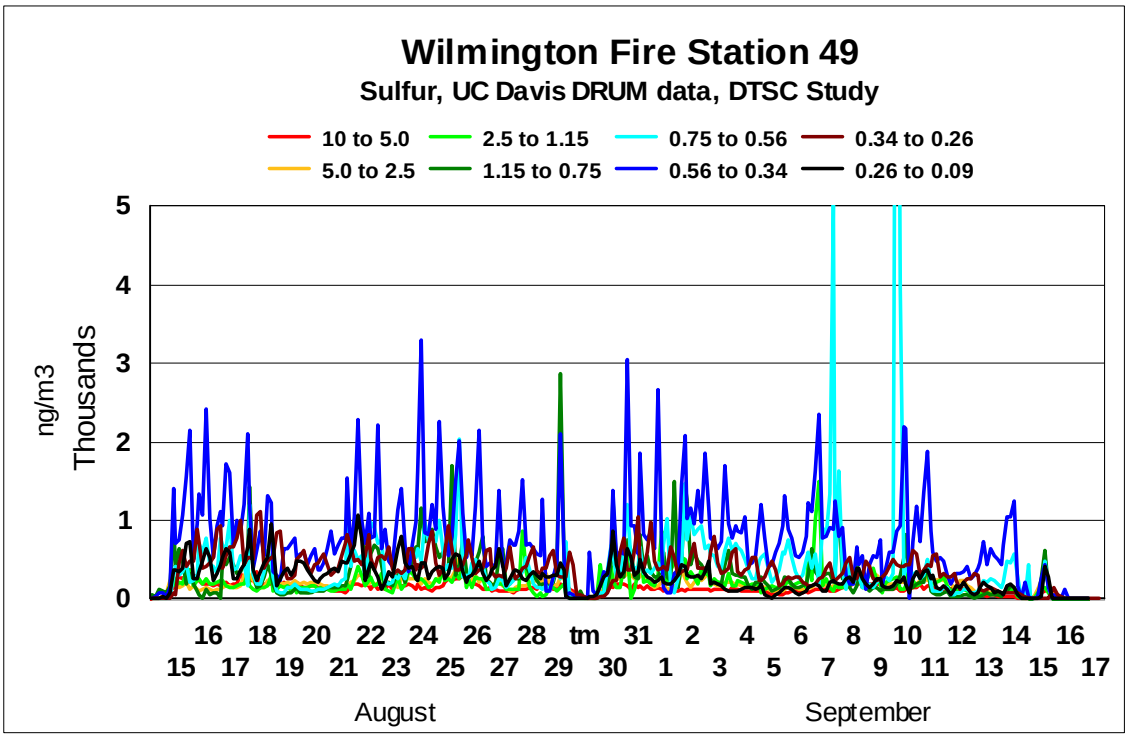


Figure 18 DRUM elemental data – sulfur

We note that in this plot and the ones to follow, influence of the ships in the port disappeared under a shift of wind to the east around August 21, followed by a massive soot plume (see the optical signal). This period will be examined to see if any unusual events occurred near Fire Station 49 and to better establish non-shredder background.

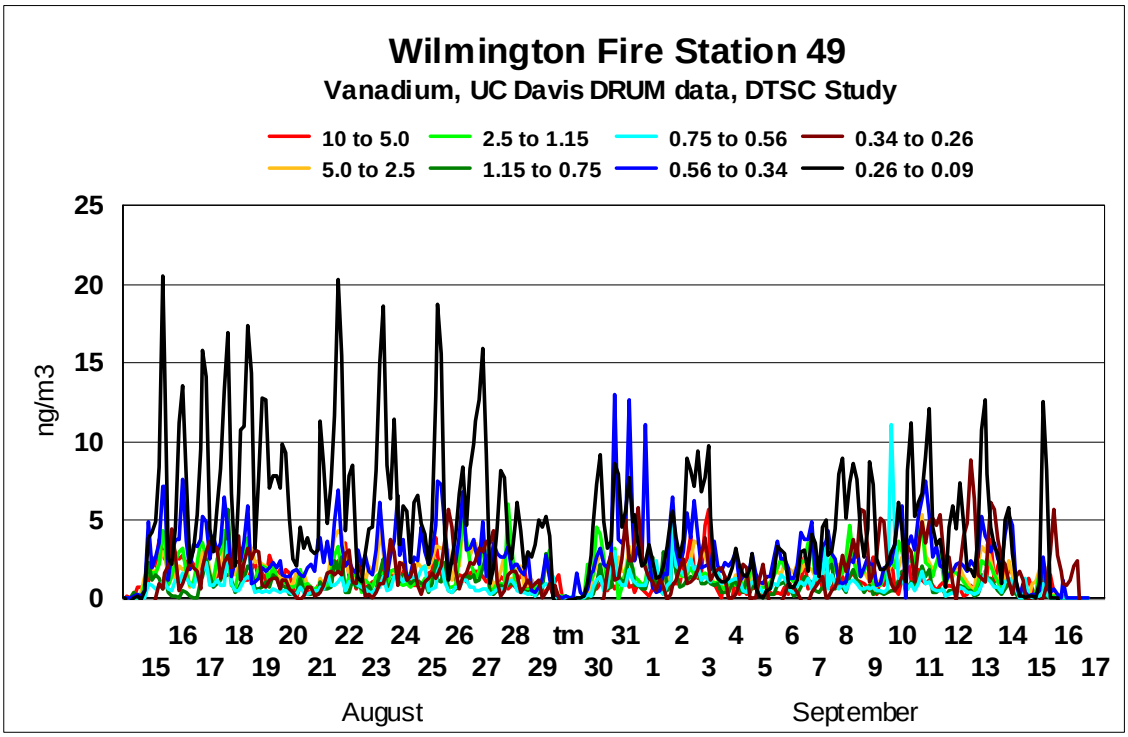


Figure 19 DRUM elemental data – vanadium

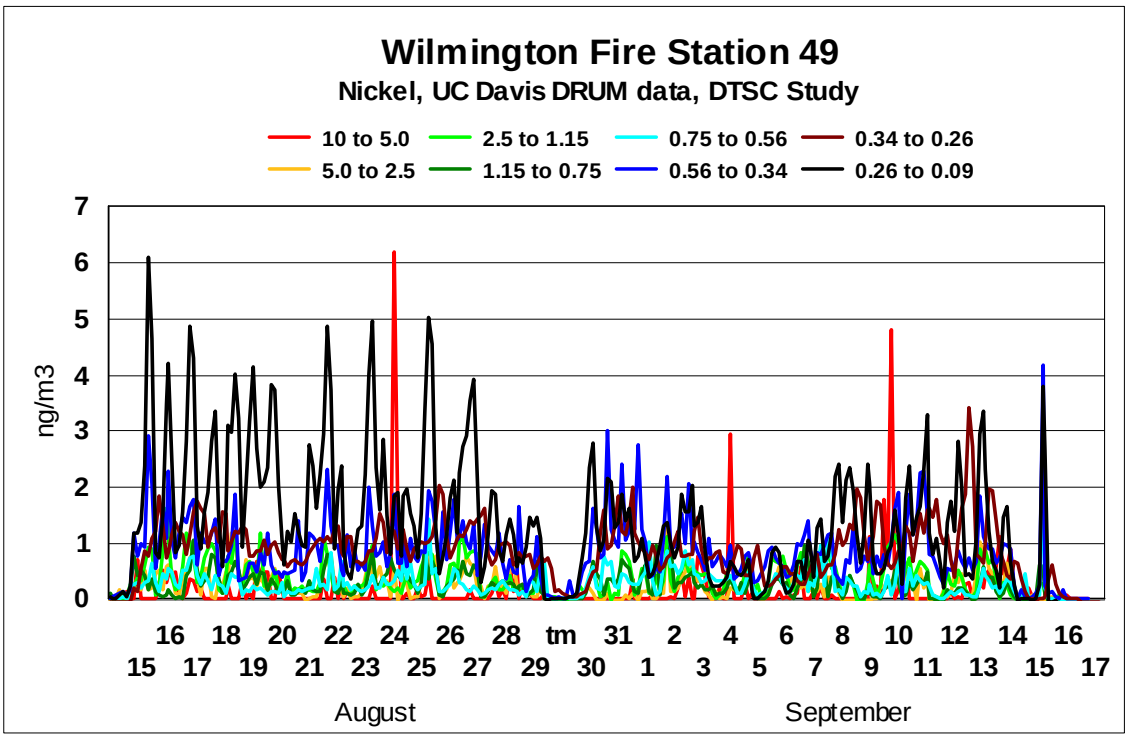


Figure 20 DRUM elemental data – nickel

This elemental set has a unique source the combustion of heavy, sulfur rich bunker oil in ocean going ships. This is shown below in the joint vanadium-nickel plot.

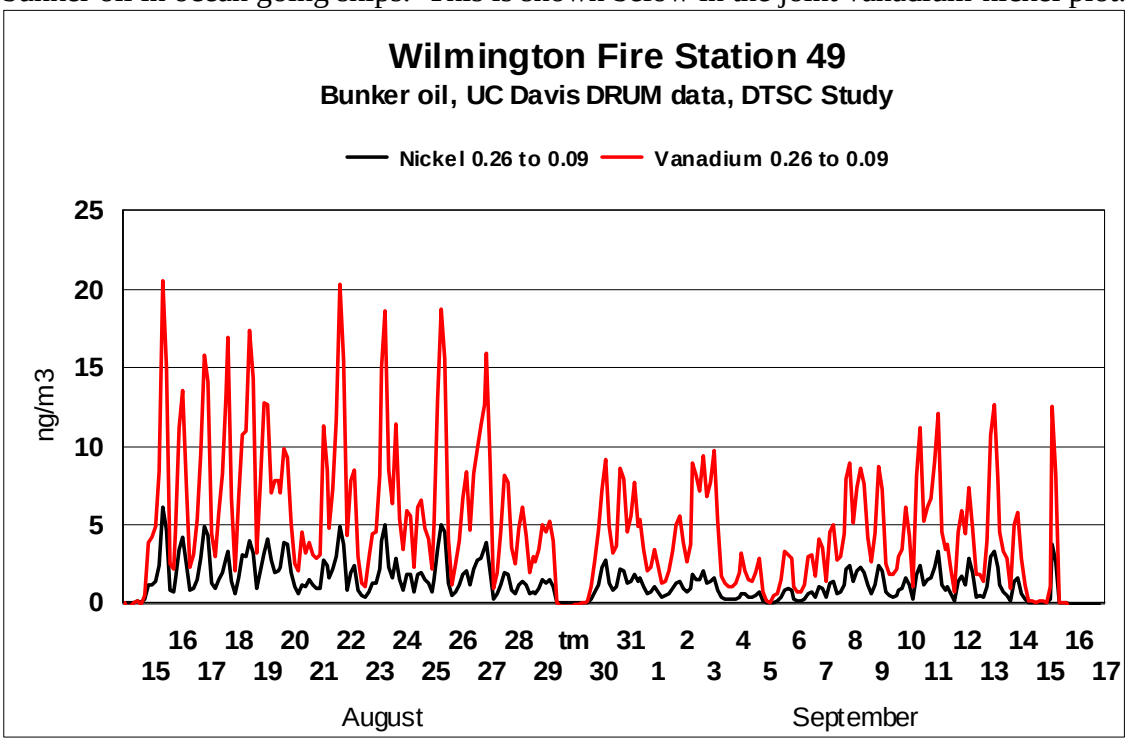


Figure 21 DRUM elemental data – nickel and vanadium

The importance of this result is that it provides an industrial tracer of sources upwind of the shredder, thus identifying trajectories that cross the shredder site before they arrive in Wilmington. This supports the meteorological analysis above.

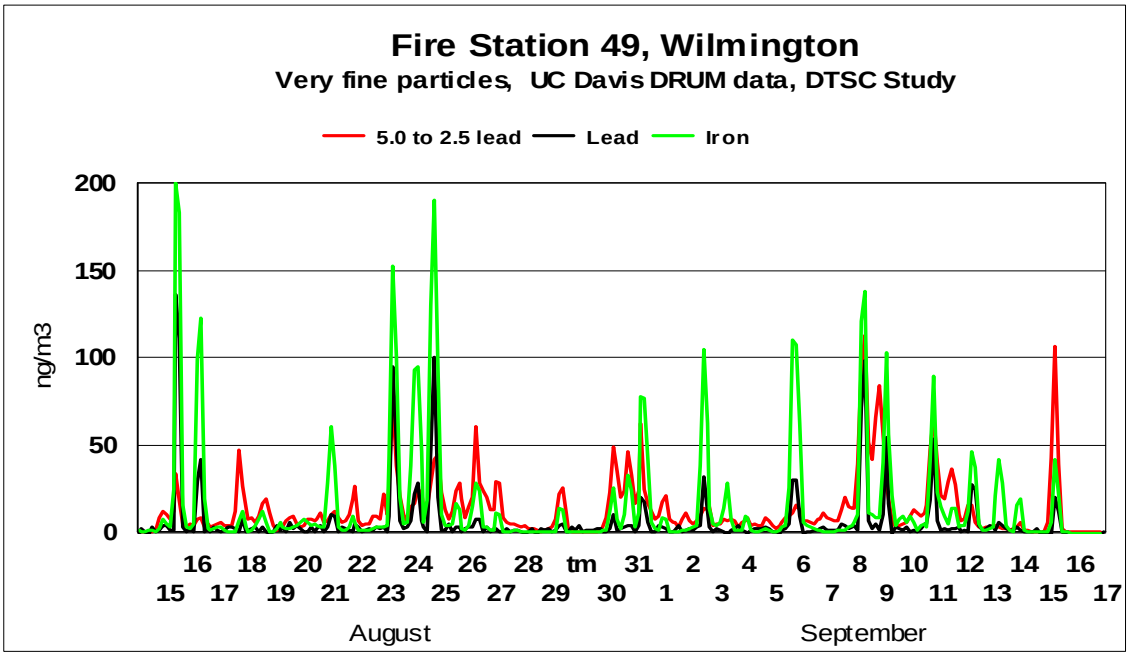


Figure 22 DRUM elemental data – coarse lead, very fine (< 0.25 μm) lead and iron

We can now examine the suite of elements that is correlated with the fine iron. The very fine iron is associated with both very fine lead and coarse lead, but it is clear that the ratio changes from episode to episode. This is most likely due to the varying nature of the feed stock. This is shown below for additional elements zinc and copper, both widely used in cars and appliances. Note the high zinc episodes of August 25 and 26, with little lead. There are no major lead sources in appliances, as an example.

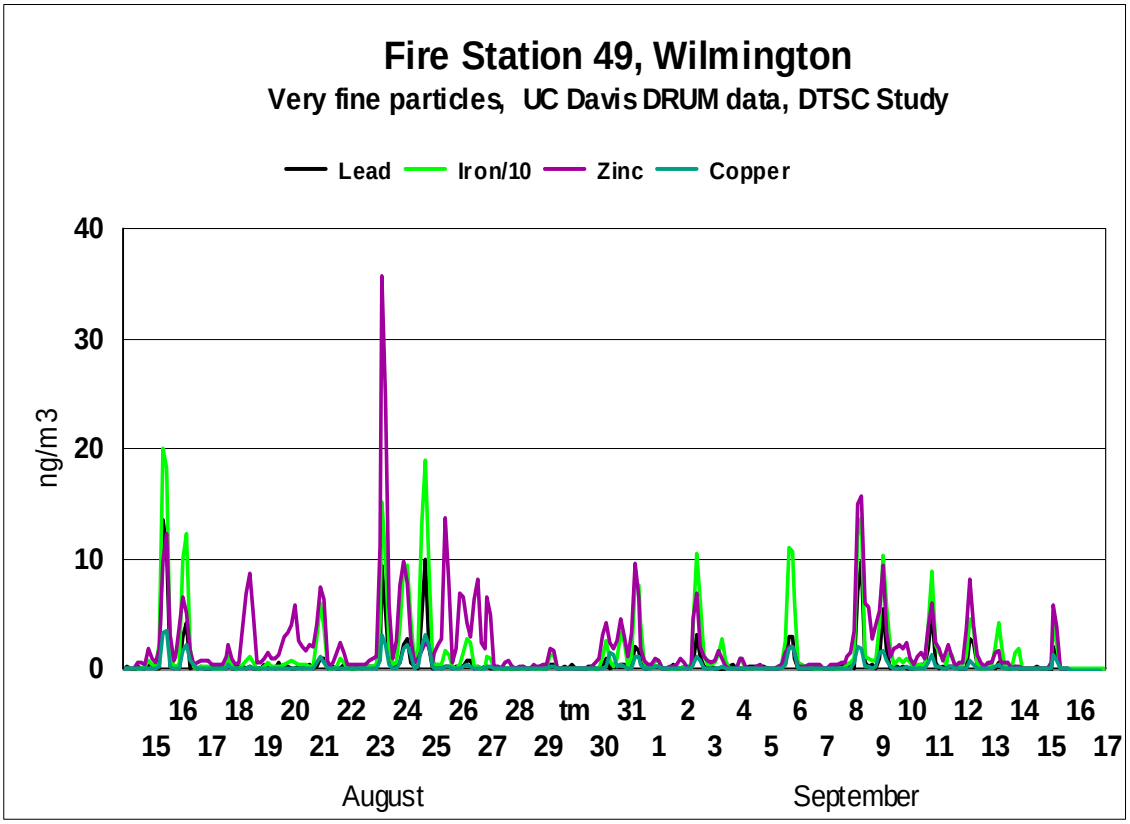


Figure 23 DRUM elemental data – very fine (< 0.25 μm) lead, iron, zinc, and copper

2. Long term toxic concentration data

With the availability of aerosol mass and compositional data, we can calculate the fraction concentration of toxic elements throughout the study period. The coarsest particle measured, 10 to 5.0 µm diameter are show below in Figure 24.

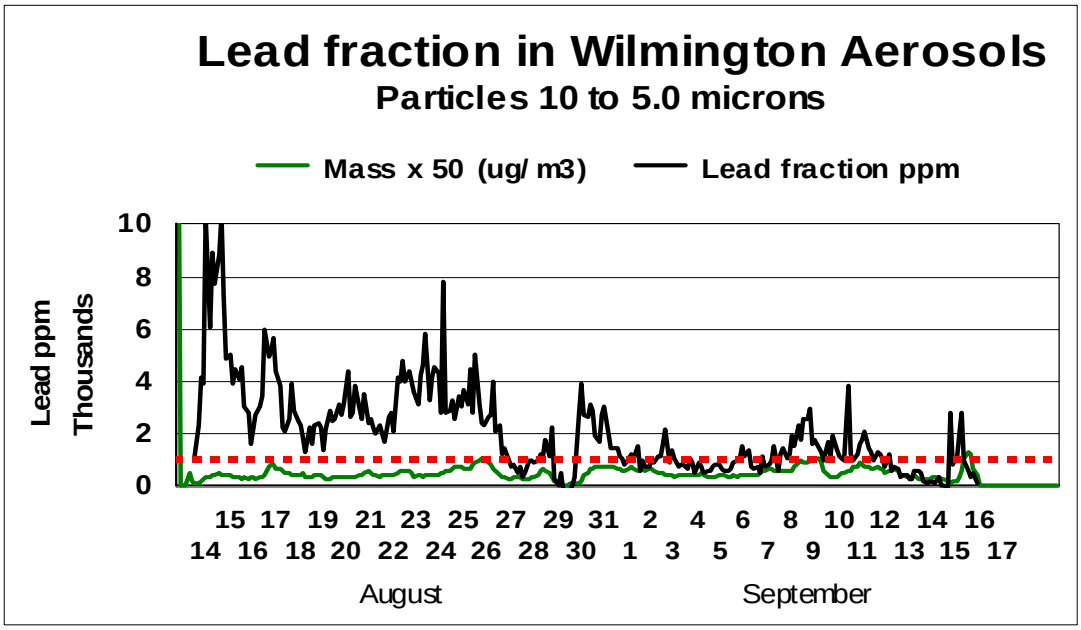


Figure 24 DRUM mass and elemental data –10 to 5.0 µm lead (ppm)

As can be seen in Figure 24, the aerosols measured at Wilmington Fire Station 49 exceeded the 1,000 ppm DTSC standard for almost all hours, but with sharp episodes of up to 10,000 ppm correlated with shredder operations.

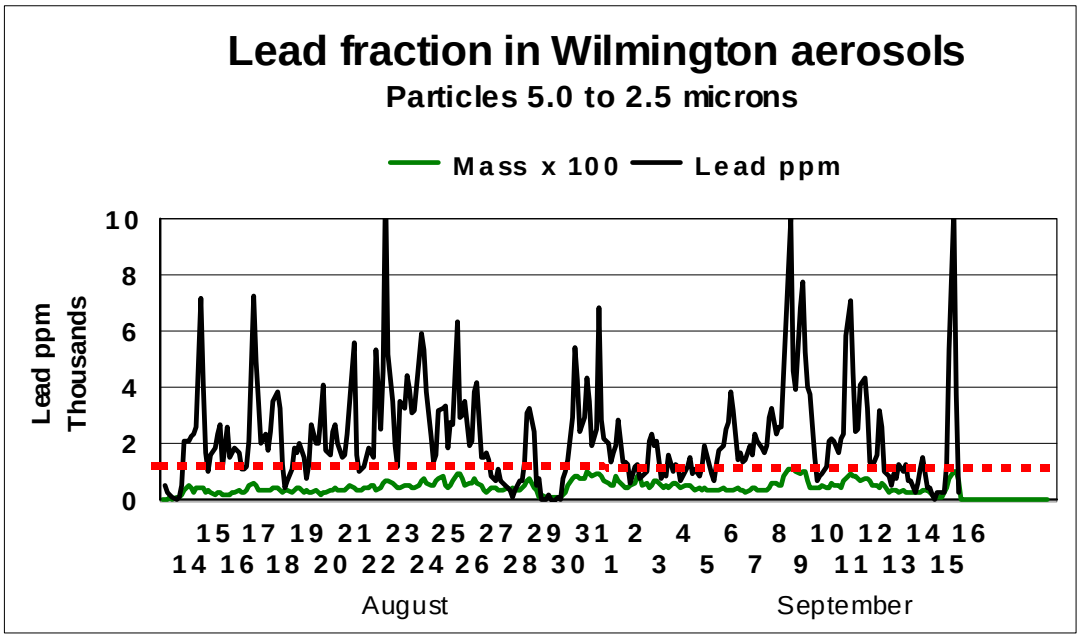


Figure 25 DRUM mass and elemental data –5.0 to 2.5 µm lead (ppm)

A similar result is seen for particles from 5.0 to 2.5 µm diameter, but with sharper lead peaks as the DRUM time resolution improves.

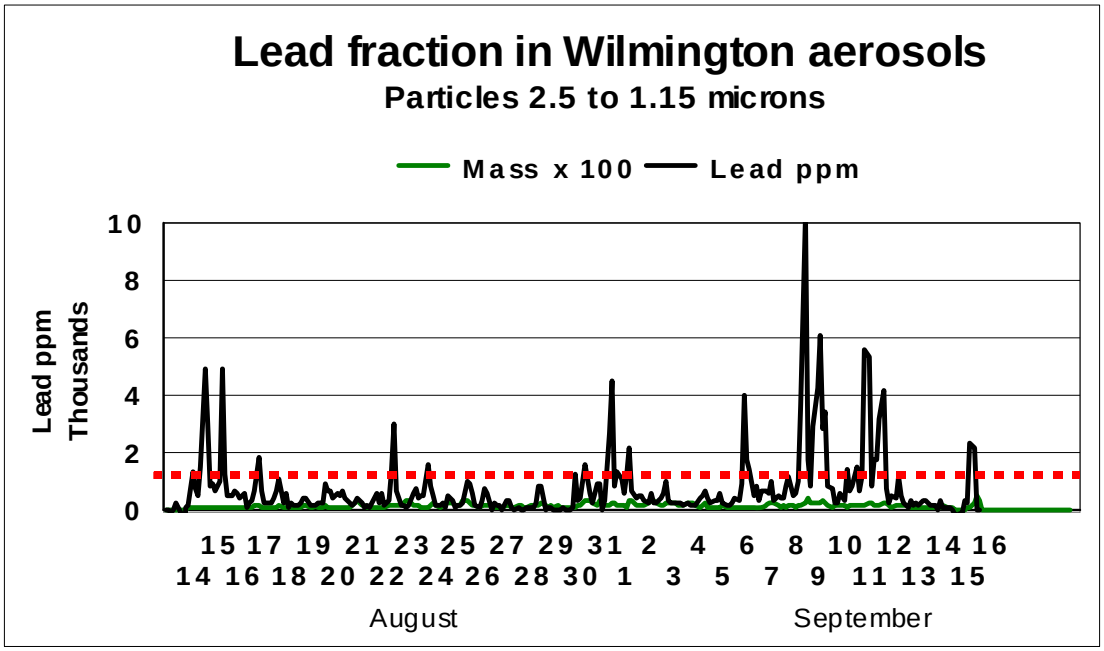


Figure 26 DRUM mass and elemental data – 2.5 to 1.15 µm lead (ppm)

For particles from 2.5 to 1.15 µm, peaks as high as 10,000 ppm still occur for a few hours at a time.

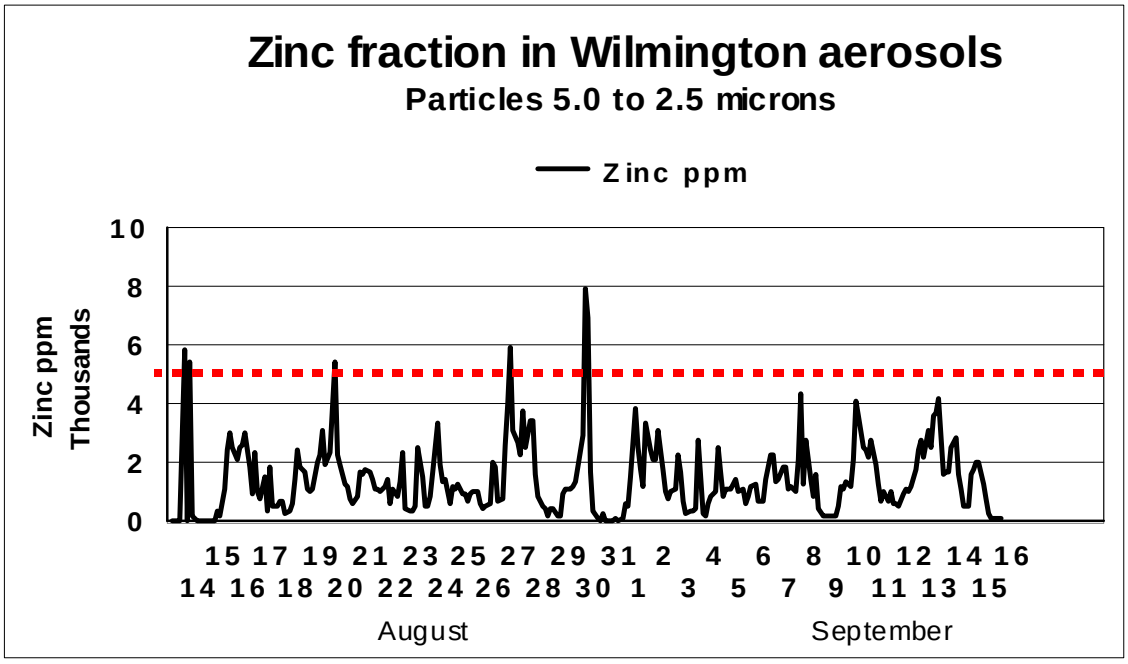


Figure 27 DRUM mass and elemental data –5.0 to 2.5 µm zinc (ppm)
Zinc also violates DTSC 5,000 ppm standards on occasion.

These data only tell part of the story. The flat distribution in size or, on some days, sharp rise in lead mass as one reaches a size of 10 μm (see August 16) indicates that there is additional lead at sizes above 10 μm, perhaps much more, on some occasions. Looking to smaller particles, the abrupt rise in lead and iron concentrations as one approaches 0.09 μm indicates that there is probably considerable mass of these elements in the dangerous ultra fine particle mode.

3. **High time resolution studies**

From the data above, we can prepare a summary table of lead and zinc concentrations versus date.

Date (Aug. - Sept.) (based on very fine iron tracer)	Lead ppm 10 to 5.0 μm	Lead ppm 5.0 to 2.5 μm	Lead ppm 2.5 to 1.15 μm
15	8180	5679	4013
16	9612	2531	3103
18	5477	6115	1268
21	3439	3567	851
23	4442	8236	2182
24	5279	5660	1278
25	5229	4635	459
26	4082	4052	1016
29	1691	3224	864
31	3325	4873	1394
2	1280	2526	3616, 1475
6	1285	3535	2919
8	1356	2259	6972
9	2802	9157	5202
11	2541	6481	5485
15	2399	7903	2302

Table 2 Lead concentrations versus particle size – 16 episodes

The amount deposited can be readily calculated by introducing the settling velocity (Seinfeld and Pandis 1997)

Details of the transport to the Wilmington sampling site can be established by combining the local meteorological data with the time resolved DRUM data. Three periods will be examined in detail, August 14 to August 19, August 21 to August 24, and September 7 through September 10.

a. August 14 to August 18 episodes

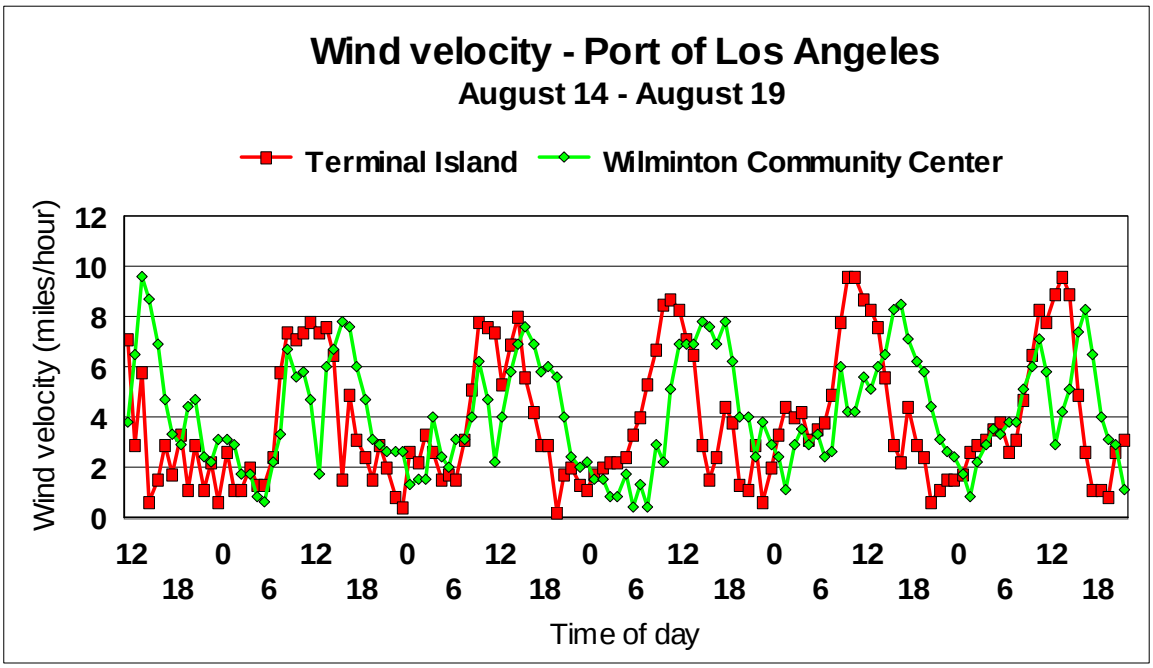


Figure 28 Local wind velocity – August 14 to August 18

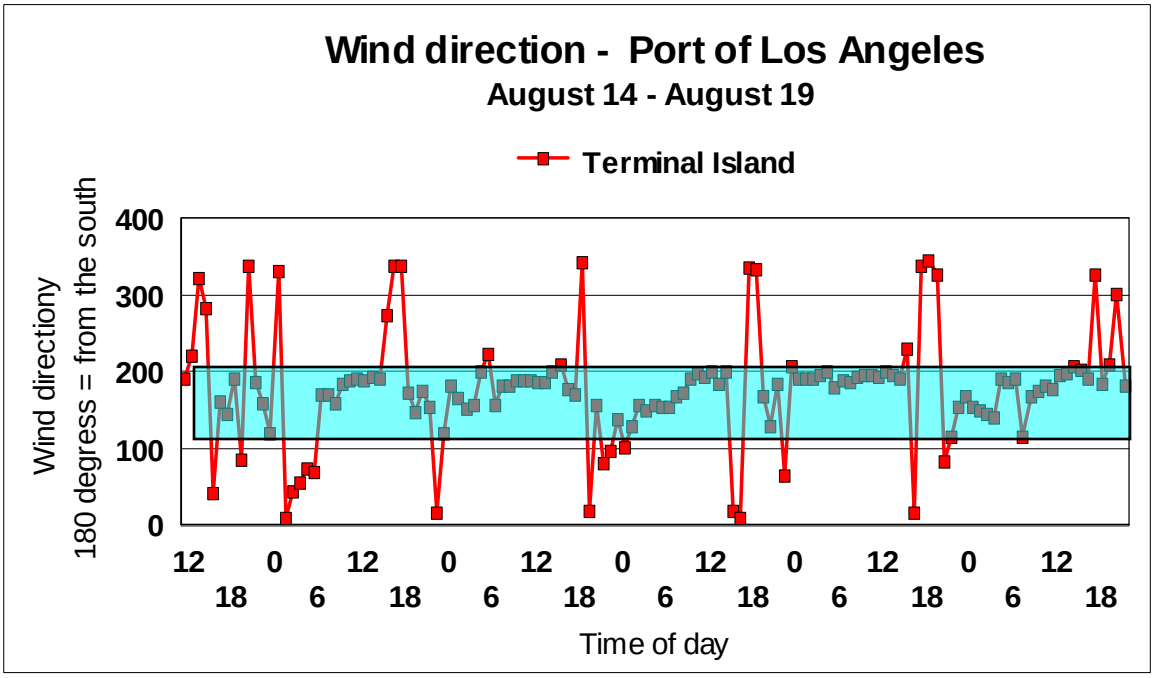


Figure 29 Local wind direction – August 14 to August 18. The shaded area is ± 45° from the direction of the shredder.

As shown below, both lead and iron were seen when winds were optimum for transport to Wilmington.

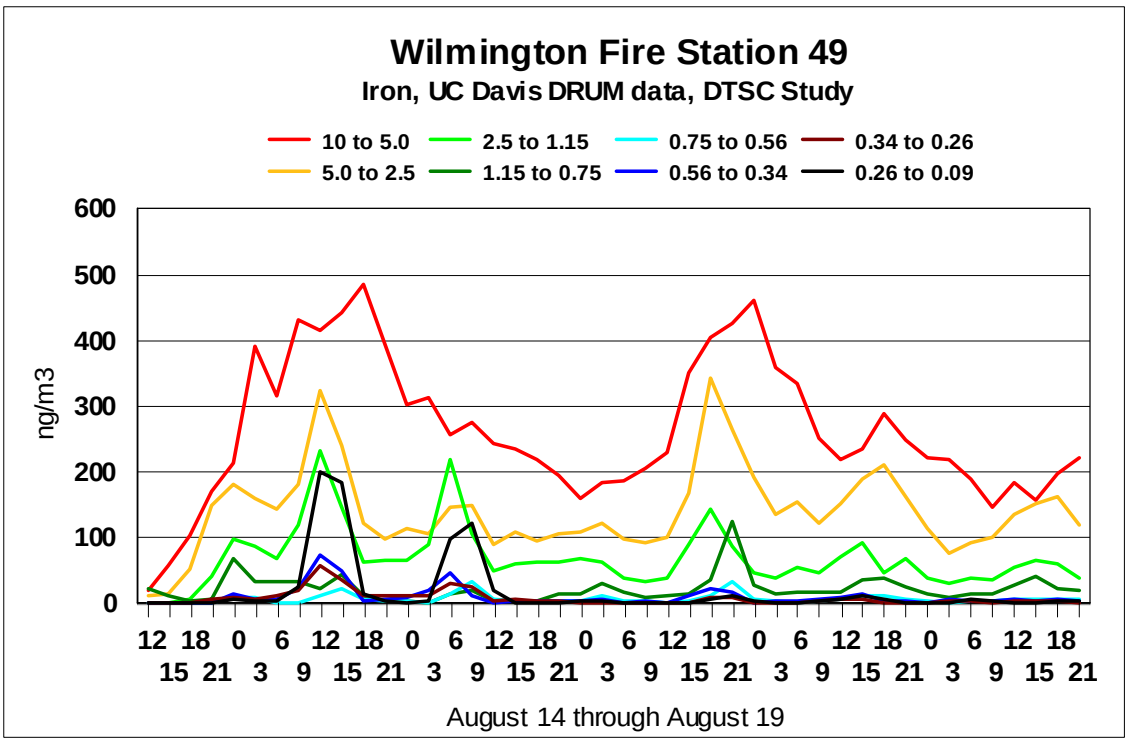


Figure 30 DRUM/S-XRF elemental data, iron, August 14 to August 18

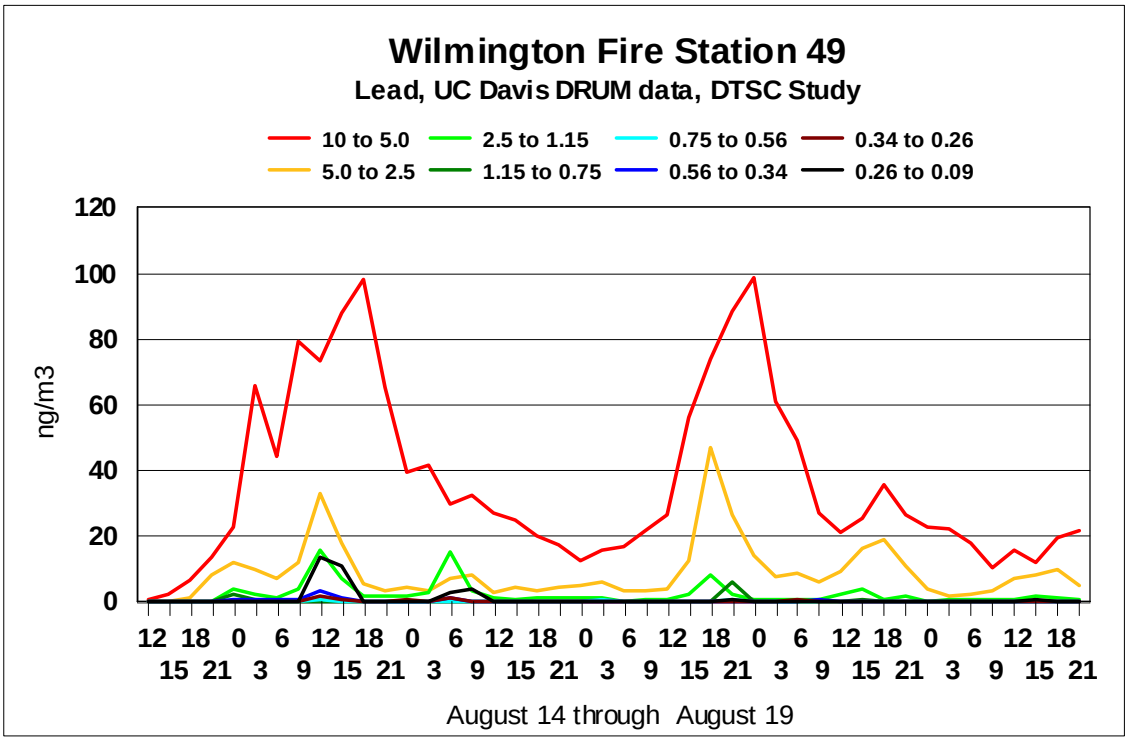


Figure 31 DRUM/S-XRF elemental data, lead, August 14 to August 18

b. August 21 to August 24 episodes

We now examine short time period analysis for the four days, August 21 through August 24, on a 3 hr basis.

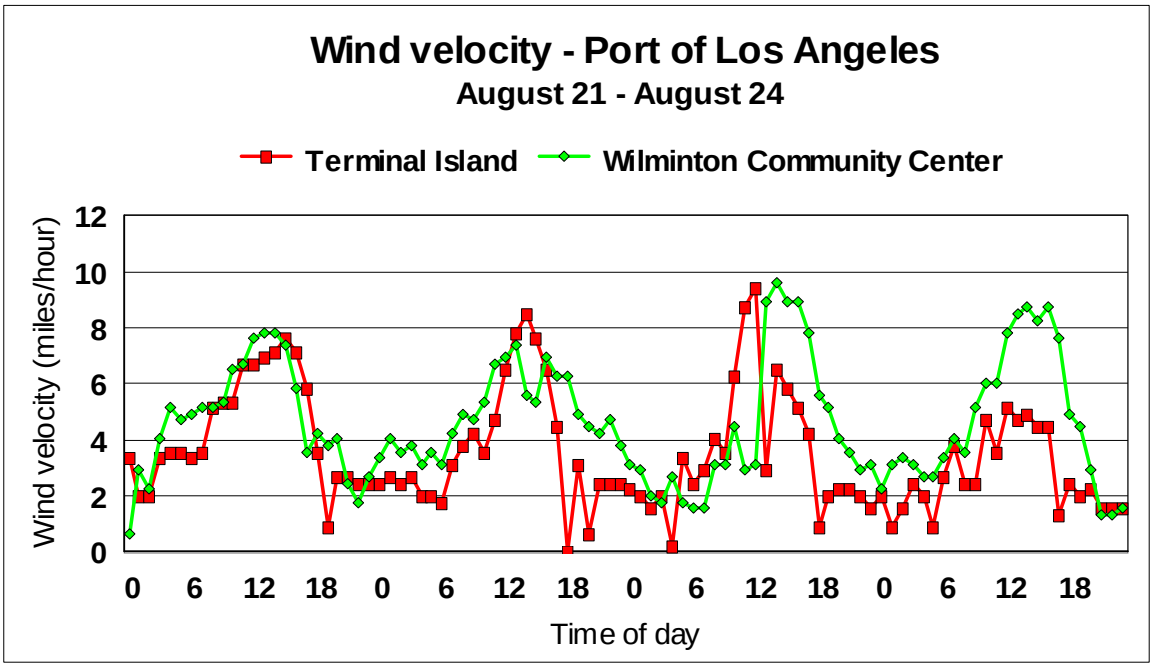


Figure 32 Local wind velocity – August 21 to August 24

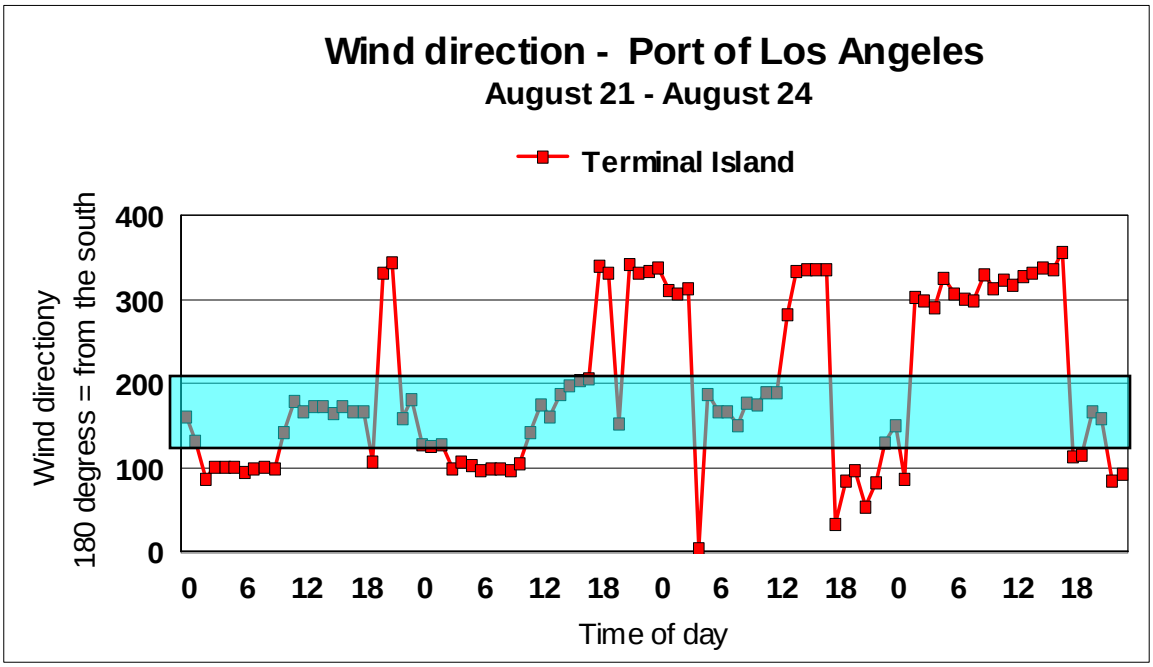


Figure 33 Local wind direction – August 21 to August 24

The first element is chlorine from sea salt.

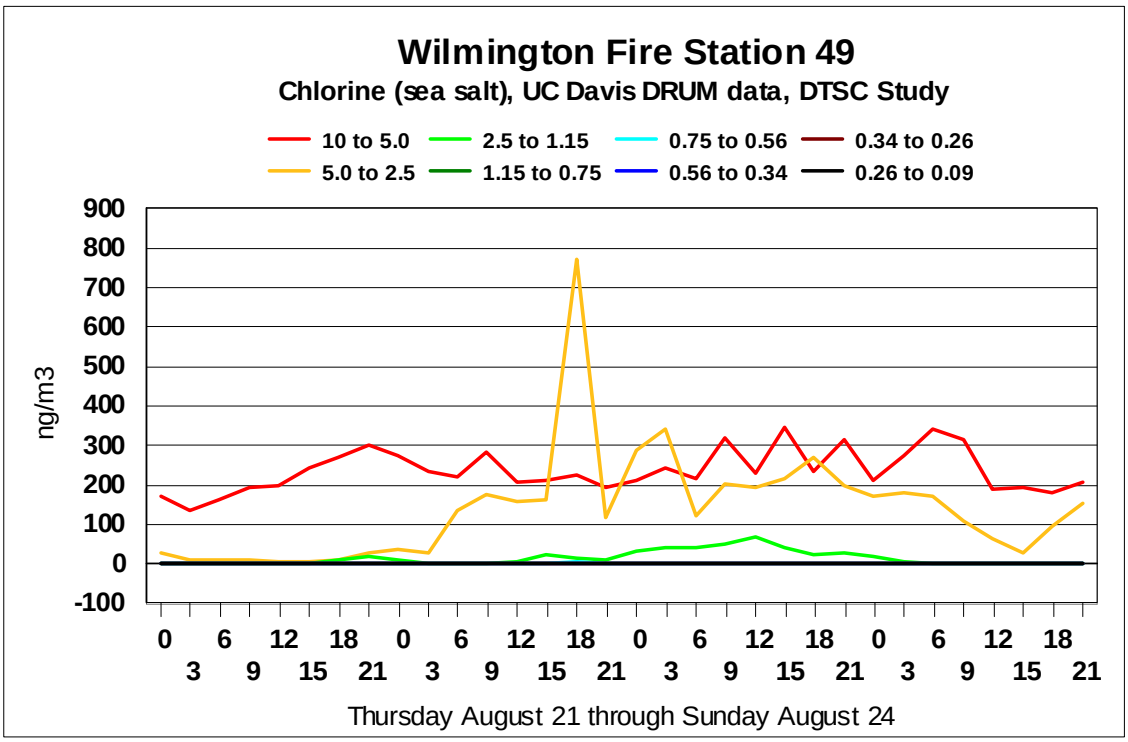


Figure 34 DRUM/S-XRF elemental data – chlorine

The coarse sea salt is essentially constant, but the finer sea salt starts on August 22 and peaks on August 23.

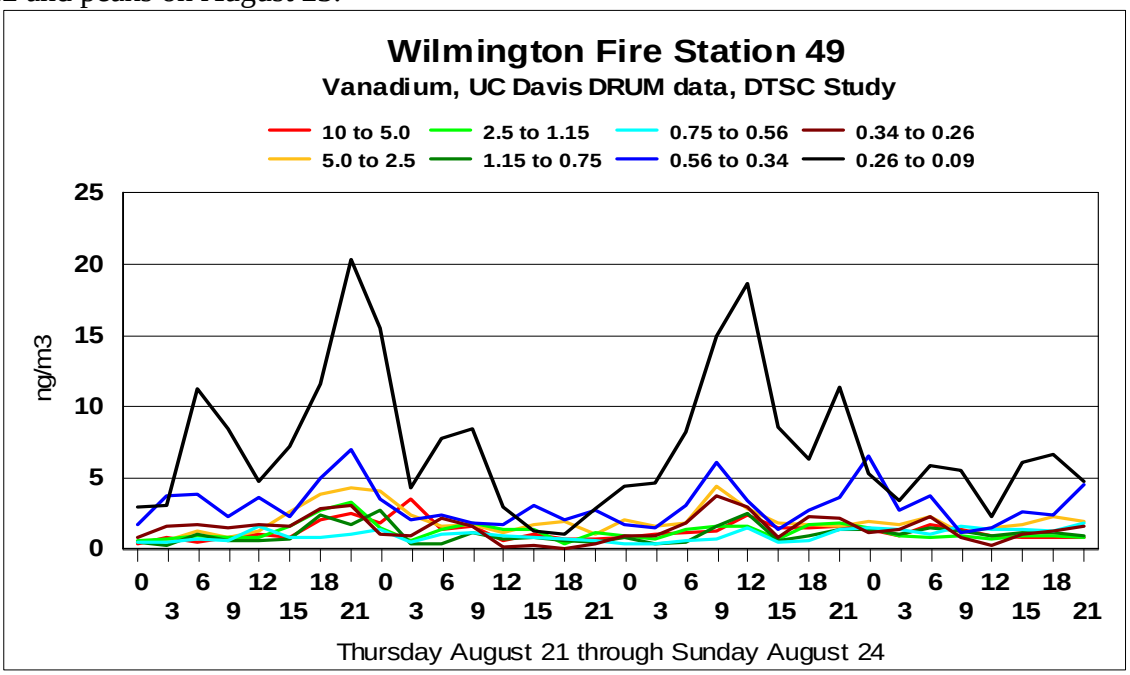


Figure 35 DRUM/S-XRF elemental data – vanadium

Another tracer of upwind air that must pass over the shredder to reach the Wilmington site is vanadium from heavy bunker oil used in ocean going ships. Note there are major impacts on the daytimes of August 21 and August 23, but the fine chlorine only occurred on August 23.

The iron during this period has an essentially constant source with the very fine spike occurring on the 23rd and 24th. The second of these spikes occurred in conjunction with the finer chlorine and vanadium. Lead has a similar behavior.

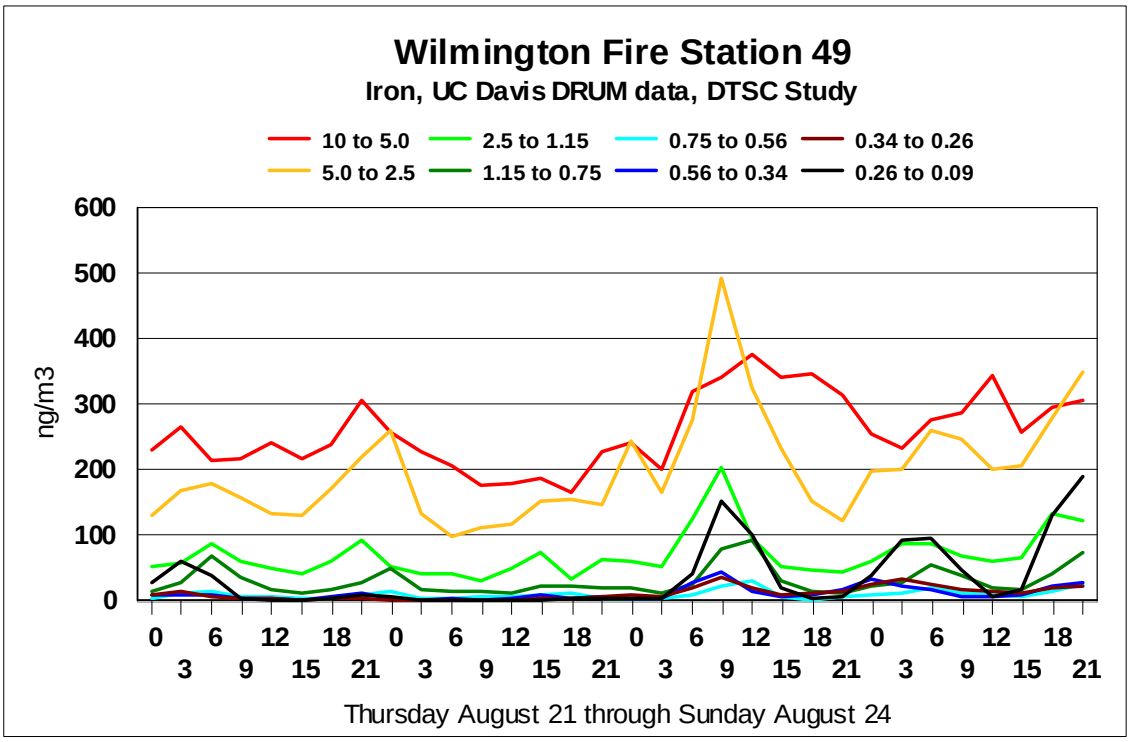


Figure 36 DRUM/S-XRF elemental data – iron

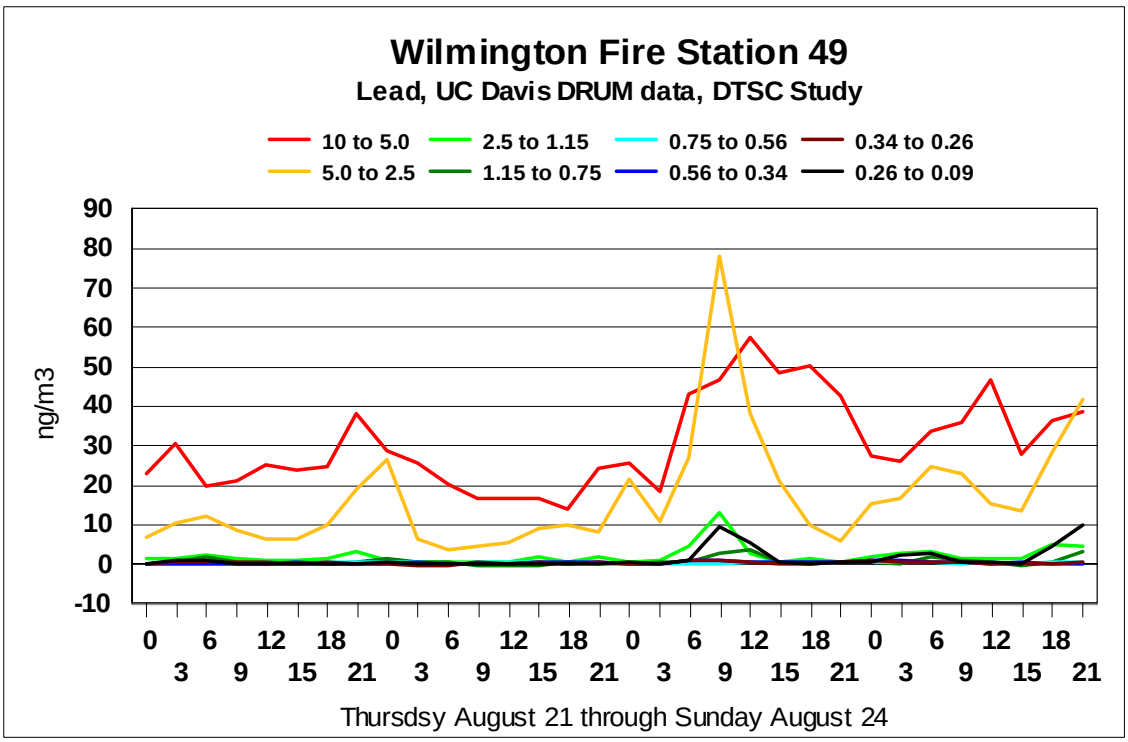


Figure 37 DRUM/S-XRF elemental data – lead

The high concentration and excellent correlation between lead and iron indicate a polluted soil source, but the elemental ratios are very iron rich, roughly a factor of 4 more than soil. This indicates a long-term impact of the shredder on the surrounding area.

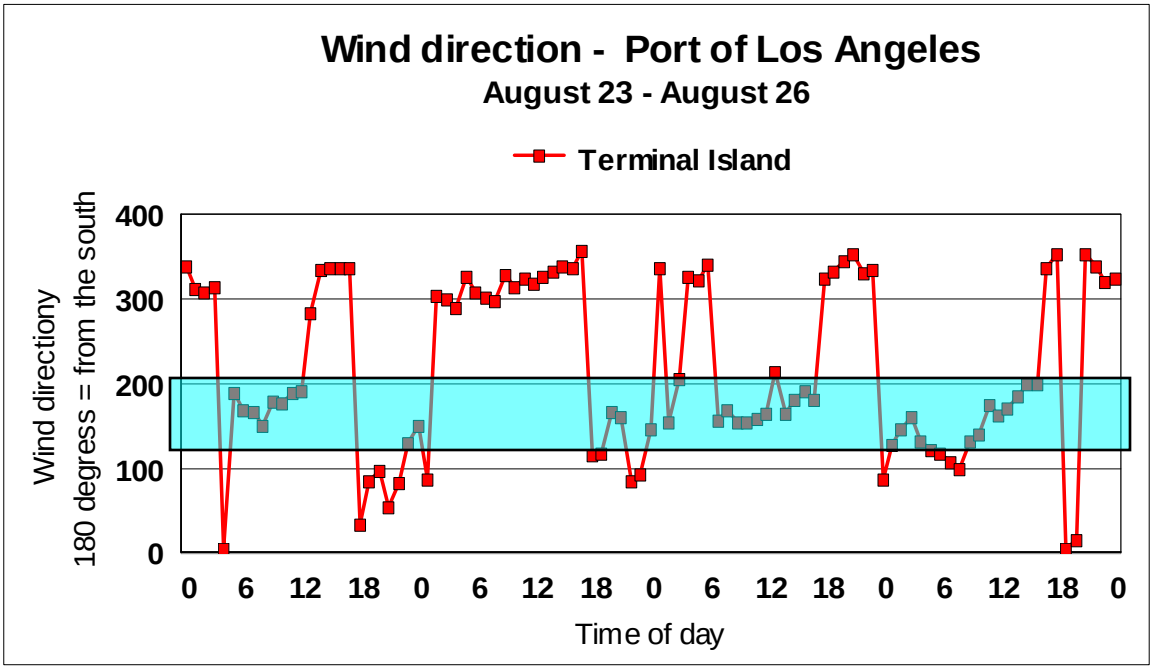


Figure 38 Wind direction data with shredder direction overlay

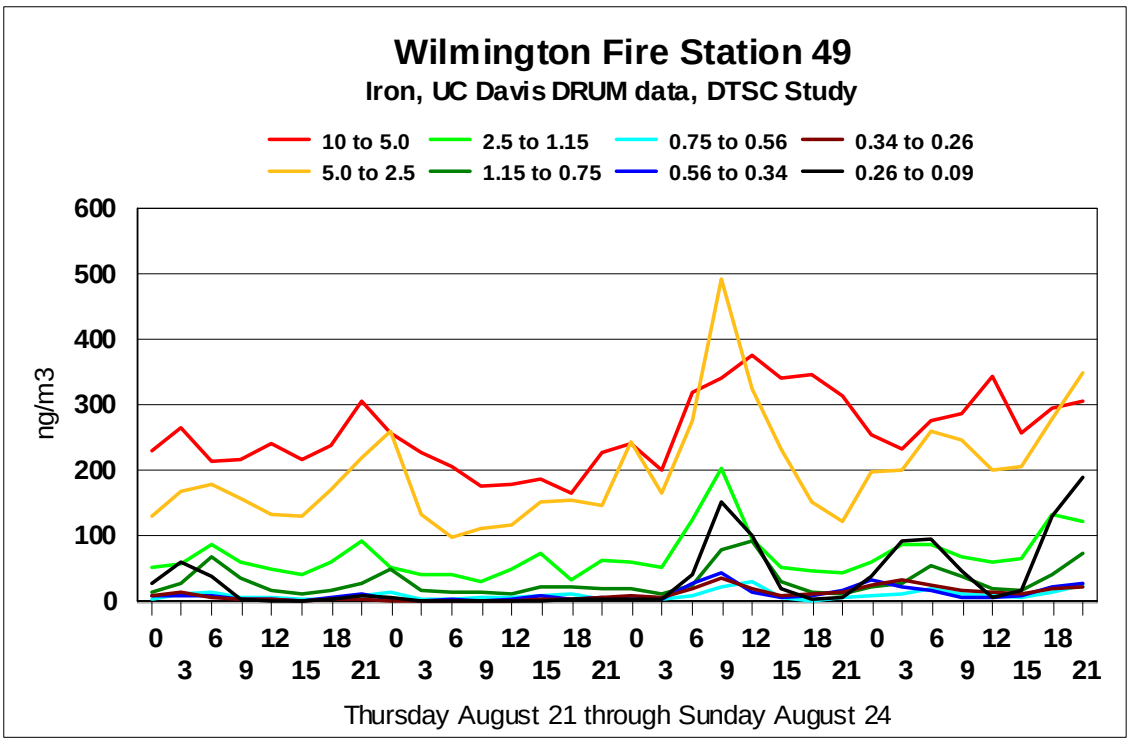


Figure 39 DRUM/S-XRF elemental data – fine iron

The presence of the very fine iron indicates a high energy and/or high temperature process, as iron from soil is essentially absent from aerosols below 1 μm in size. The fact that this tracks with very fine lead and occurs only on winds from the shredder identify the shredder as the source.

c. September 7 through September 10

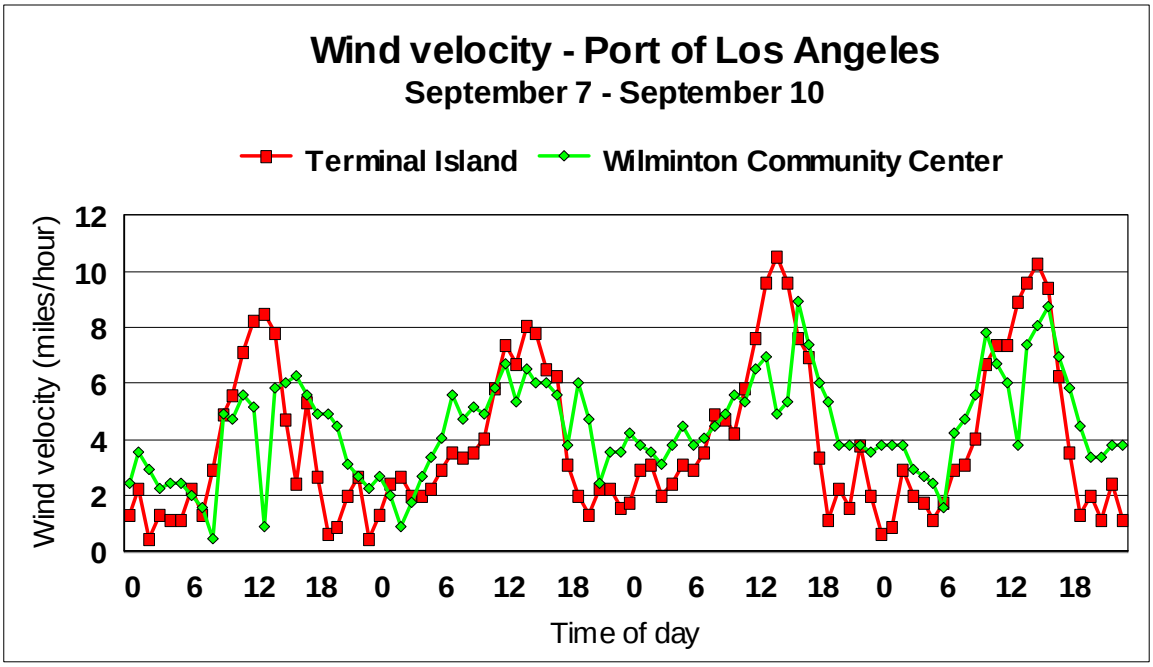


Figure 40 Local wind velocity – September 7 through September 10

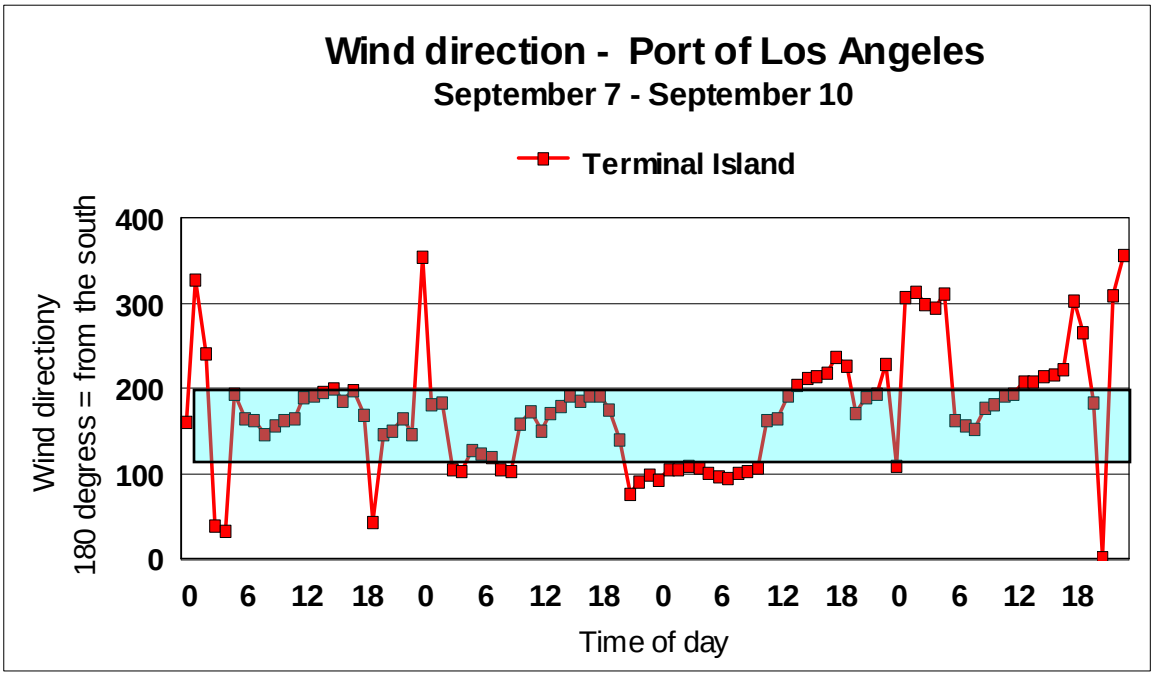


Figure 41 Local wind velocity – September 7 through September 10

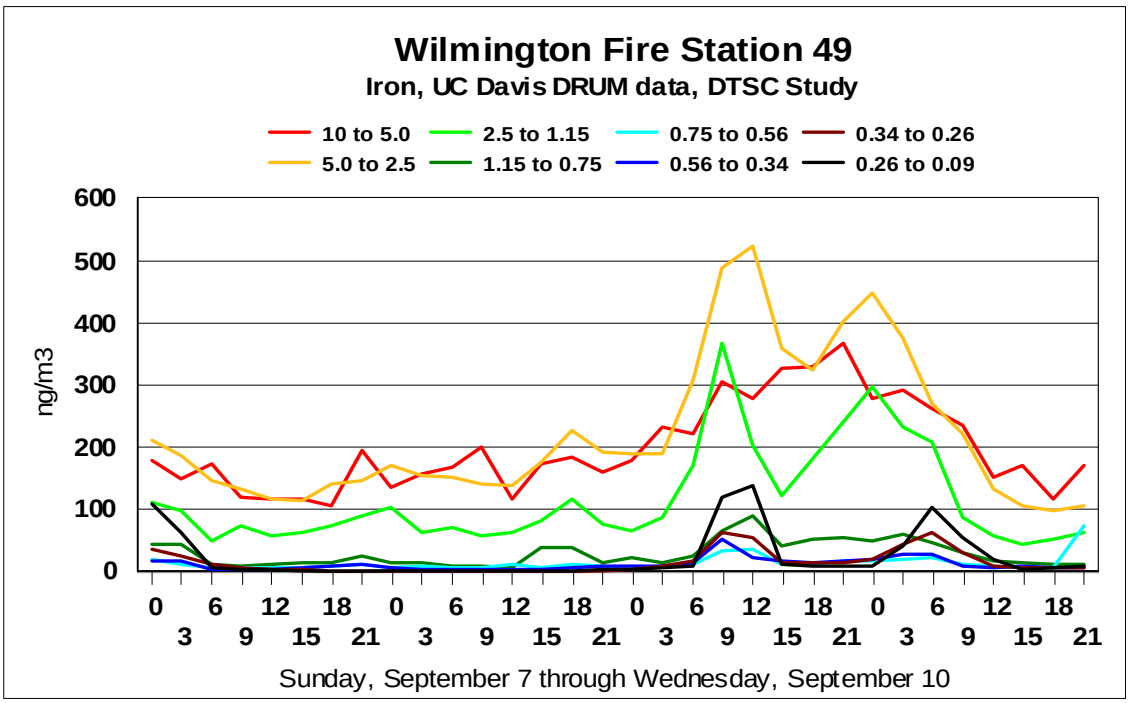


Figure 42 DRUM/S-XRF elemental data – iron

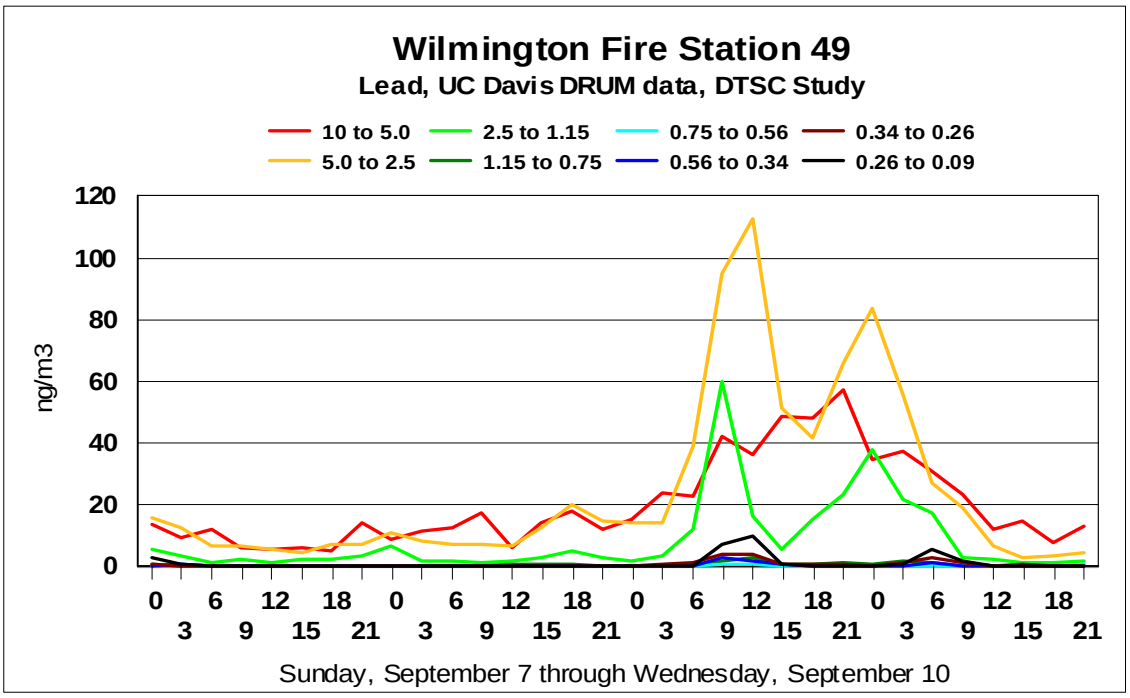


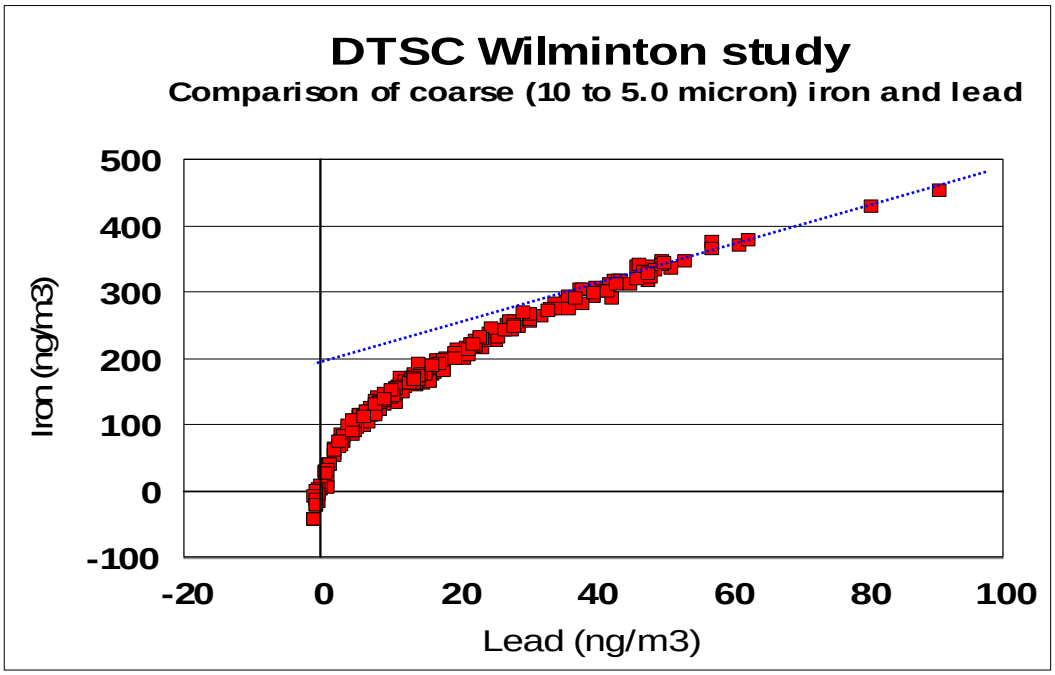
Figure 43 DRUM/S-XRF elemental data – iron

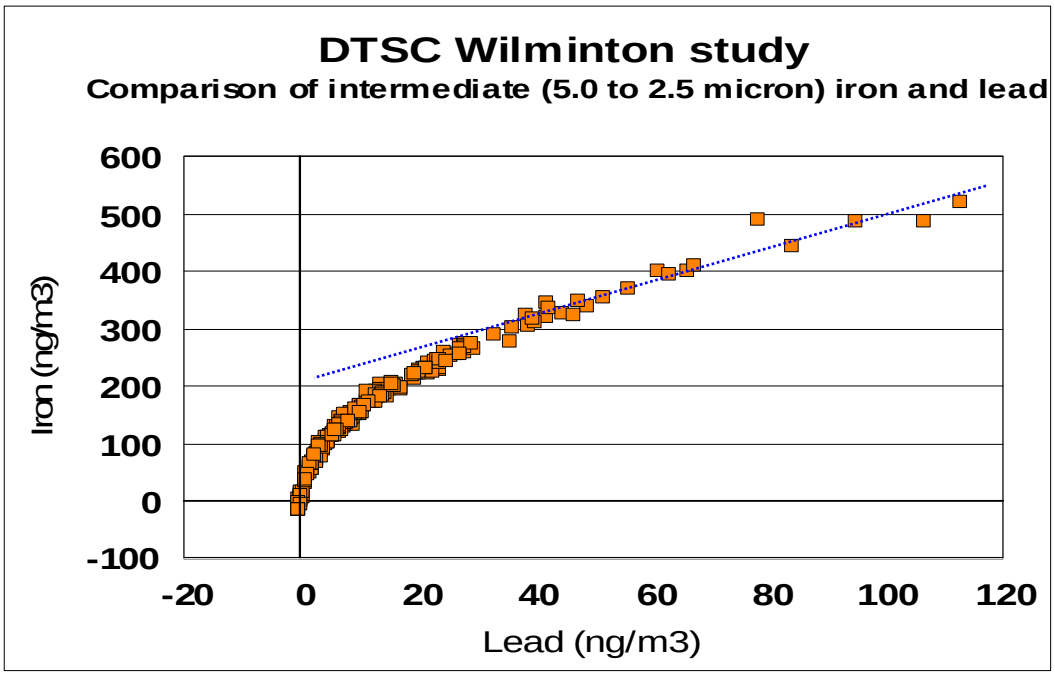
This period is interesting because despite favorable meteorology, there was minimal shredder source impact on Sunday and Monday. Clearly, details of shredder operations and feed stock are key to further analysis.

Additional topics:

1. **Coarse mode aerosols**

Establishment of natural background versus shredder materials in the coarse mode can be examined by performing a regression between the iron and lead for the 10 to 5.0 and 5.0 to 2.5 µm size modes. The assumption is that the natural soil has little lead.





The non-linear behavior of the graphs show that there is an intercept at which there is iron but no lead (circa 200 ng/m^3), – this could be the natural soil background. This soil, however, may also be from the shredding operations on dirty cars.

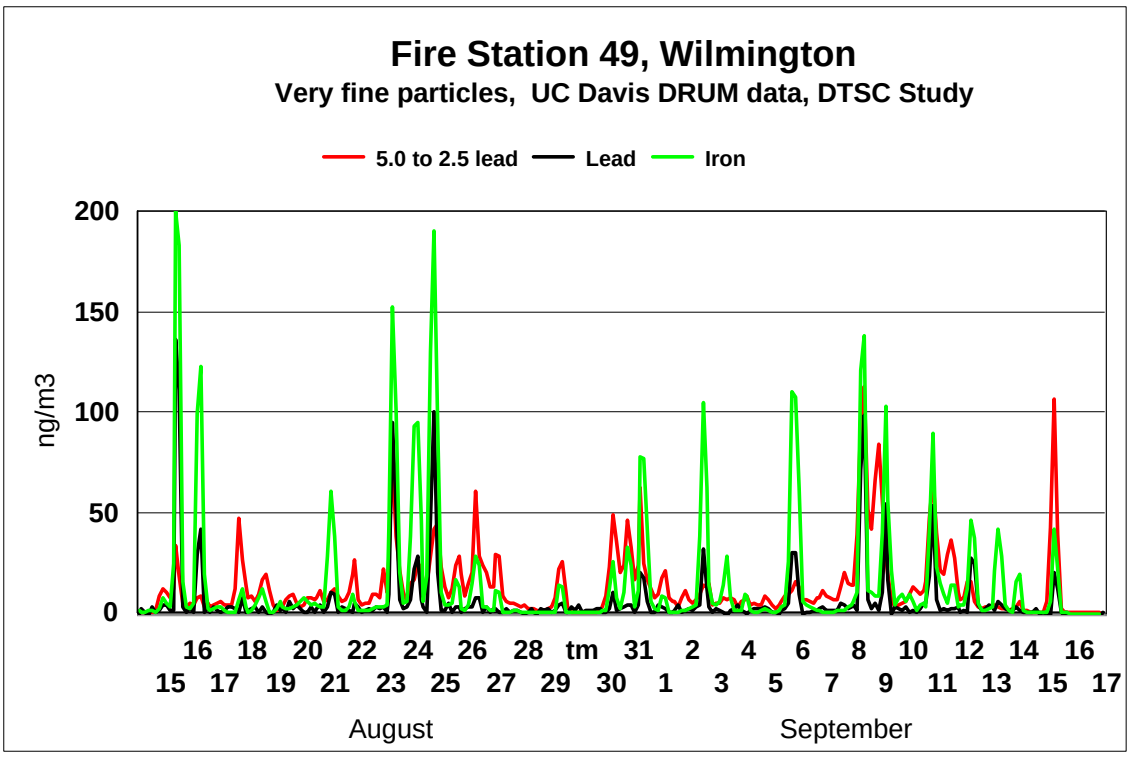
2. Overlap between DTSC Title 22 threshold concentrations and DELTA detectable limits for elements

Element	DTSC Total Threshold Limit Conc. (mg/kg)	DELTA Sensitivity (ng/cm^2)
Antimony (Sb)	500	Interferences limit sensitivity
Arsenic (As)	500	0.1
Barium (Ba)	10,000	1.0
Cadmium (Cd)	100	Interferences limit sensitivity
Chromium & Chromium III (Cr, Cr III)	2,500	0.1
Cobalt (Co)	8,000	0.2
Copper (Cu)	2,500	0.1
Lead (Pb)	1,000	0.6
Mercury (Hg)	20	0.5
Molybdenum (Mo)	3,500	3.3
Nickel (Ni)	2,000	0.2
Selenium (Se)	100	0.1
Silver (Ag)	500	Interferences limit sensitivity
Vanadium (V)	2,400	0.1
Zinc (Zn)	5,000	0.1

Table 3 Overlap of DTSC toxics and DELTA Group MDLs

3. Fine Iron (Fe) particles and known health impacts

We are seeing 100 – 200 ng/m^3 of Fe in air this would normally be approximately 1 ng/m^3. DTSC Toxicologist will determine relation of fine Fe to known health impacts.



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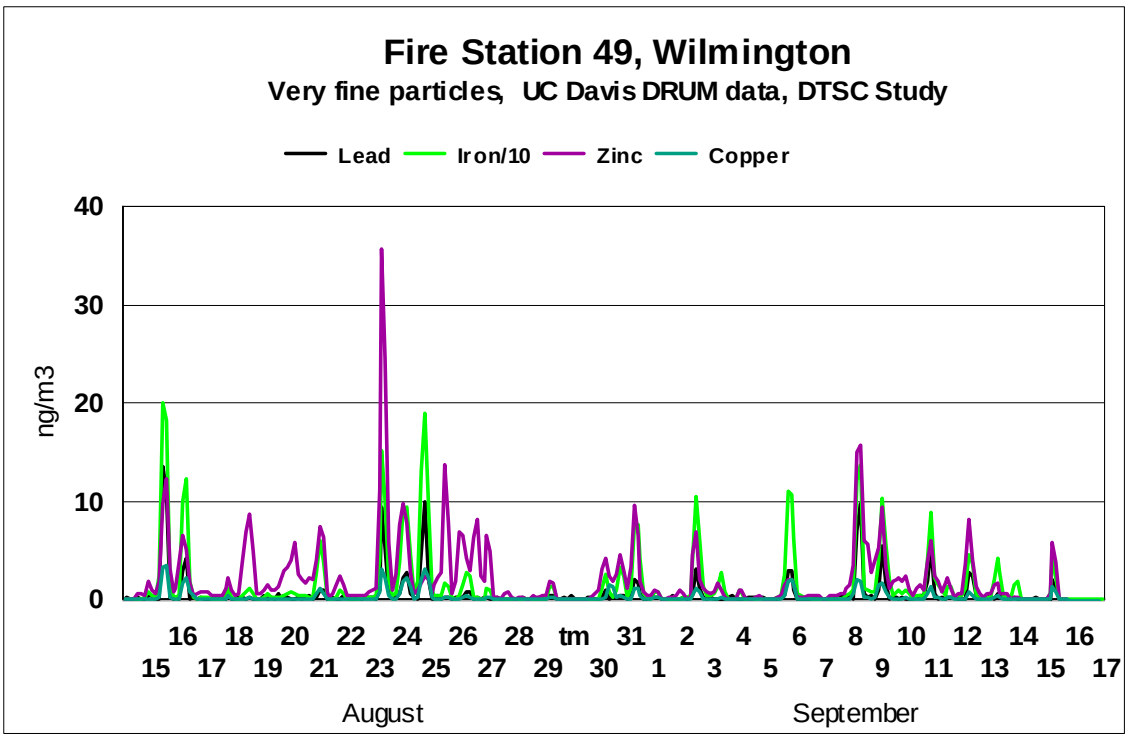
4. Can we distinguish diesel and auto emissions from Shredder emissions?

Yes. There are two methods to use; 1) The differing spatial distribution of diesel sources in the Los Angeles Port area, and 2) trace metals in the shredder waste and diesel exhaust**.**

Diesel emissions from trucks, trains, and fork lifts in the area are widely distributed, including north and east of the Wilmington site, while the shredder lies SSE of the sampling site. Diesel tracers are Zinc (Zn), Phosphorous (P), and Sulfur (S) (Zielinska et al, 2004), and thus these would show up in the record when the winds are in all directions other than from the shredder. No such signature is seen, limiting the impact. Using the measured non-shredder zinc background of 0.3 ng/m^3, and using the Zielinska zinc to mass value for diesel trucks, we predict about 0.5 μg/m^3 of diesel exhaust at Fire Station 49 in Wilmington, a contributor to the 1.5 to 2 μg/m^3 of very fine mass we measured, but dwarfed by the 10 the 40 μg/m^3 of shredder mass.

Shredder waste is known to have the following elements: Lead (Pb), Copper (Cu), Zinc (Zn), Iron (Fe), Cadmium (Cd), Mercury (Hg), and Arsenic (As). Since zinc is common to both diesel and shredder waste, we can examine how much zinc occurs that is not associated with lead and iron. In the figure (below) we show that every zinc peak but one (August 27) occurs with the typical shredder elements, and thus des not come from diesels.



5. Can PCB's and other organics be measured using this sampling technique?

This requires a separate (identical) sampling unit, with separate substrates and requires 2 weeks for a detectible signal (the result is an average value at each size mode for the sampled interval, therefore partial day/night or wind selective sampling may be required)

The species that we have measured to date, using this method, include about a dozen PAHs (including specifically benzo[a]pyrene), n-alkanas (petroleum), sugars (including levoglucosan, wood smoke tracer), and fatty acids (including cholesterol from cooking meat.). An example from Roseville rail yard is shown below for PAHs.

Table 3 Concentrations (pg/m^3) of particulate PAHs observed at the Roseville Rail Yard in the summer of 2005.

Compound	8-stage DRUM (8/5 - 9/27)	8-stage DRUM (scaled x 2.6) (8/5 - 9/27)	Early Lundgren (9/27 - 10/7)	Late Lundgren (10/7 -10/17)
Phenanthrene	21	*55*	110	100
Anthracene	<MQL	*<MQL*	20	20
1-methylphenanthrene	<MQL	*<MQL*	32	28
Fluoranthene	57	*147*	160	160
Pyrene	74	*190*	310	300
Benz[*a*]anthracene	[a]	*[a]*	[a]	[a]
Chrysene+ triphenylene	24	*62*	130	130
Benzo [*b*+*k*]fluoranthene	68	*175*	350	330
Benzo[*e*]pyrene	90	*231*	360	350
Benzo{a}pyrene	68	*175*	270	280
Perylene	<MQL	*<MQL*	35	36
Indo[1,2,3-*cd*]pyrene	84	*216*	240	230
Dibenz[*a*,*h*]anthracene	100	*257*	270	270
Benzo[*g*,*h*,*i*]perylene	230	*591*	650	650
Coronene	175	*450*	380	370

[a] Unable to quantify compound due to analytical problem, namely excessive enrichment of chrysene-d_{12} that saturated the ion trap mass spectrometer.

These studies showed that diesel trains had 5.5 ±0.7 times more benzo[a]pyrene emissions per unit mass than diesel trucks. We are aware that an enormous amount of diesel exhaust contaminates the Long beach area, and such data would be extremely useful.

6. Can this analysis provide detection of Mercury (Hg) and Cadmium (Cd)?

Mercury

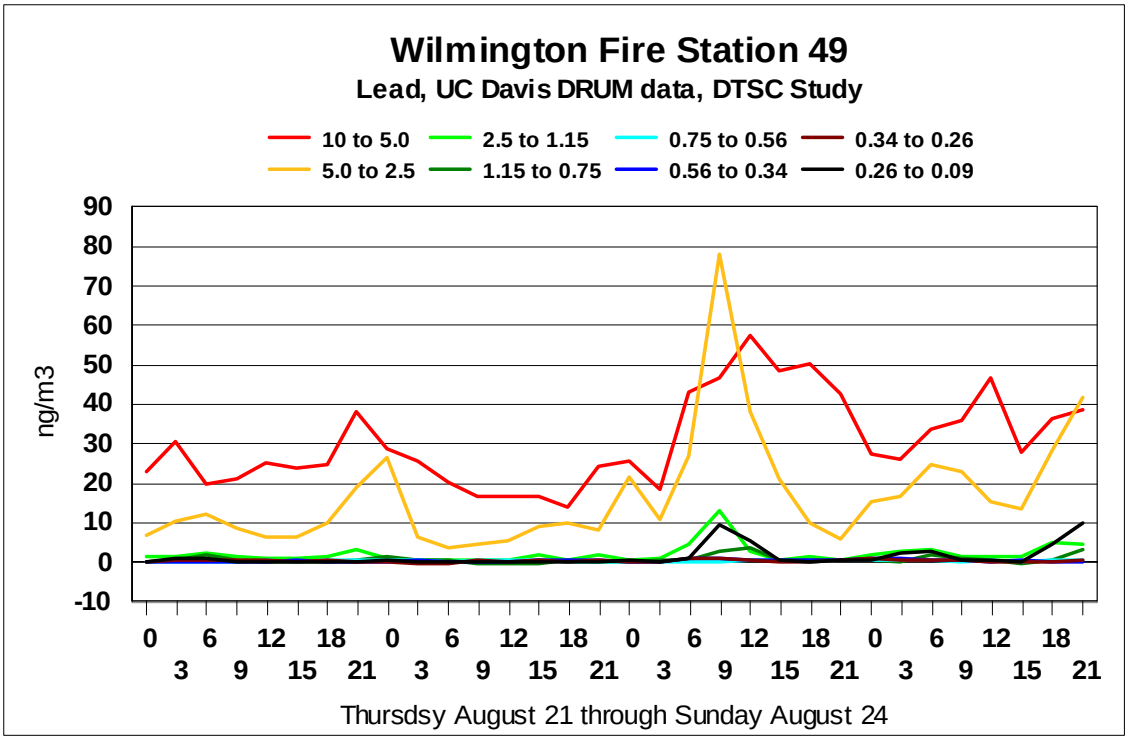
Because Mercury readily moves between the vapor, liquid, and a solid state; we can provide a lower limit only, due to potential evaporation in the analysis chamber. If a Mercury lower limit is desired from our analysis, it must be specifically requested.

Cadmium

There is an elemental interference in the spectrum due to the proximity and domination by the fine K line. This can be overcome in the future using an analysis setup at SSRL @ Stanford.

7. **Can we distinguish between emissions from the piles and the emissions when the shredder is operating?**

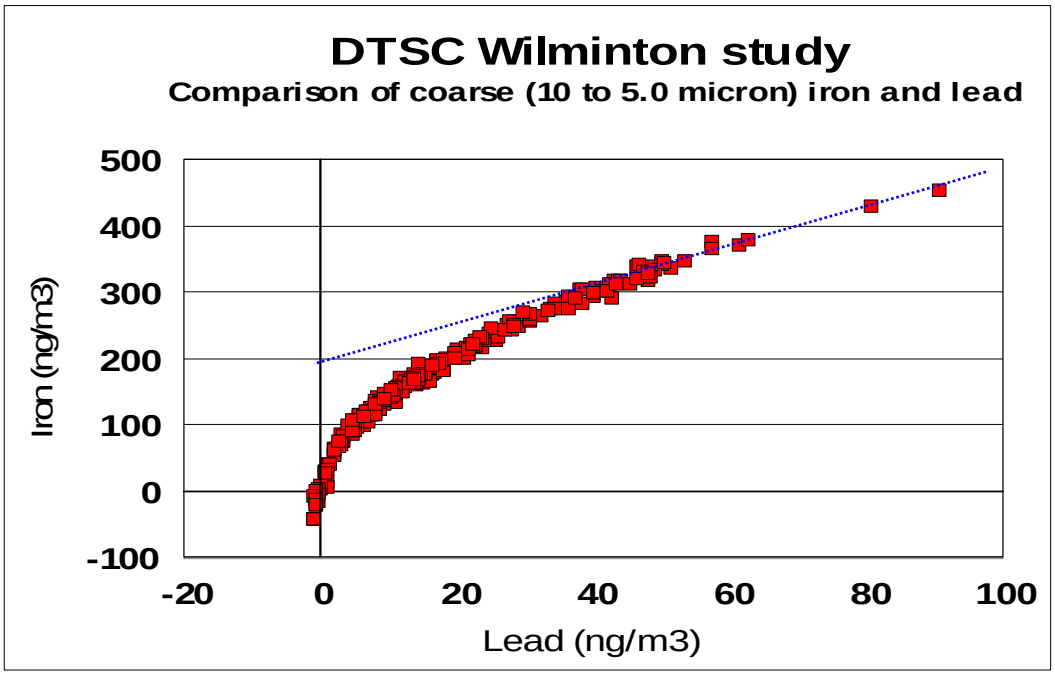
(See Progress report #2, page 19)

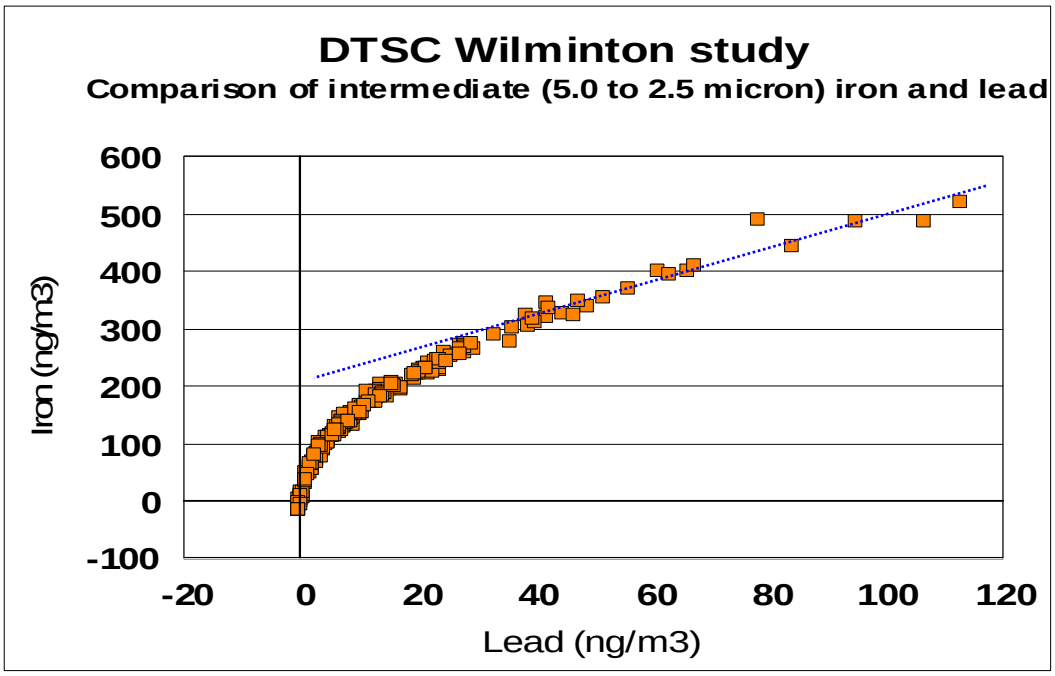


The shredder operating information allows us to identify 3 sources of lead in this one episode, However, every episode must be analyzed independently.

1. "Background" source – about 15 to 20 ng/m^3 in to the 10 to 5.0 mode, 5 ng/m3 in the 5.0 to 2.5 mode, seen at Fire Station 49 even when the wind was blowing the shredder plume away from the station. The source of this material is fugitive or resuspended dust (see the iron graph) from years of contamination. This will include both lead from car exhaust, but it had been decades since this source was active, and recent tons of shredder waste.
2. "Shredder product pile fugitive dust" – about 30 to 35 ng/m^3 in the 10 to 5.0 micron mode only, very little, < 5 ng/m^3 in the 5.0 to 2.5 mode, when the wind blows from the shredder to Fire Station 49 but the shredder itself is not operating, as shown by the lack of very fine iron.
3. "Shredder operations" – hard to completely separate this from the shredder product pile fugitive dust with out more detailed wind data. I could be essentially zero to perhaps 10 ng/m^3 in the 10 to 5.0 micron mode. In the 5.0 to 2.5, it is easily seen at the level 40 to 80 ng/m^3.

Another approach is to use the very strong iron-lead correlation. Then coarse iron is "enriched" above standard Earth crustal soil averages by up to a factor of 4, indicating that it is not normal soil. We examine this in the two plots below.





The 10 to 5.0 micron aerosol mode, (which has inputs to coarse aerosols when the shredder is not running), and the 5.0 to 2.5 micron mode, which is only present when shredder is running and wind is from the south, has exactly the same iron-lead relationship (slope of the line), and includes the same 200 ng/m3 of iron with no lead.

This proves that all the lead seen in any wind direction is caused by shredder operations, current and past.

8. **What is the deposition exposure, as defined by deposit/area/time?**

This topic is under development by Dr. Barnes and Ms. Smeltzer, but a rough idea can be gained by a simple line source dispersion calculation. Using the downwind measured dispersion for a modestly (20m) elevated source from the San Diego freeway quite near the port, (Cahill et al, 1974, Feeney et al 1975), and the settling velocities from Seinfeld and Pandis 1997, the measured daytime wind velocity, and an assumed 100 foot maximum plume height from the shredder photos, we can estimate the distance by which ½ the plume mass has impacted the ground:

Particle size	Settling velocity	Distance to 50% settling
10 to 35 microns	1 cm/sec	2.8 miles
5 to 10 microns	0.5 cm/sec	5.6 miles
2.5 to 5 microns	0.3 cm/.sec	9.4 miles
1.15 to 2.5 microns	0.2 cm/sec	14.1 miles

Thus, all of Wilmington and well inland will receive shedder waste deposited onto surfaces. This also means that on the typical night NW winds, shredder aerosols will impact much of the City of Long Beach.

9. Can we predict what the emissions were for the 120 days of no controls?

One can do a calculation based on stated efficiency of controls and corresponding annual removal amount as follows: At 80% efficiency, 68.87 tons/year are controlled (from New Terminal Island Emission Calculator with MegaShredder.xls, "shredder" estimate). Therefore, 100% uncontrolled emissions correspond to 86.08 tons/year. Said another way, this is the amount released with no air pollution control system for a year.

So for the 120 days with controls one can estimate,
86.08 tons/365 days = .236 tons/day x 120 days = **28.3 tons** for the 120 day interval.

10. Summary of operations:

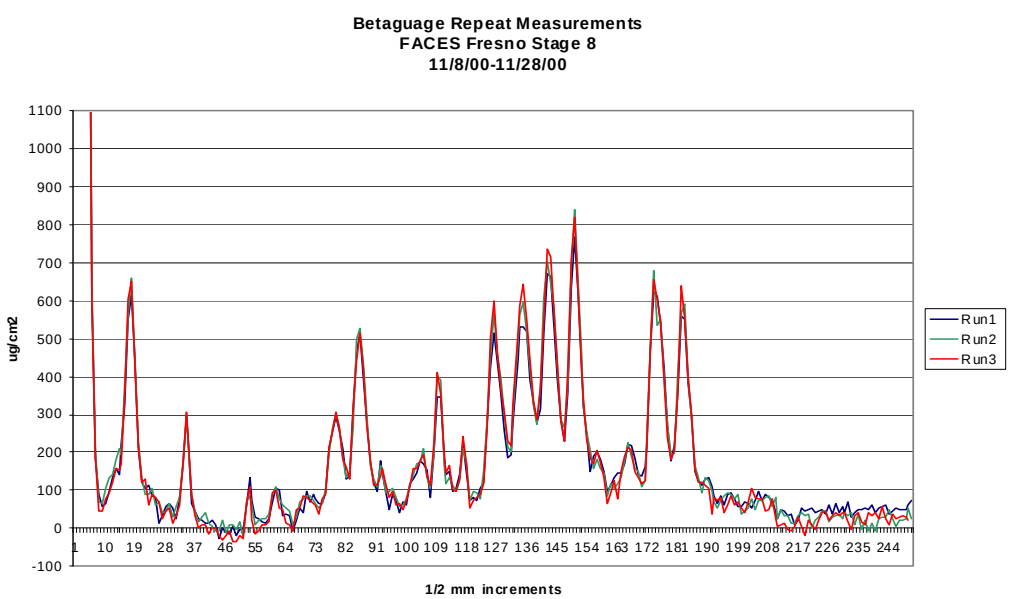
The combinations of the metrological, mass, and elemental data show that the shredder is routinely impacting the Wilmington site with elements, some toxic, which will settle to the ground.

Appendix A

DRUM quality assurance summary

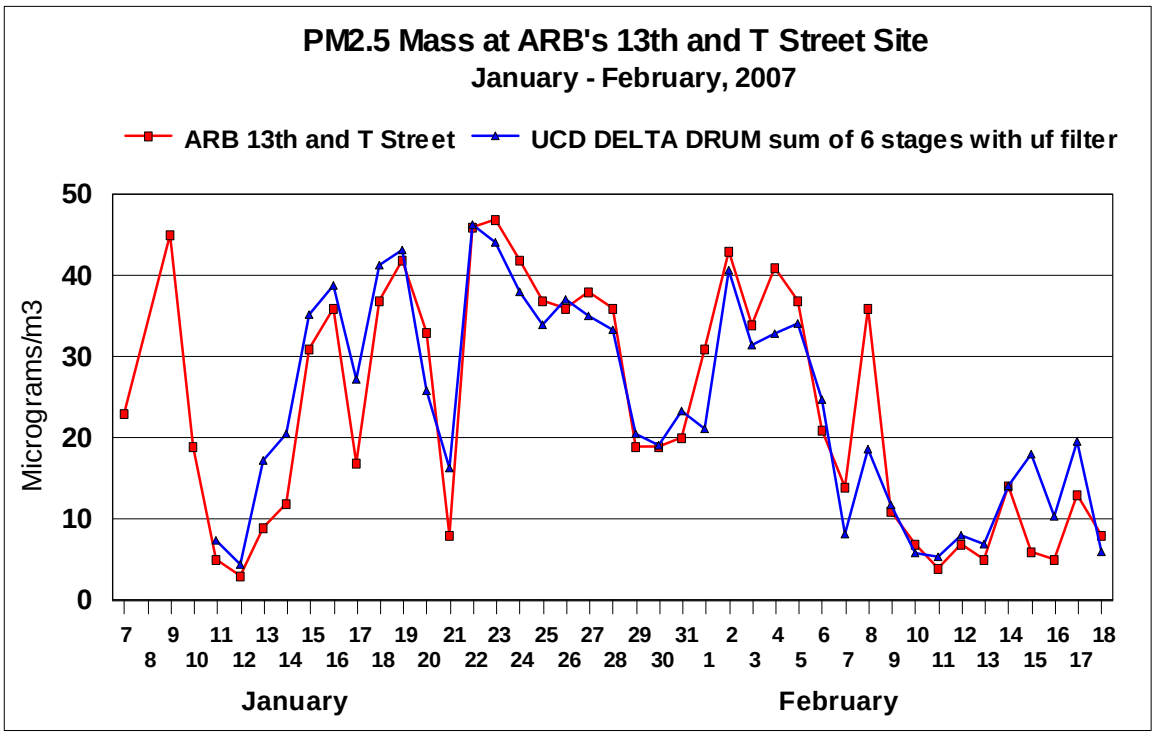
Continuous analysis of aerosols by size, time, and composition are now thought to be essential for understanding the causal factors behind the statistical association between PM mass and mortality/morbidity since current EPA protocols, 24 hr PM_{10} and $PM_{2.5}$ mass on a 1-day-in-3 schedule, obscure important health related parameters in time of day, particle size and composition (Devlin, 2003). Obtaining such data by enhancing filter based methods is prohibitively expensive (Lippmann, 2009) Physical impaction and subsequent non-destructive analysis, long used in research studies, can easily fill the needs of health based research community. However, this requires new levels and enhanced protocols of quality assurance. For example, if data are taken by an impactor every 3 hr, and particles are collected in 6 sub-2.5 μm size modes, 48 individual vales for mass or composition are required to match a single 24 hr $PM_{2.5}$ filter,

One potential device that meets the need of health scientists is the **D**avis **R**otating-drum **U**nit for **M**onitoring (DRUM) sampler has the advantage that the particle sizes are established from basic aerodynamic principles so measurements are a validation, not a calibration (Raabe et al, 1988) Further since most DRUM mass and compositional measurements are non-destructive reanalysis protocols and transfer of samples to other laboratories is allowed and encouraged. These techniques are contained in the 140 page DRUM Quality Assurance Protocols ver. 1/08, 2008 (DQAP 1/08) maintained by the UC Davis DELTA Group for the worldwide collaborators of the DELTA Group. Some examples are given in this section but the entire volume is an essential part of the proposed study. The precision of the soft beta gauge mass measurements are shown below for very fine ($0.26 > D_p > 0.09$ μm) diameter particles, the size range with most diesel and smoking car exhaust.

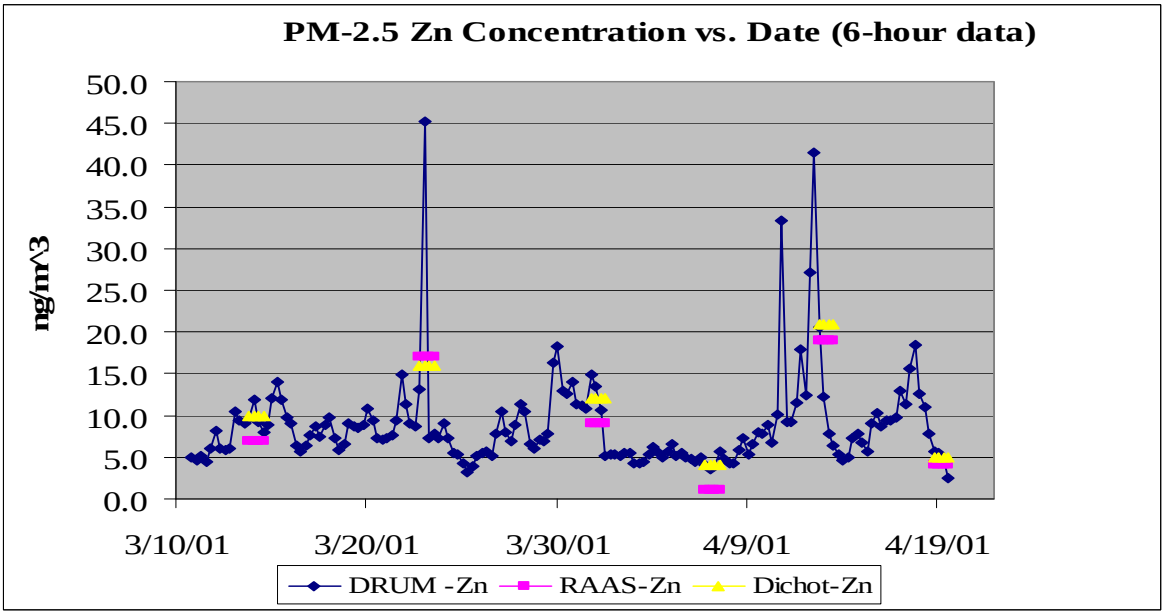


A

Accuracy has been established in a recent comparison to ARB FRM filter samplers at the Air Resources Board 13th and T Street test site in Sacramento.



One of the first examples of S-XRF elements versus filters is from the Fresno Asthmatic Children's Environment Study (FACES, ARB, 2001). The 24-hour filter data are superimposed. One can see both ht excellent DRUM – filter agreement, including both sampling and S-XRF analysis, and how much information is lost in 24 hr filter data.



Finally, below we summarize all DELTA Group S-XRF inter-comparisons in the past 5 years (DQAP v. 8.02, pg 32) We also give averages below without the ARB RAAS data, as these have been found to have problems. A comparison was also done with IMPROVE in the Yosemite study (2002) but this comparison is not included since IMPROVE has also since identified serious deficiencies in data from that period (White et al, AAAR 2004)

Study and date	Methods	**Average ratio, Al to Fe**	Std. dev.	**Average ratio, Cu to Pb**	Std. dev.
BRAVO, 1999	PIXE vs S-XRF	**0.99**	0.04		
BRAVO, 1999	CNL XRF vs S-XRF			**1.24**	0.14
FACES, 2001	ARB XRF vs S-XRF	**0.93**	0.21	**1.02**	0.08
FACES, 2001	ARB RAAS vs S-XRF	**(0.98)**	0.27	**(0.74)**	0.23
ARB LTAD 2005	DRI XRF vs S-XRF	**1.037**	0.085	**0.907**	0.009
All prior studies	**Average** (no RAAS)	**0.984** (0.985)	**0.15** (0.11)	**0.977** (1.055)	**0.115** (0.076)