Deposition of coarse toxic particles in Wilmington, CA for the Department of Toxic Substances Control (DTSC): Summer, 2008, and Spring, 2009

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Thomas A. Cahill 5/11/2011

Abstract:

The Terminal Island shredder is the major source of stationary source emissions on the island, with 3.78 tons/year PM_{10}, (Appendix A), which is about ½ the total of all stationary facilities, plus about ½ of the cadmium, lead, mercury, copper and nickel aerosols.

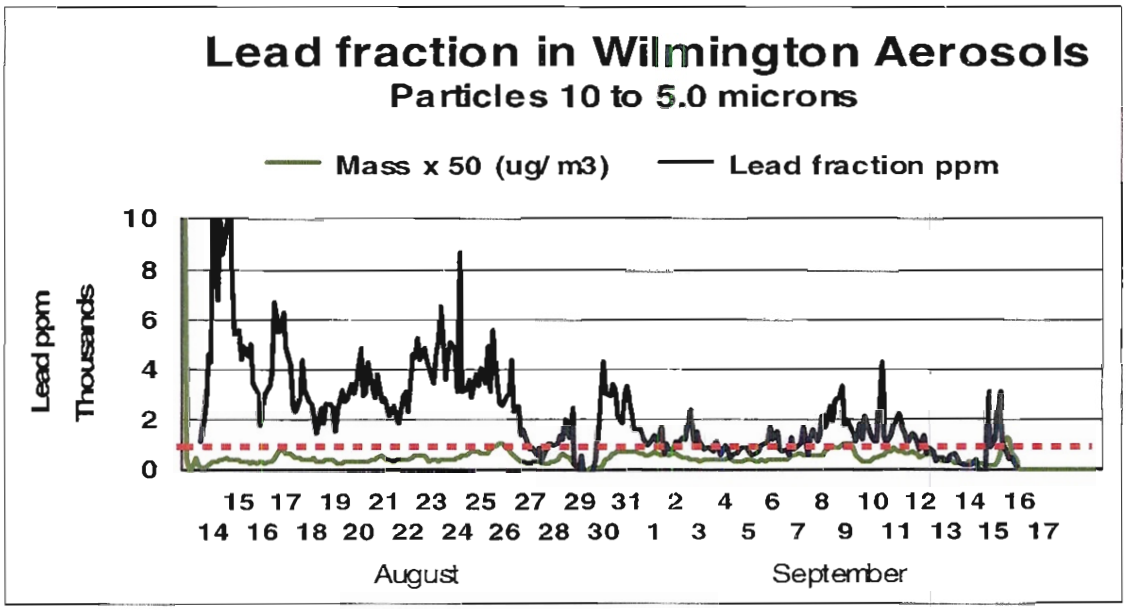
In order to evaluate the impact of these materials downwind in Wilmington, CA, and specifically the deposition of toxic metals onto surfaces and the soil, a study was begun in Summer, 2008 to measure the source materials at the shredder, their transport as aerosols downwind into Wilmington, and their deposition impact onto surfaces including playground structures. Specifically, the study posed the question of the toxic potential of airborne deposition.

On August 20, 2008 samples were collected from the Terminal Island shredder's pollution reduction system during the execution of a criminal search warrant by DTSC and later analyzed for elemental content by synchrotron-induced x-ray fluorescence (S-XRF) (Appendix C)

Aerosols were collected and analyzed downwind of the Terminal Island car/appliance shredder for mass and elemental content every 3 hrs in 8 size modes (10 to 0.09 μm) over a period of 5 weeks in August and September, 2008, and in 9 size modes

(35 to 0.0 μm) over a period of 4 weeks in May and June, 2009. The aerosols measured in 2008, identified as originating from the shredder, contained lead and zinc, with lead averaging 96 ng/m^3 in the 16 major episodes (6 hr. duration each). In addition, an unusual very fine iron aerosol was seen coming from the shredder.

The amount of deposited particles was calculated by introducing the settling velocity (Sehmel, 1981, Seinfeld and Pandis 1997) for the aerosols. DTSC's regulatory thresholds only apply to deposited particles, not aerosols, so the deposition-weighted values are the only relevant ones to compare with DTSC's hazardous waste thresholds. We note that over all hours during the 6 week study the coarse (10 to 2.5 μm) lead values were 2,369 ppm, dominated by the episodes coming from Terminal Island, which averaged 4,446 ppm Pb. The deposited levels of both lead and zinc were in excess of DTSC's hazardous waste threshold limits, 1,000 ppm and 5,000 ppm respectively. Below we show the continuous lead data in aerosols in the size mode that provides 83% of all deposited lead.



Ship activity in the Port of Los Angeles was seen in the sulfur, vanadium, and nickel aerosols from ships in the harbor, with potential health impacts. However, these levels were somewhat less in 2009 than in 2008, perhaps reflecting less ship traffic, or less likely due to improvements in emission rates from ocean going ships.

In terms of aerosols tied to the shredder in the 2008 study, measurements in spring, 2009, showed massive reductions in the very fine particles coming from the shredder. Very fine iron was only 9% of the 2008 level, while lead was reduced by 40% from the 2008 values. Further, very fine iron seen in spring, 2009, was usually correlated with activities at the shredder site monitored by video camera, including smoke emissions. Thus, the sharp reductions reflect improvements in the pollution control systems. Coarser aerosol particles were about the same as in 2008 or even slightly higher, likely reflecting resuspension of contaminated soils as the source.

Wipe tests of impervious surfaces were made downwind of the shredder and into the City of Wilmington. These samples were analyzed by S-XRF and showed that the levels of lead and zinc fell off by about a factor of 2 as one moved from near-port sites into downtown Wilmington, (including the fence of a school playground), while still exceeding the lead and zinc DTSC hazardous waste threshold limits.

This report will present each of the periods separately and then perform the comparison study.

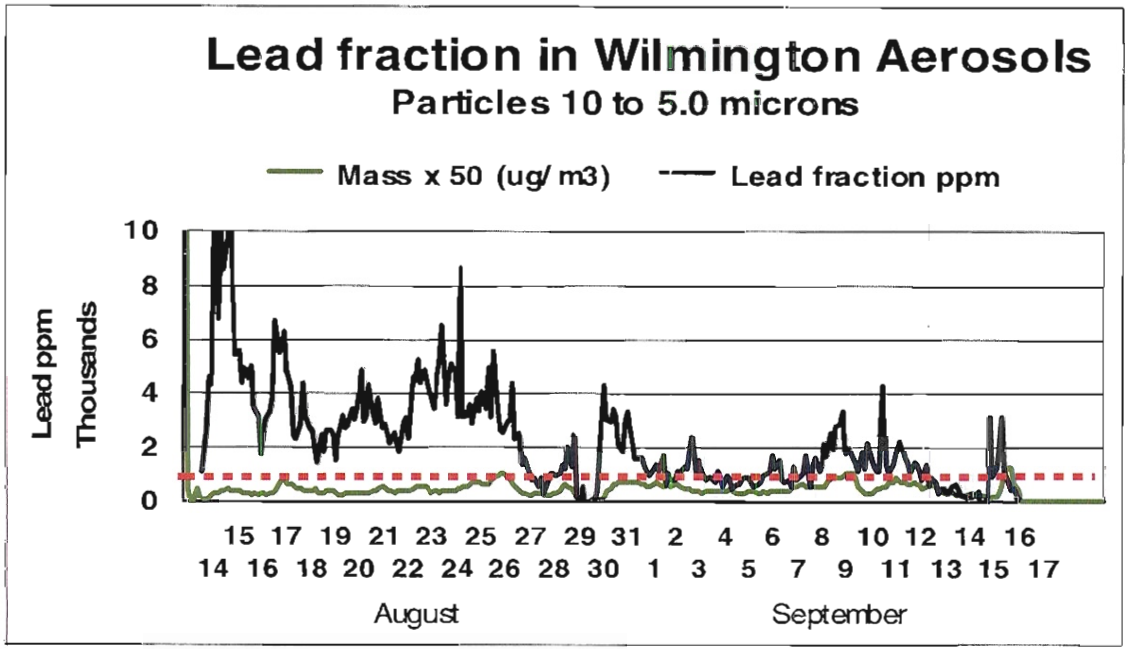
Part 1: Summer, 2008

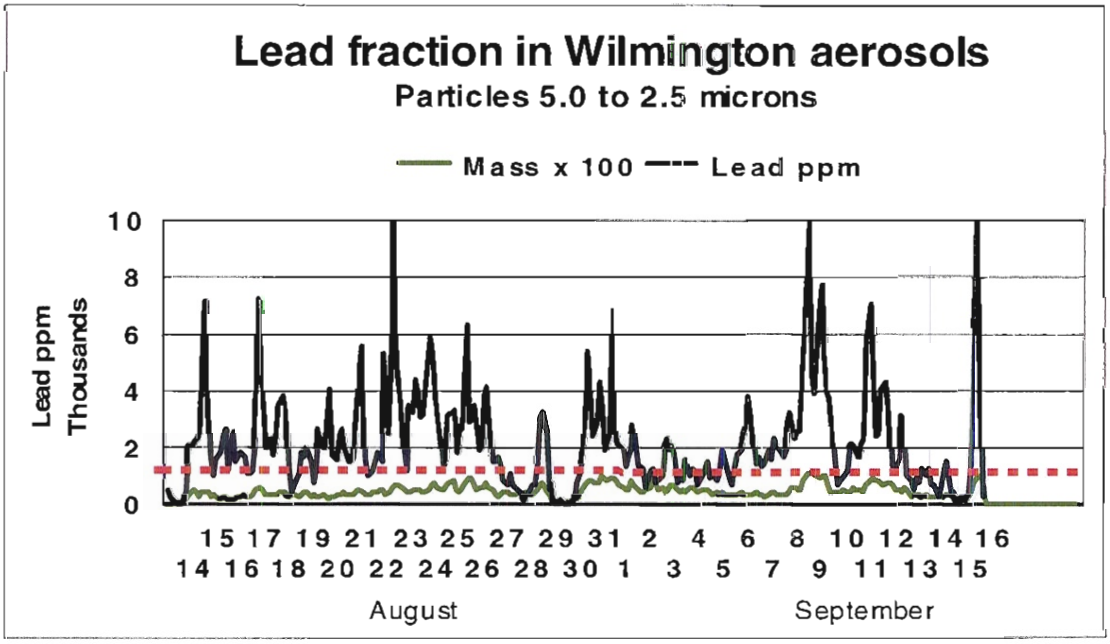
Deposition of coarse toxic particles in Wilmington, CA for the Department of Toxic Substances Control (DTSC) August – September, 2008

Executive Summary – summer, 2008:

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.

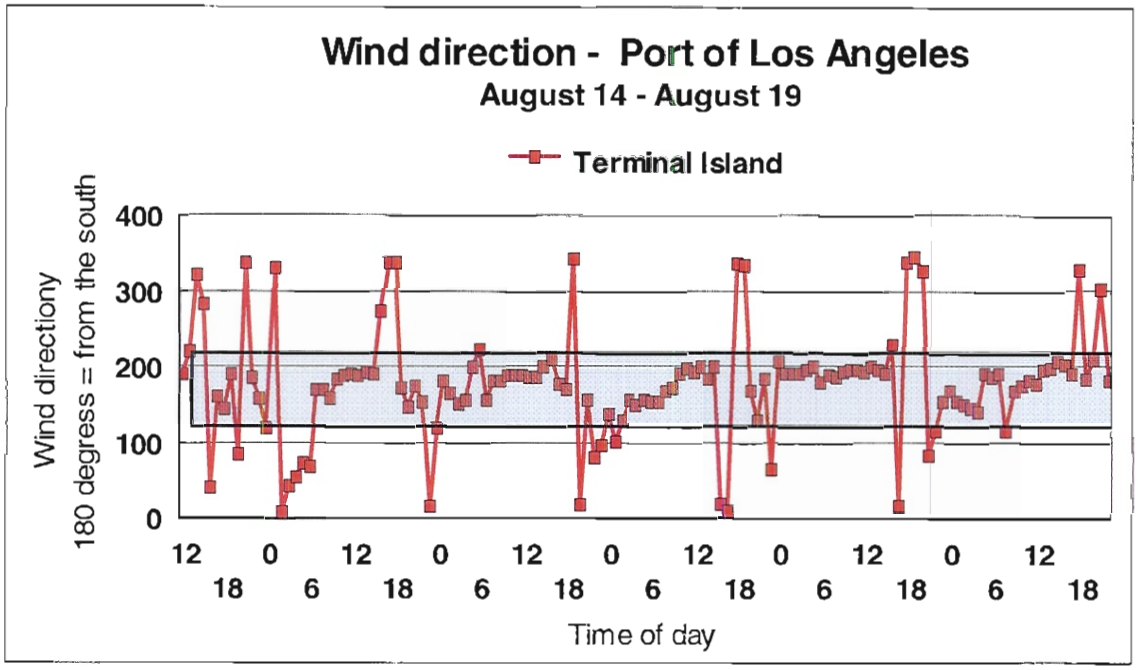
The data indicate the presence of many metals measured at the Wilmington Fire Station 49, including lead, which occur in coarse particles that will readily settle onto the ground. Two examples are shown below, including the 10 to 5.0 μm fraction responsible for 83% of all deposited lead. The DTSC 1,000 ppm lead standard shown below only applies to particles deposited onto surfaces.

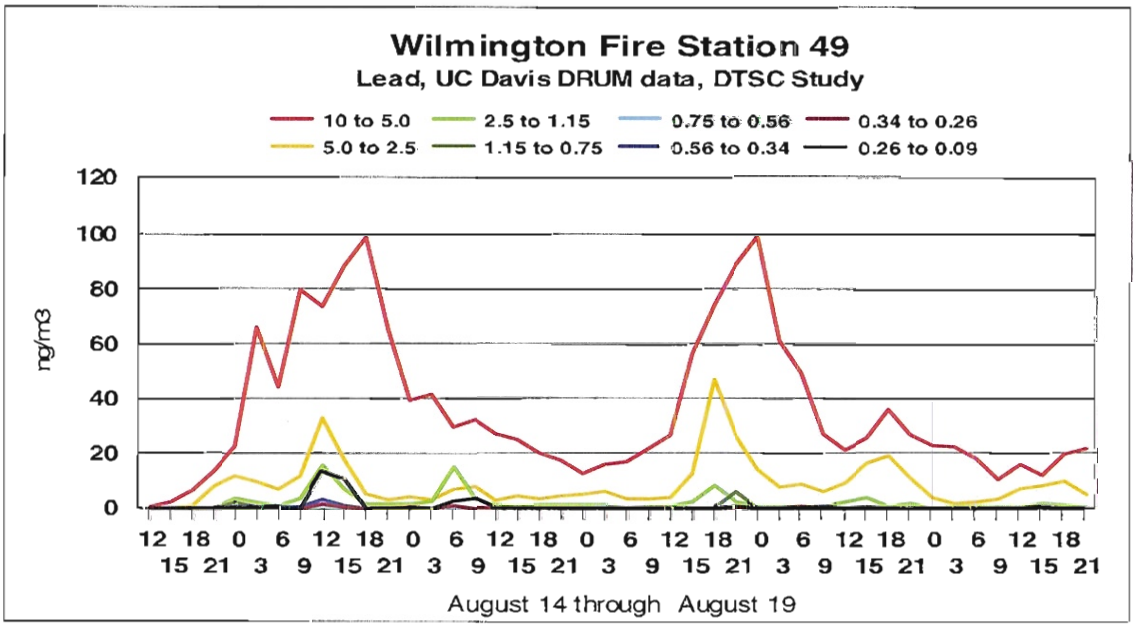




In addition to the coarse toxic elements, the very fine elements from the shredder, especially very fine iron, are themselves in concentrations and particle sizes that are capable of causing health impacts to lungs.

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 ° around the 160 ° 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 Community Center lies almost directly downwind of the Terminal Island shredder during daytime, while night winds come in from the northwest.

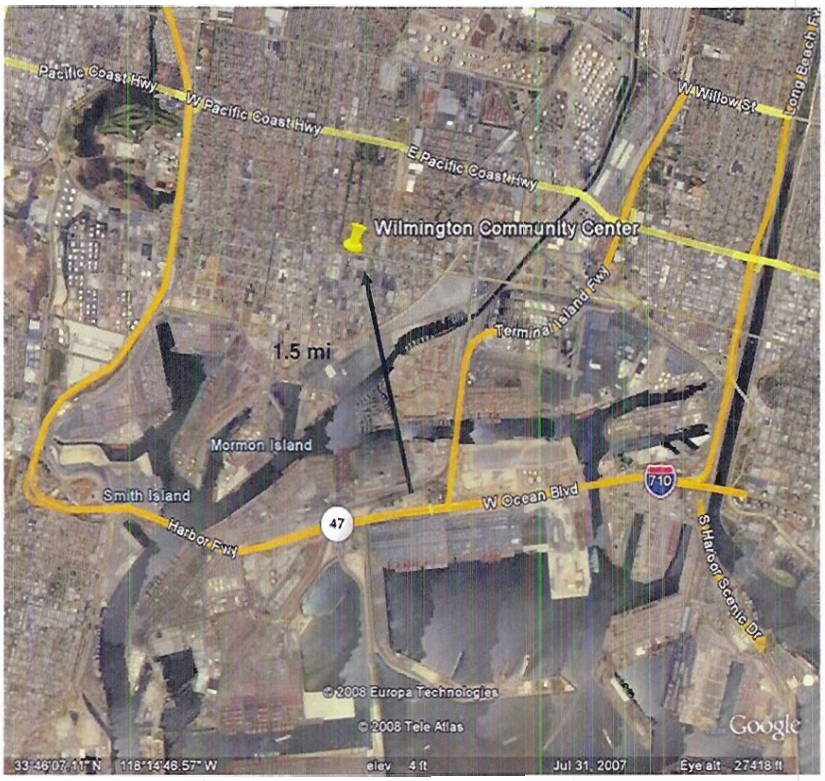


Figure 1 Satellite photo of the study area

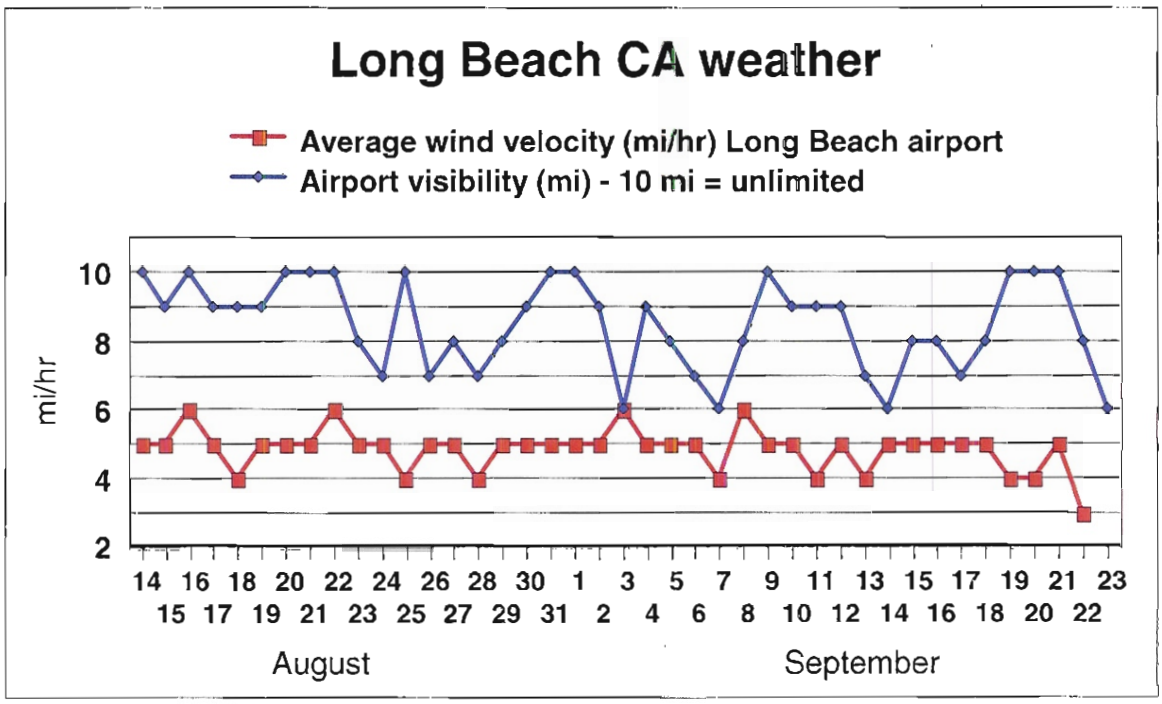


Figure 2 Regional meteorology from the Long Beach airport

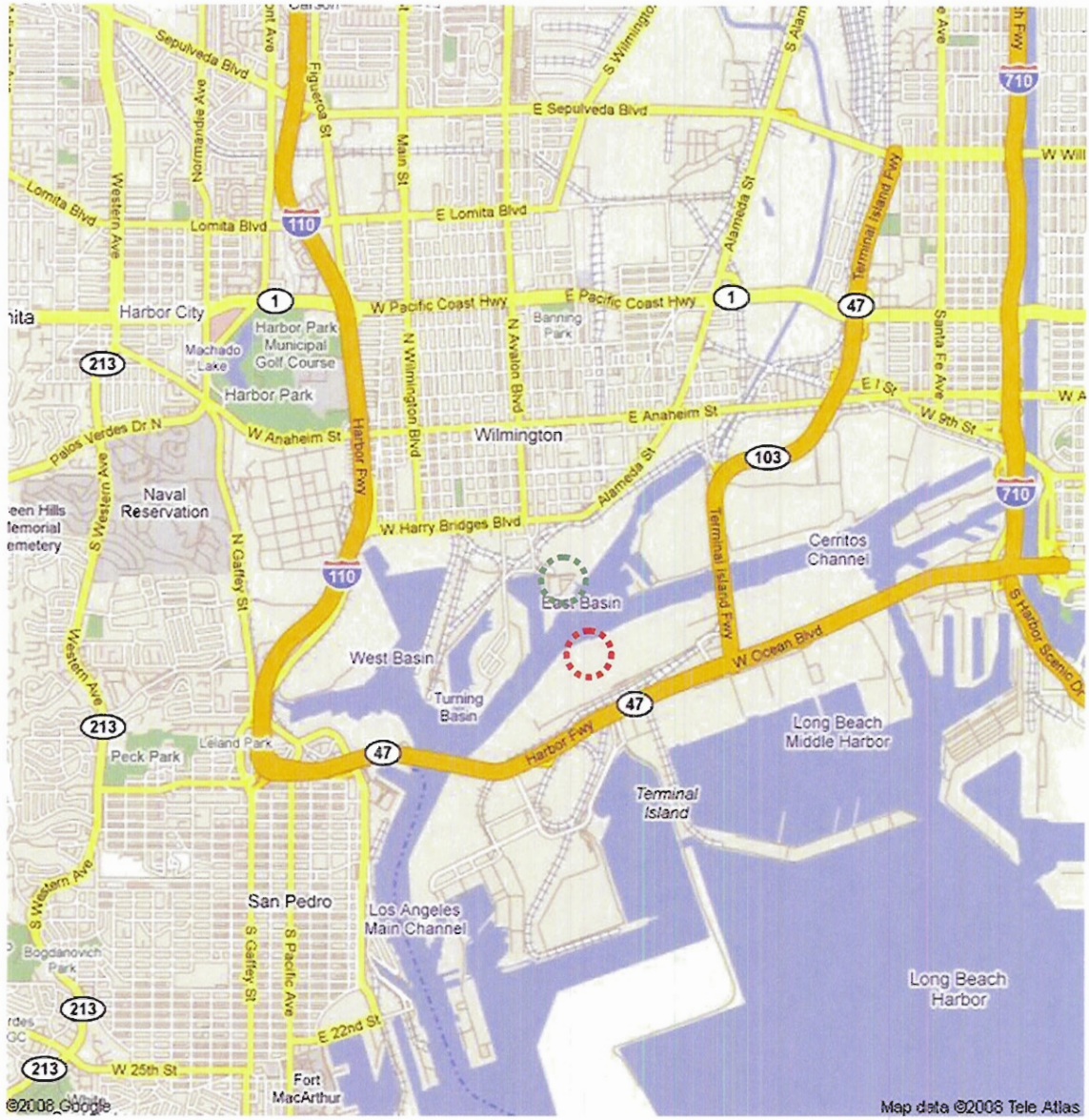


Figure 3 Street map of the study area. The approximate location of the shredder (red circle) and sampling site (green circle) are shown.

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. 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 met station network allows us to better identify local wind strength and direction.

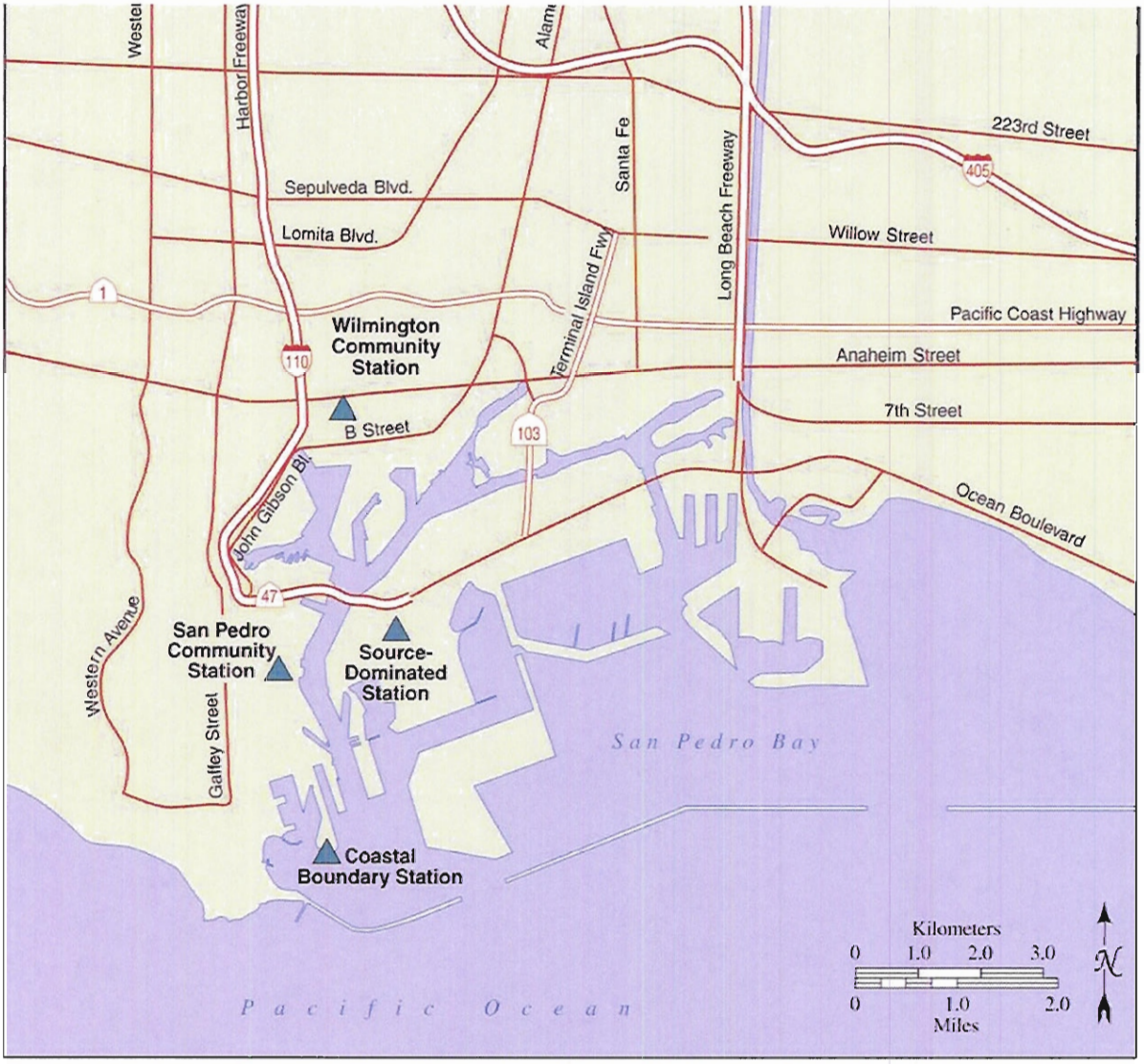


Figure 4 Local meteorology from the Port of Los Angeles network.

Two sites were chosen for our analysis, the Terminal Island (TI) Source Dominated site and the Wilmington Community Center (SP) site. The aerosol sampling station 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

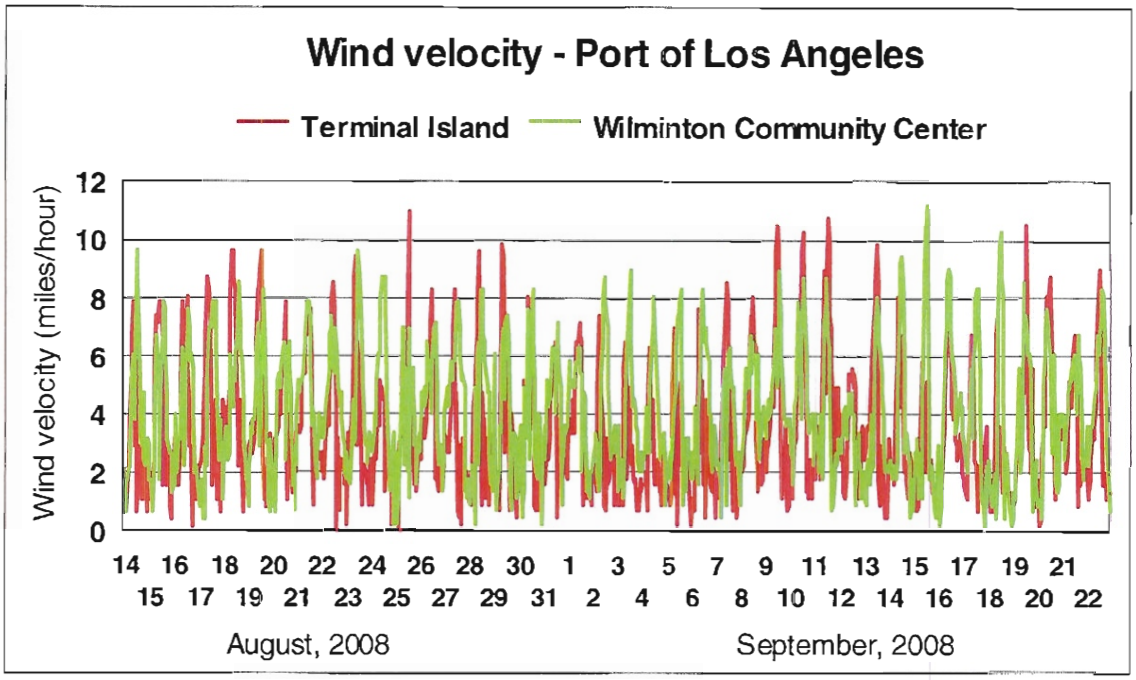


Figure 5 Wind speed for the TI and SP meteorological stations

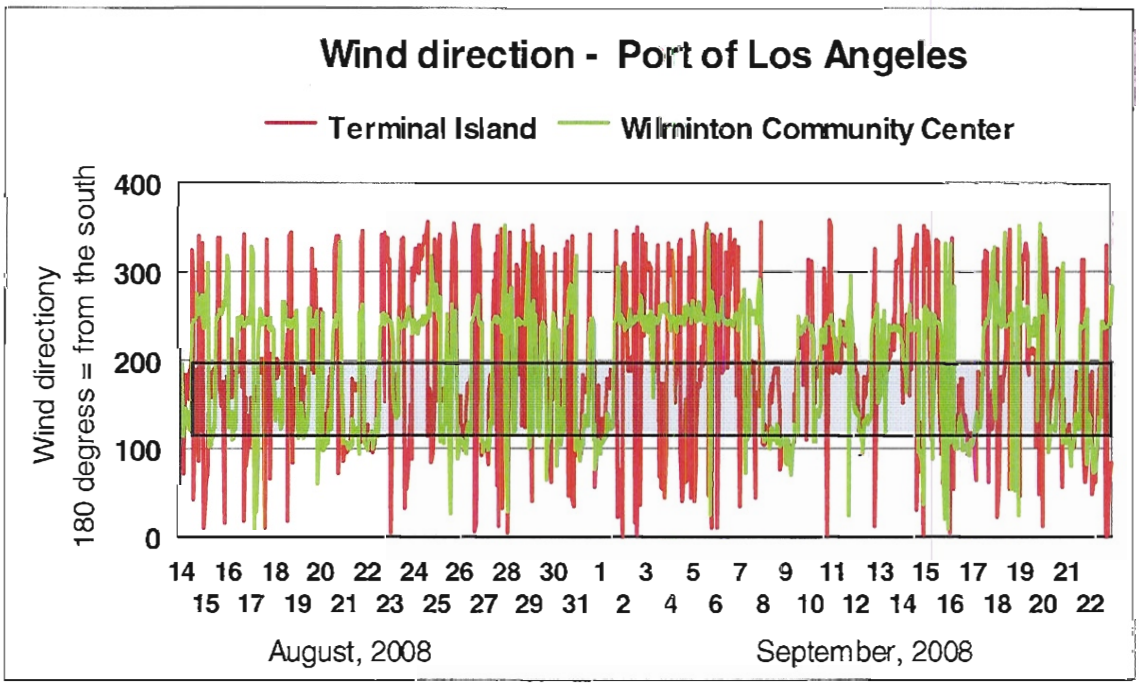


Figure 6 Wind direction from the TI and SP meteorological stations. The aqua region is ± 45 ° around the mean 160 ° direction from shredder to Fire Station 49.

The collected sample dimensions are measured to verify expected length and examined visually to detect any anomalies in sample collection. A review spread sheet is prepared for every operation (see example Table 1.)

DRUM strip mount log		START	TA Cahill	Rot rate	4.0 mm/d	DTSC=	CA Department of
8 DRUM		DATE:	10/10/08	8D-#	16		Toxic Subst. Control
Study	Site	Start	Intermediate		Intermediate	Stop	Comments
DTSC	**Wilm**	Power ou	Central blank		Other		
Date	**8/14/08**		Sept 4	Sept 4		9/23/08	vac pump on, the progr start
Hour	**12:50 PM**					09:25 AM	measured beta at 4 mm start
Flow	**10.0 nom**					39.85	days duration
Stage 8	mm (pr)	10.0	86.9	92.9	159	159.43	mm duration; 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		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		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		
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		
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		
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		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		lots of mass
10.0 to 5.0	mm (dr)	10.0	68	74	141		4 mm gap before final line
	mm (mt)						12, 43 52 to 57, 110 - 115,
							120 - 125, hvy dark not sea salt

Table 1 Characteristics of the collected DRUM samples (last column not entirely visible)

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 of the Wilmington 2008 samples are shown below. The 6 mm timing marker and clean background zone are clearly seen about midway along the deposit. The rusty color in the larger size modes is unusual. The end peak is the DRUM stop mark.

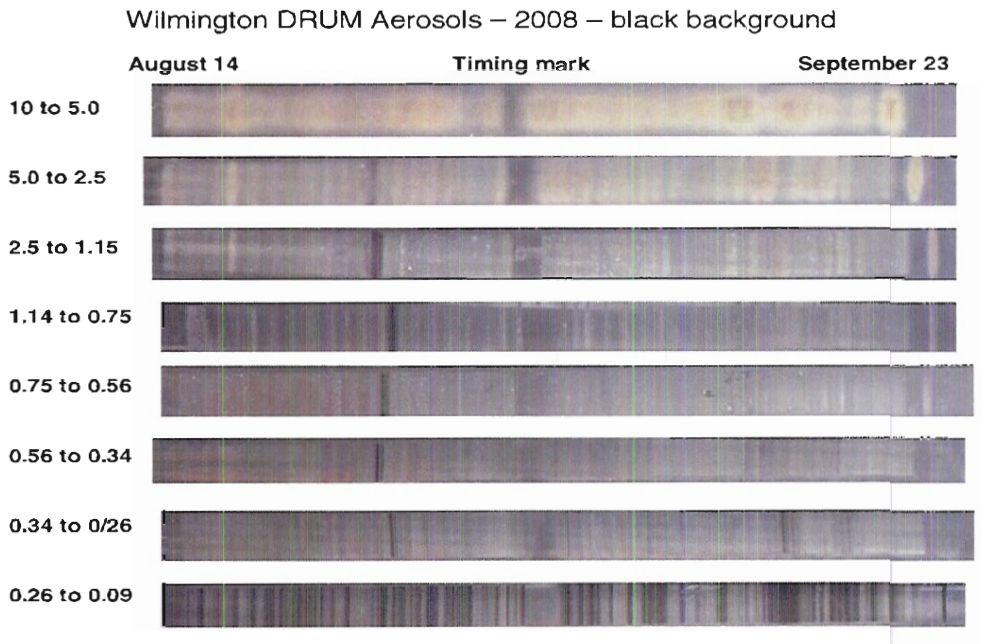


Figure 7 Wilmington DRUM aerosols – black background

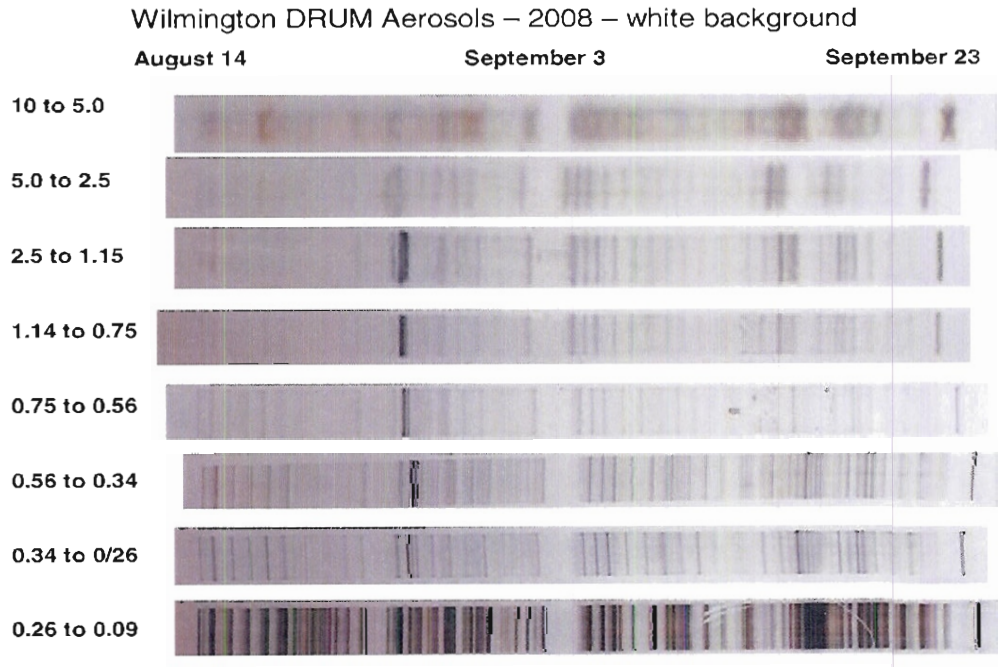
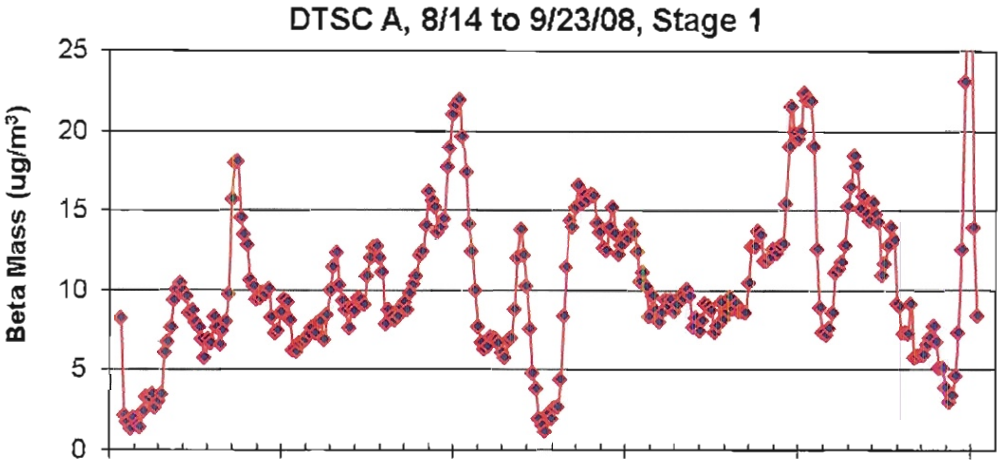


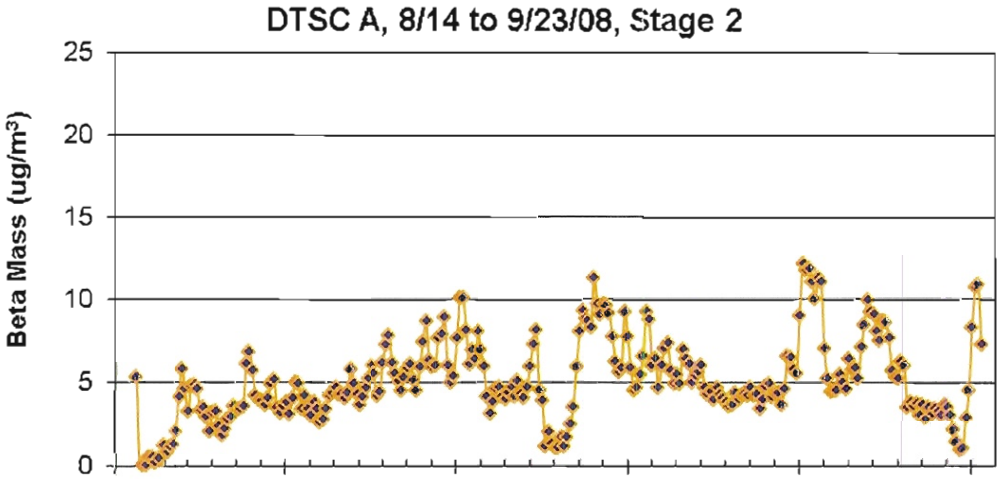
Figure 8 Wilmington DRUM aerosols – white background. Clear region near the middle is a timing/blank marker

Results – mass

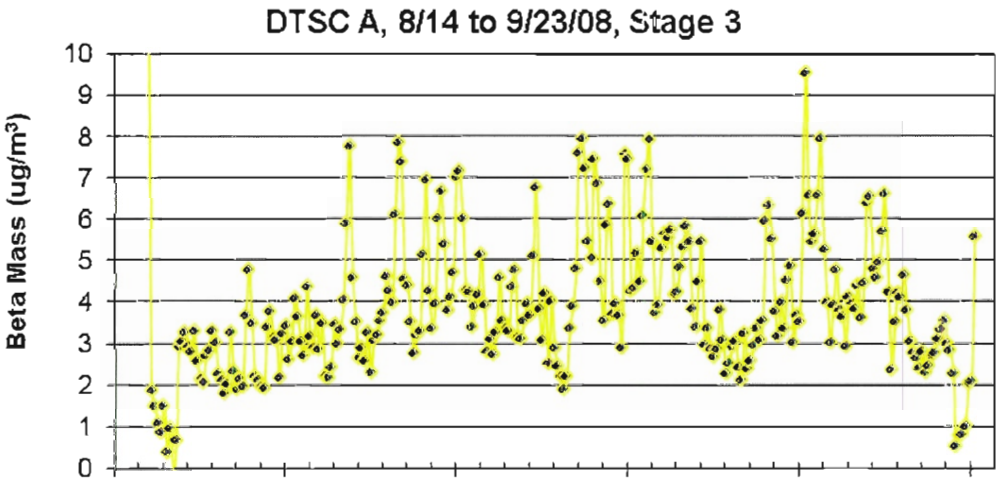
Below we show the mass of particles, from the coarsest to the finest particle sizes. These data allow calculation of ground deposition.



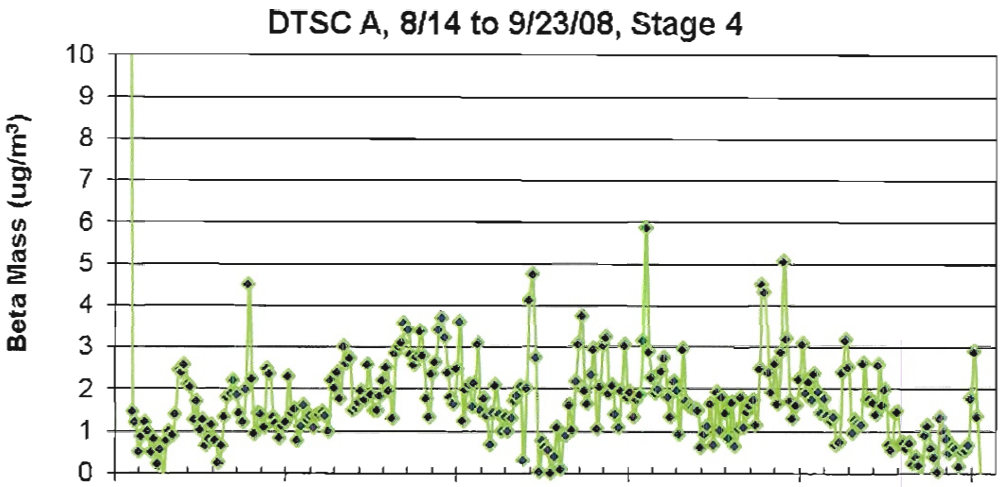
Stage 1 – 10 to 5.0 µm



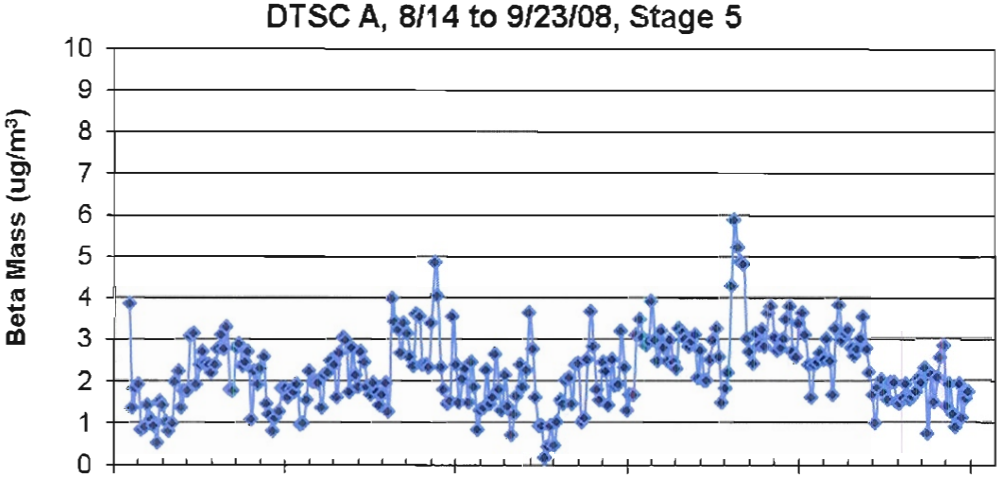
Stage 2 – 5.0 to 2.5 µm diameter



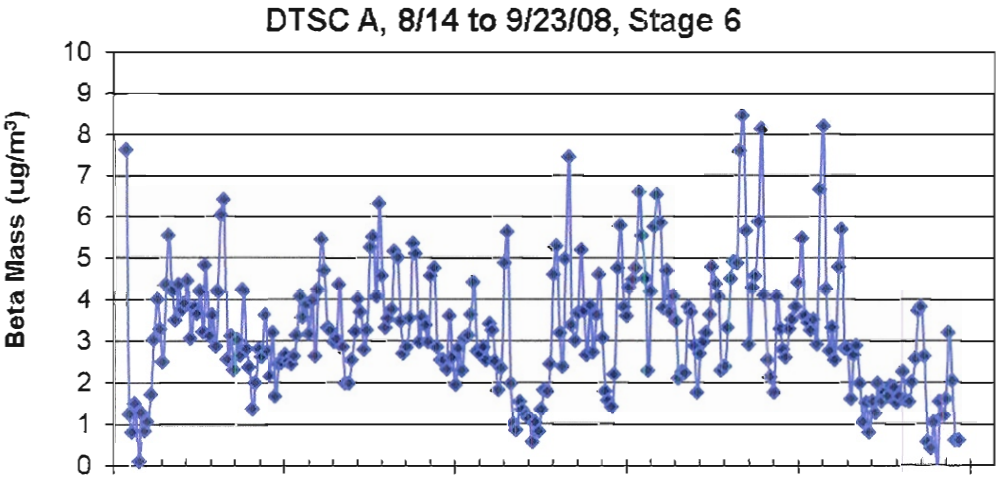
Stage 3 – 2.5 to 1.15 µm diameter



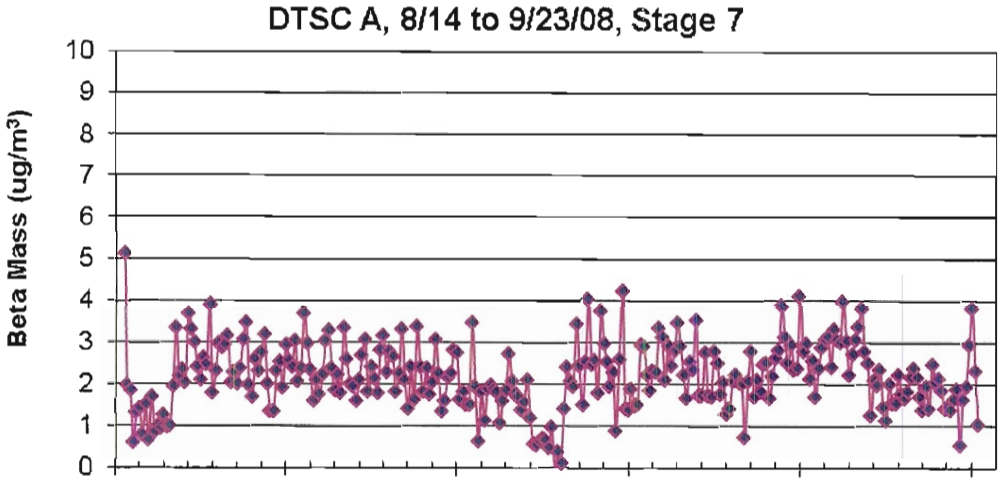
Stage 4 – 1.15 to 0.75 µm diameter



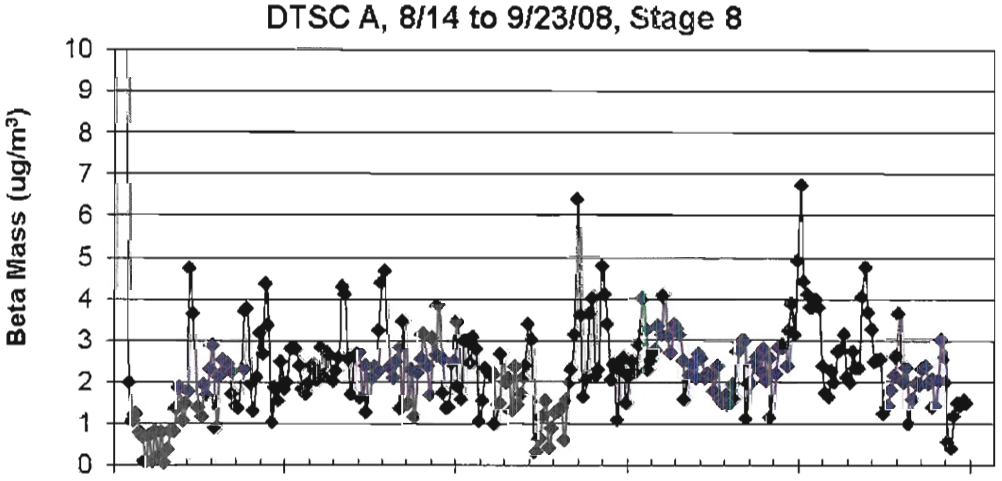
Stage 5 – 0.75 to 0.56 µm diameter



Stage 6 – 0.56 to 0.34 µm diameter



Stage 7 0.34 to 0.26 μm diameter



Stage 8 – 0.26 to 0.09 μm diameter

Figure 9 a, b, c, d, e, f, g, h – Mass versus time for the 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 C.

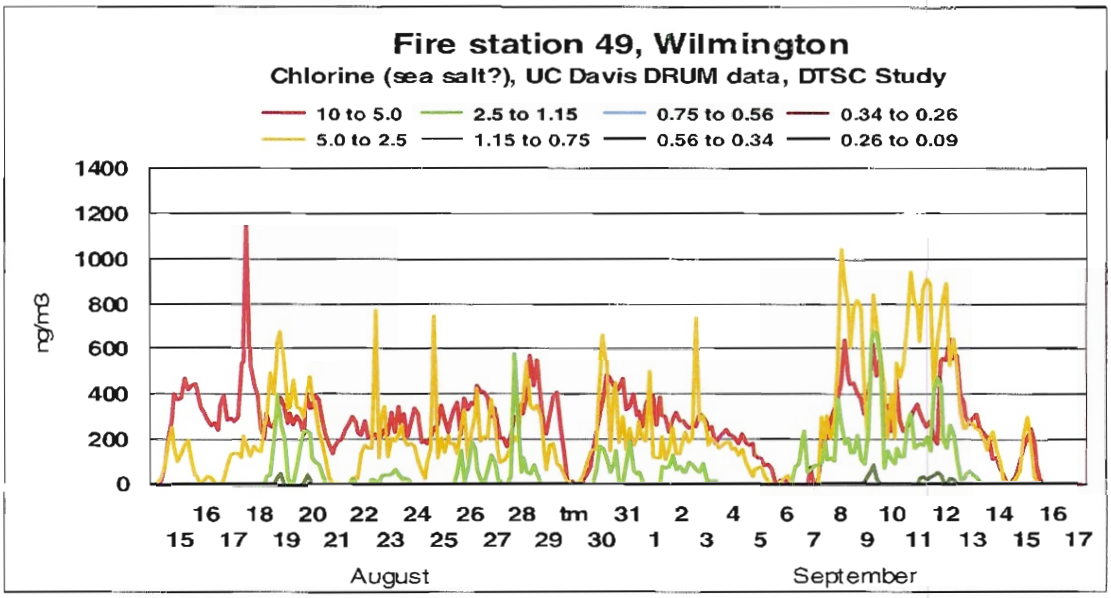


Figure 10 DRUM elemental data – chlorine (sea salt?)

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.

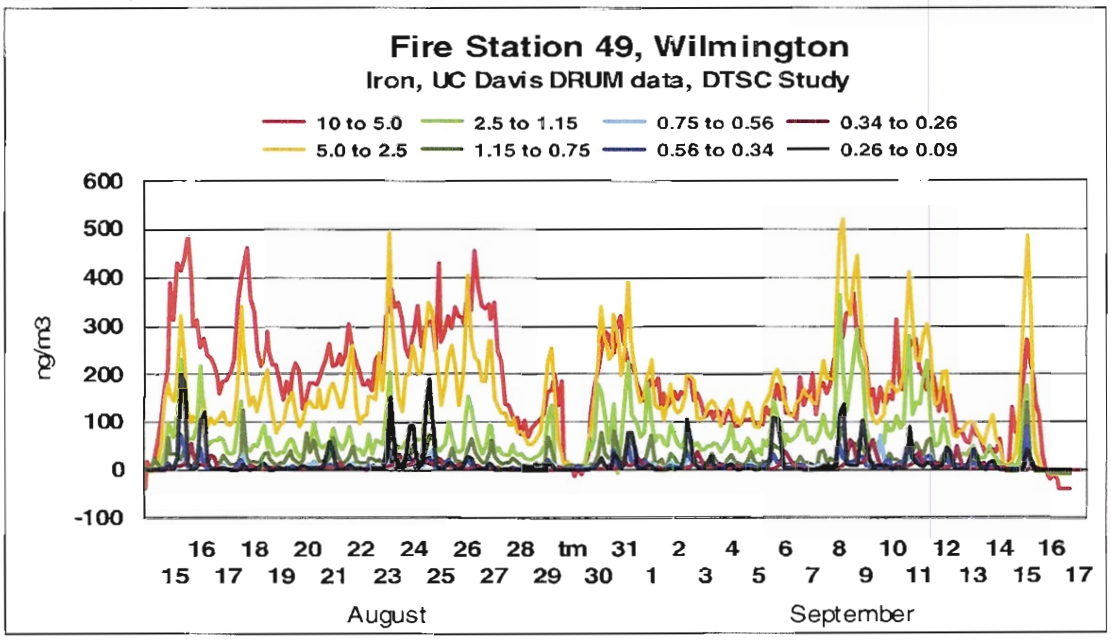


Figure 11 DRUM elemental data – iron

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 site. The fine iron signature simply should not be there.

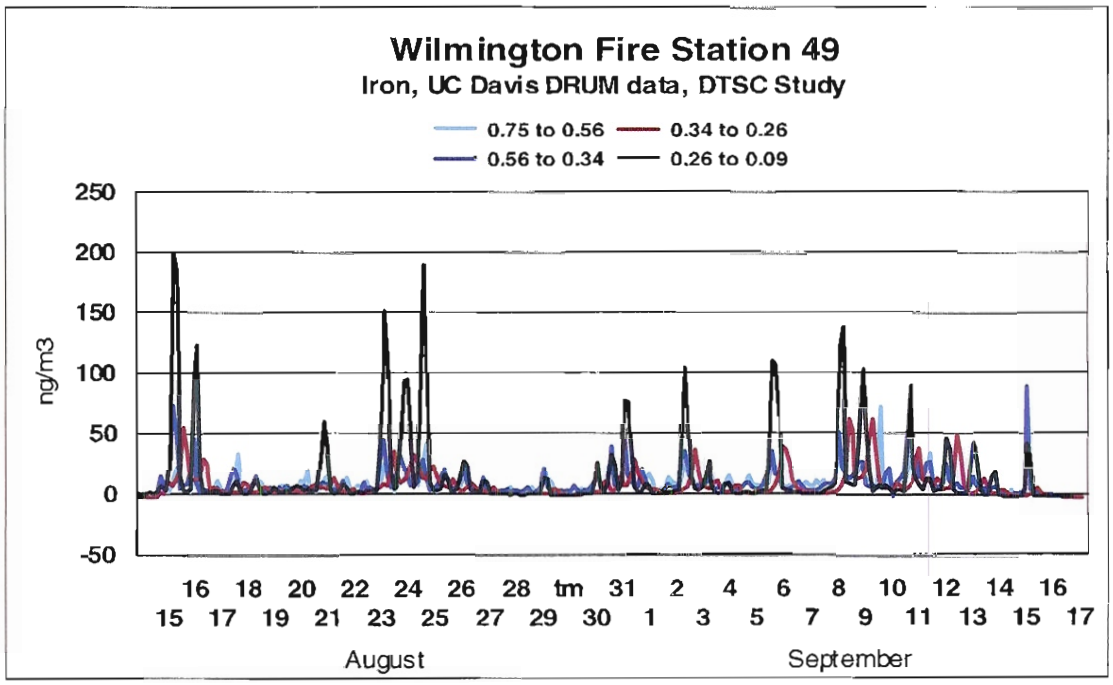


Figure 12 DRUM elemental data – fine modes of iron

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 particles while iron remains elevated.

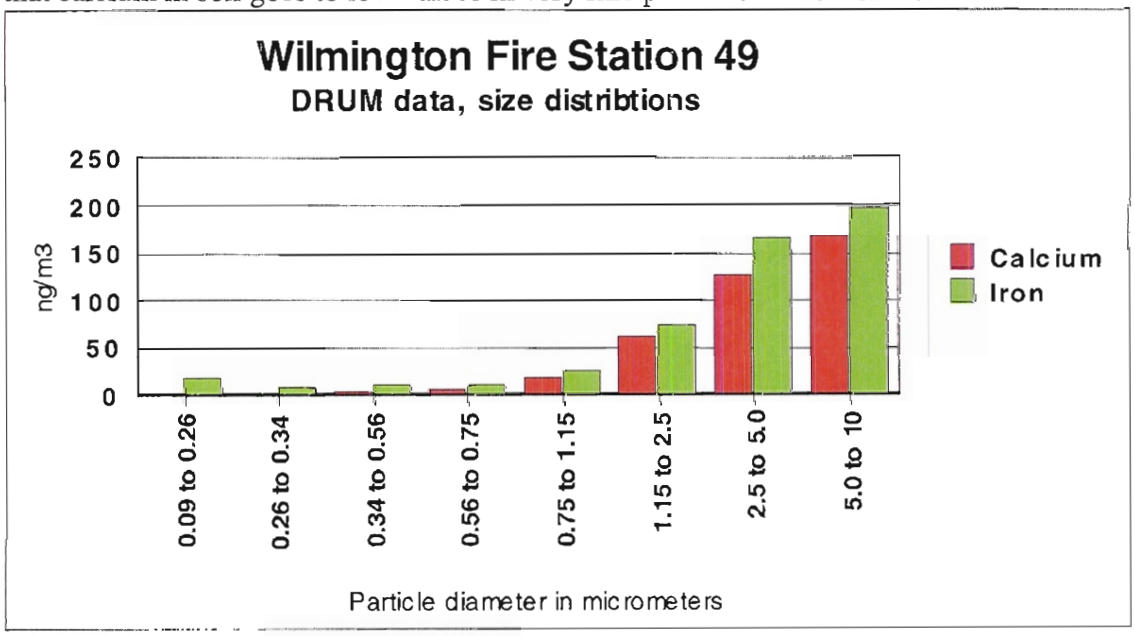


Figure 13 DRUM elemental data – size distributions of iron and calcium

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

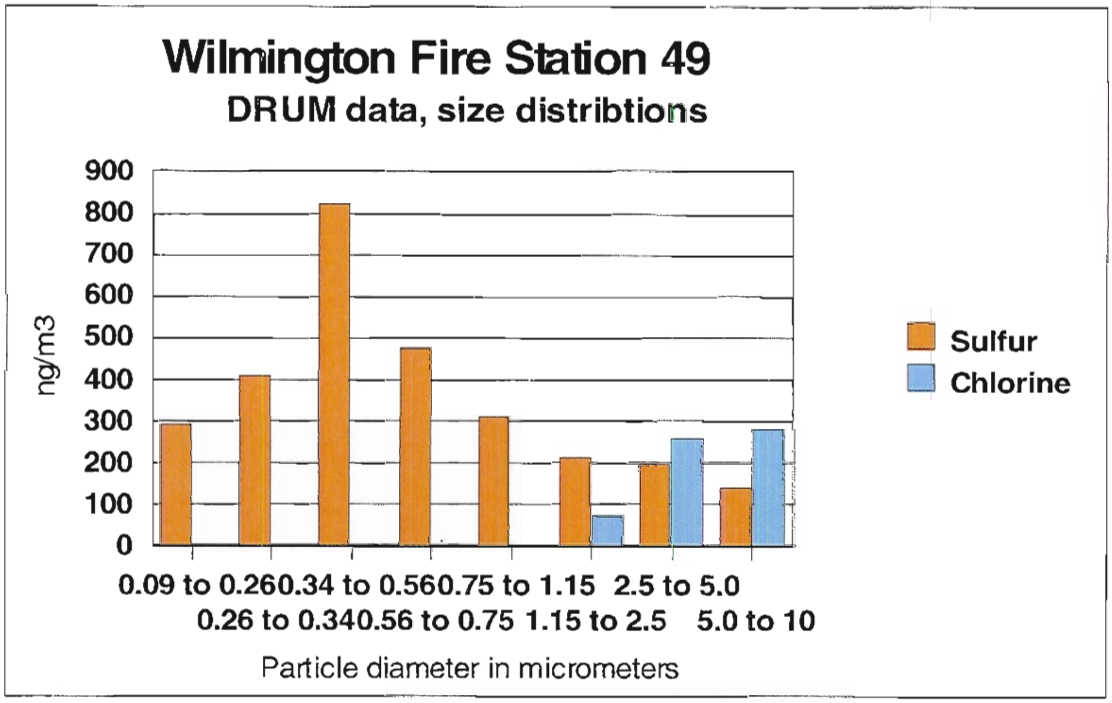


Figure 14 DRUM elemental data – size distributions of sulfur and chlorine

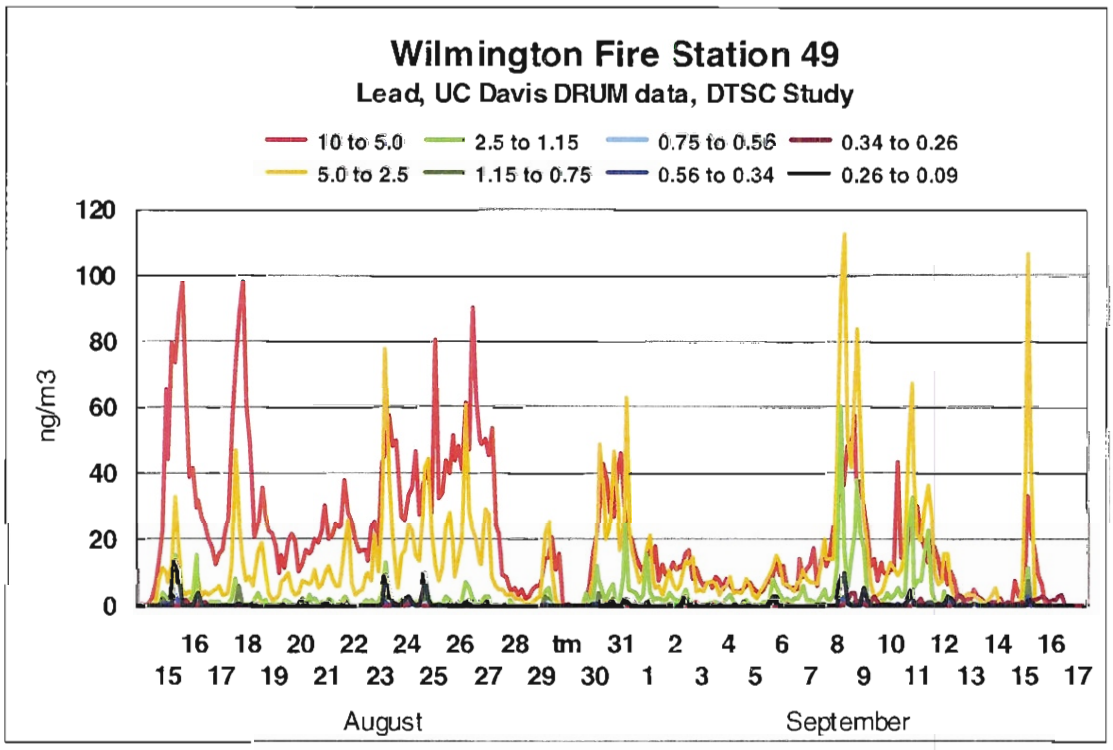


Figure 15 DRUM elemental data – lead

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

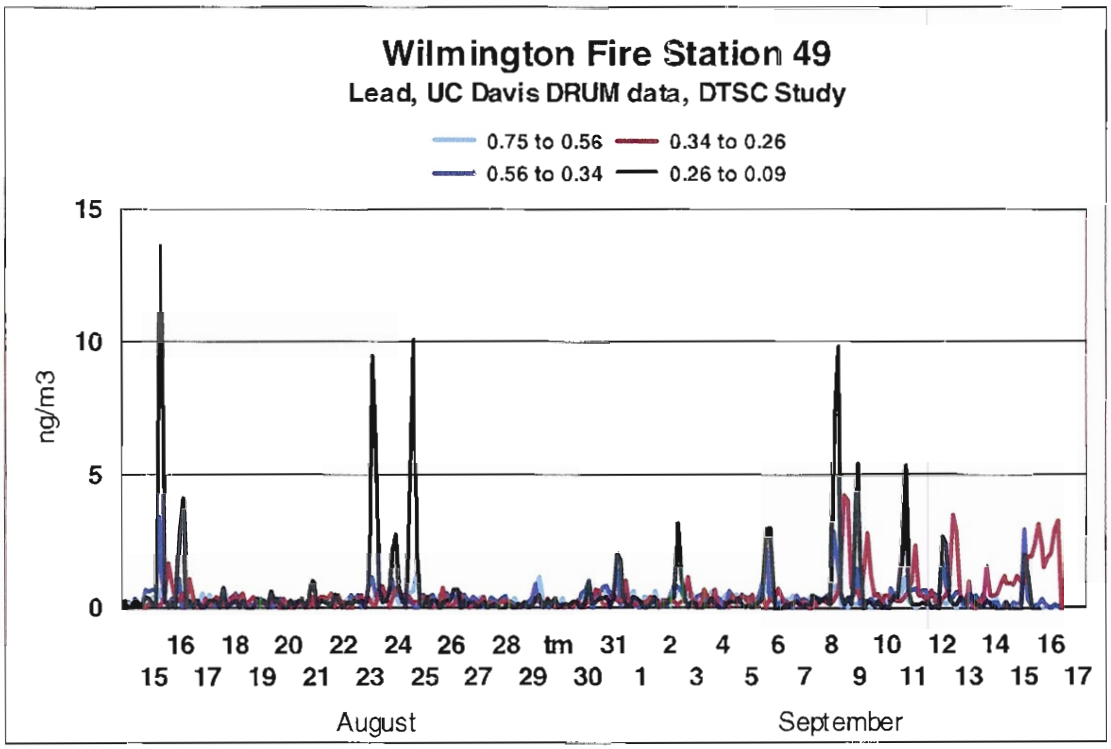


Figure 16 DRUM elemental data – fine modes of lead

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

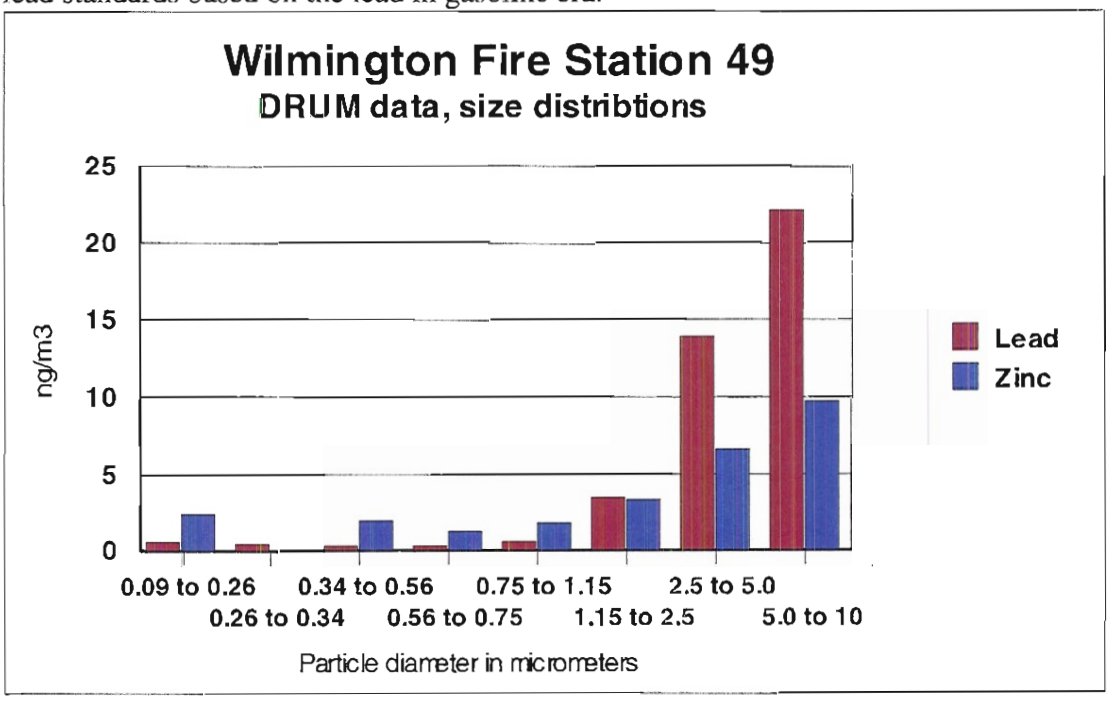


Figure 17 DRUM elemental data – size of lead and zinc

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.

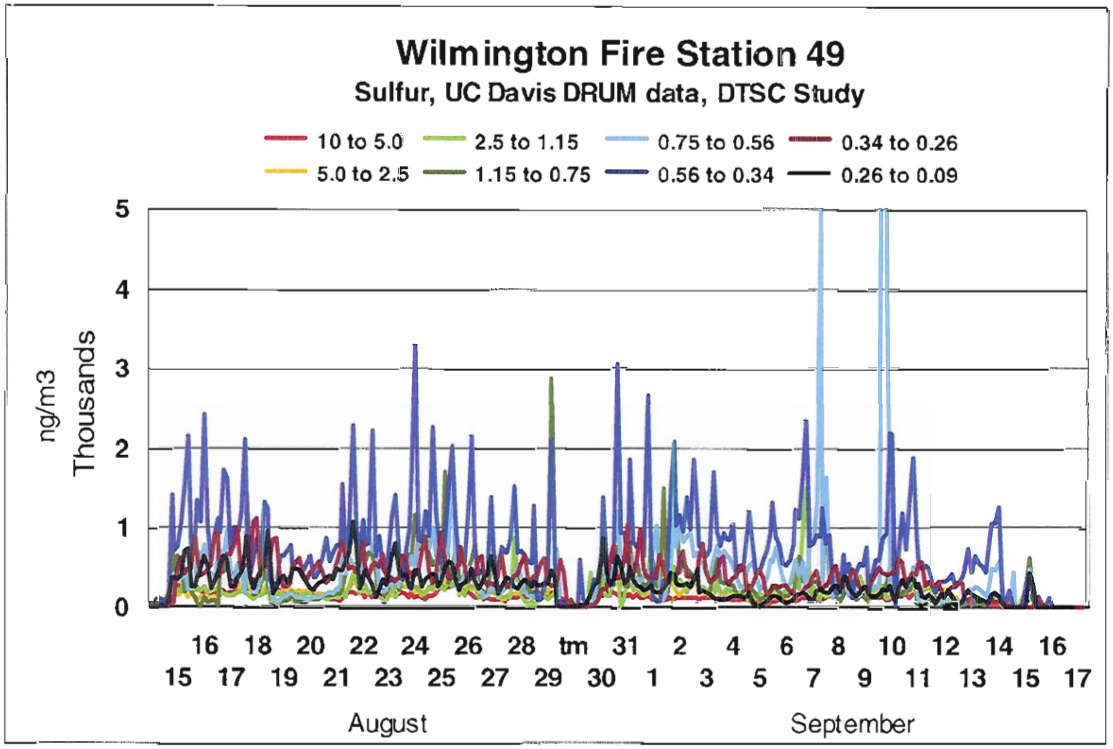


Figure 18 DRUM elemental data – sulfur

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 in figures 7 and 8). This period will be examined to see if any unusual events occurred near Fire Station 49 and to better establish non shredder background.

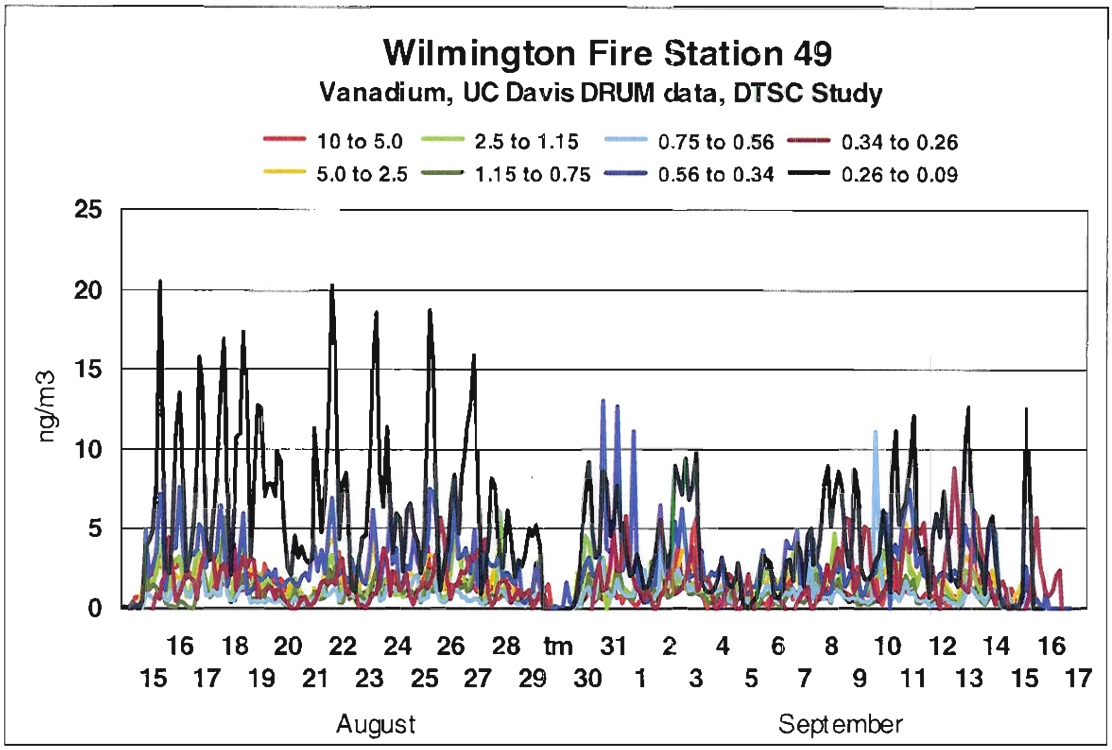


Figure 19 DRUM elemental data – vanadium

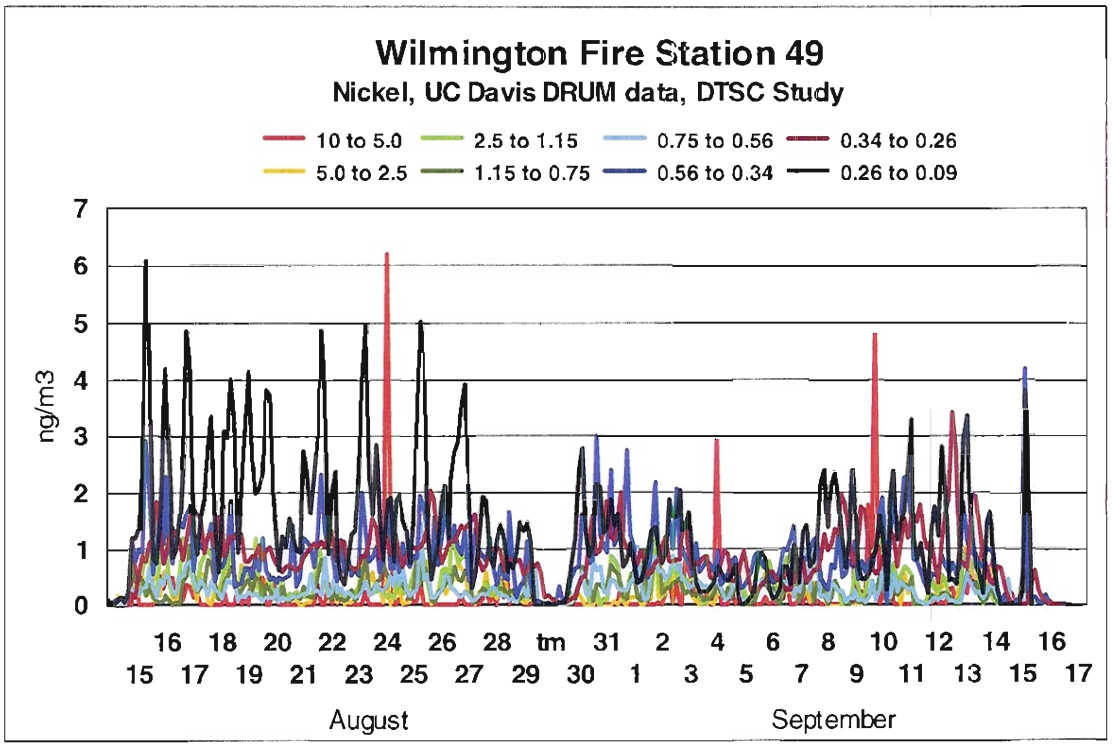


Figure 20 DRUM elemental data – nickel

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

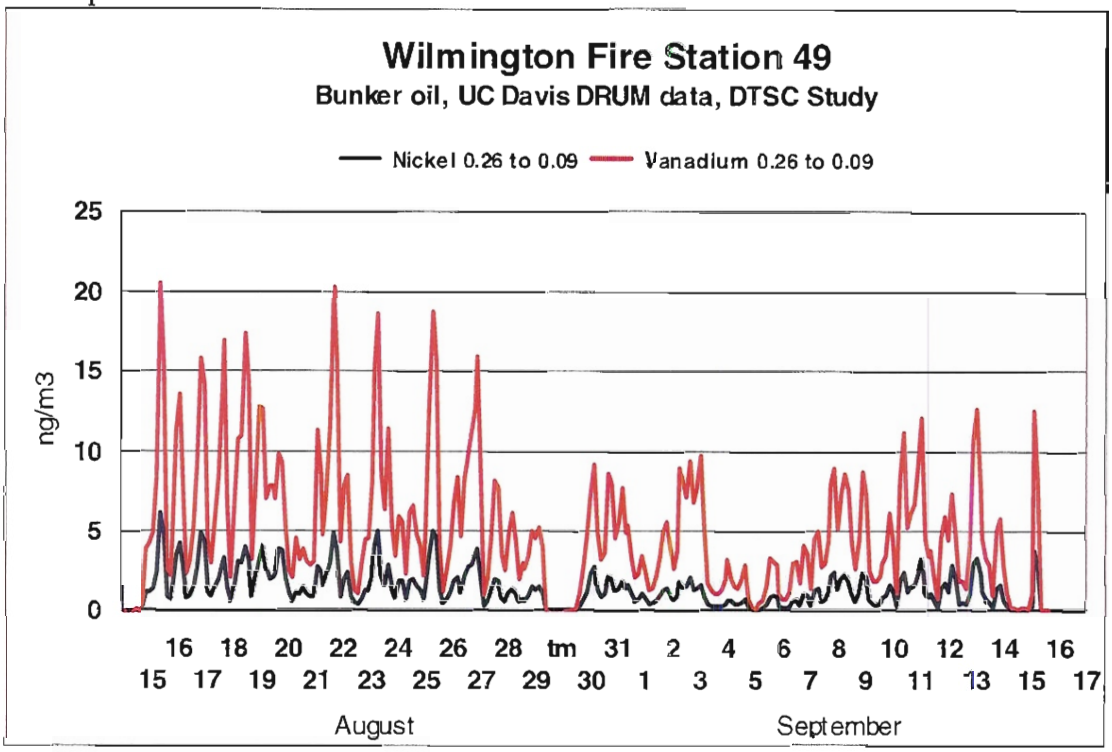


Figure 21 DRUM elemental data – nickel and vanadium

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.

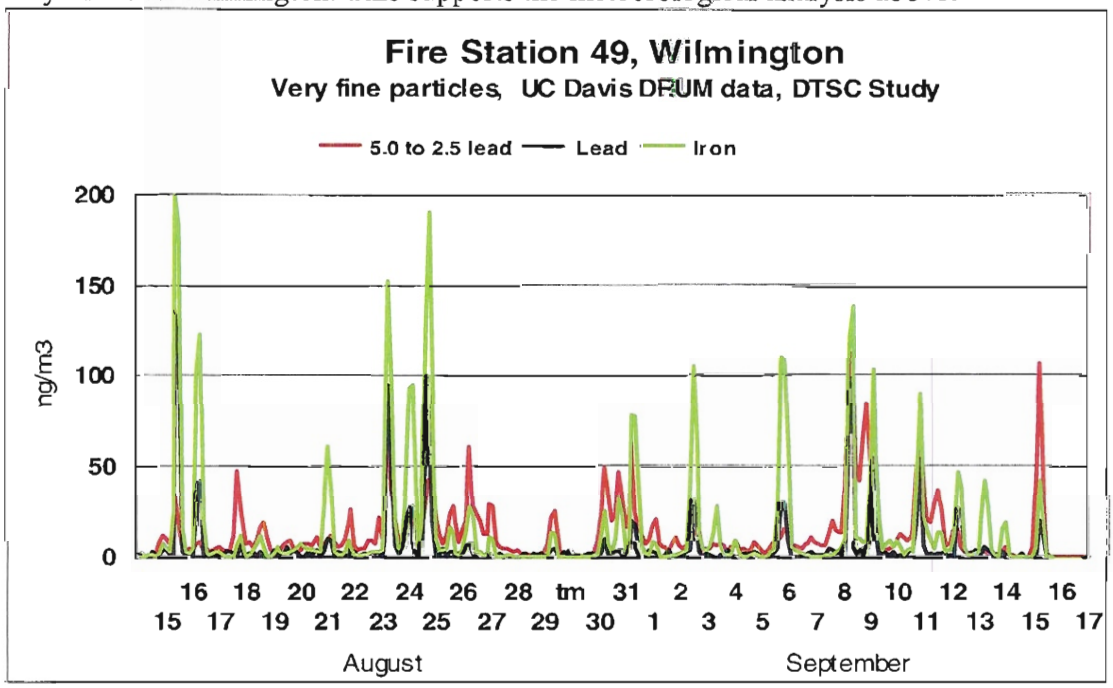


Figure 22 DRUM elemental data – coarse lead, very fine (< 0.25 μm) lead and iron

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.

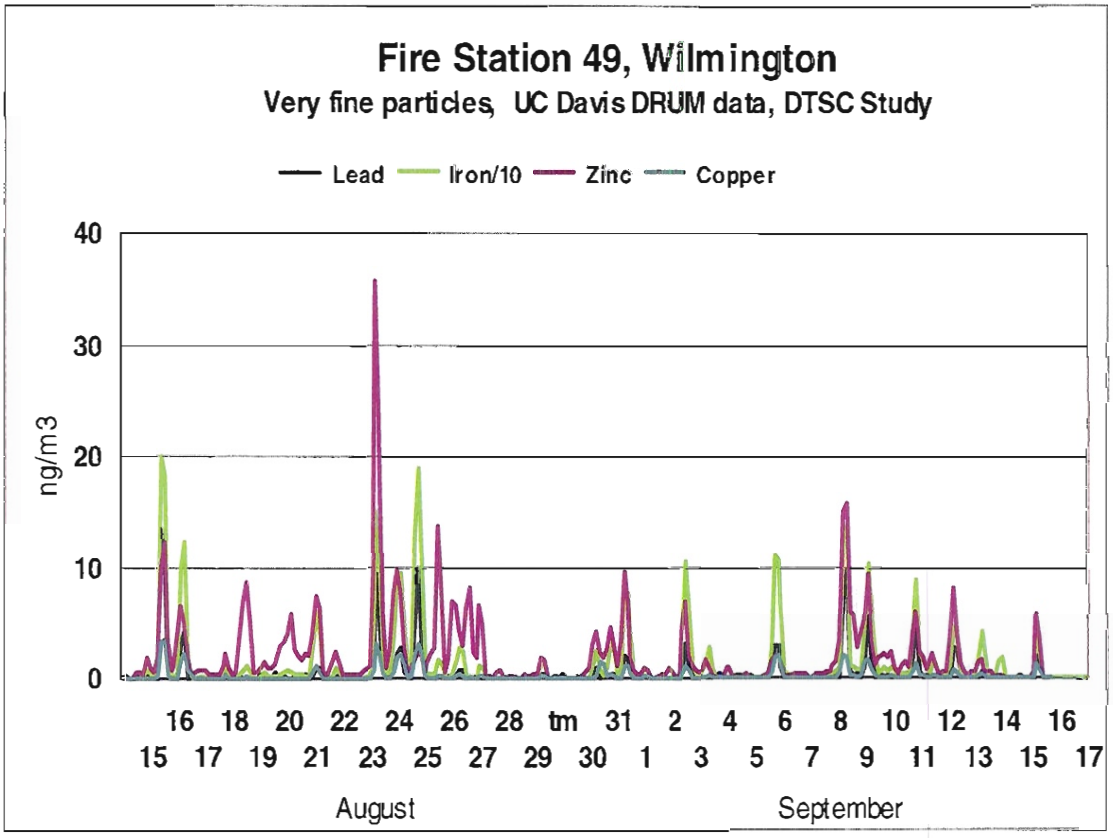


Figure 23 DRUM elemental data – very fine (< 0.25 µm) lead, iron, zinc, and copper

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 diameters are show below in Figure 24.

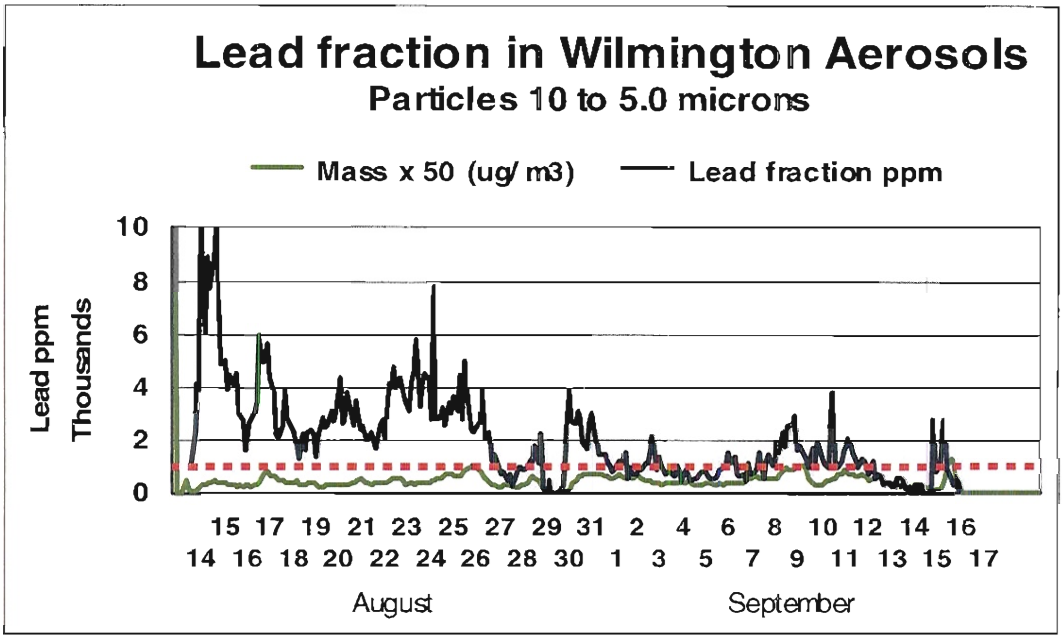


Figure 24 DRUM mass and elemental data –10 to 5.0 µm lead (ppm)

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

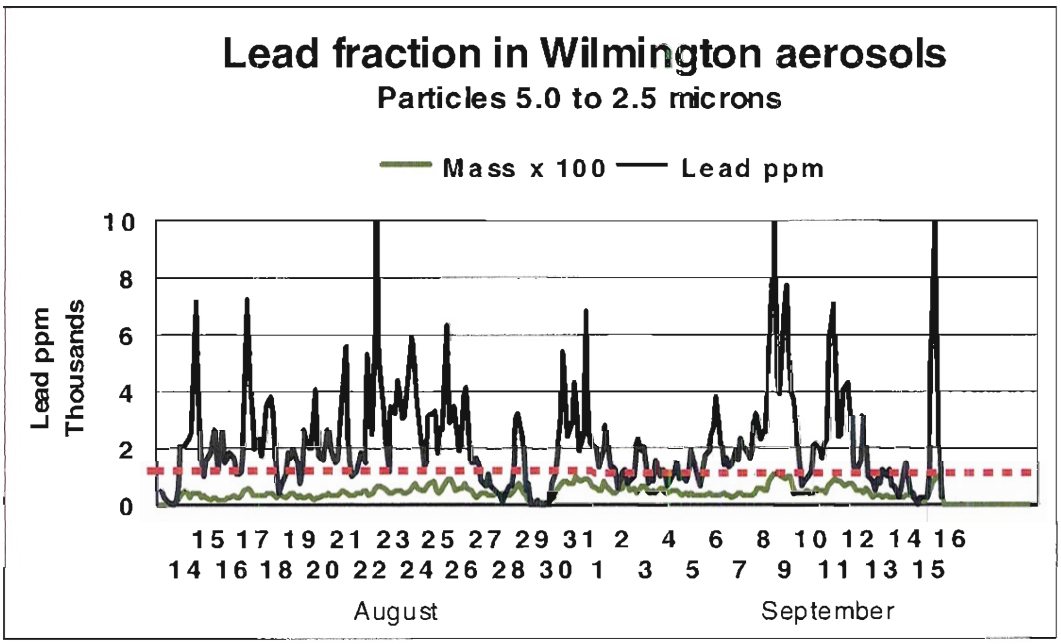


Figure 25 DRUM mass and elemental data –5.0 to 2.5 µm lead (ppm)

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

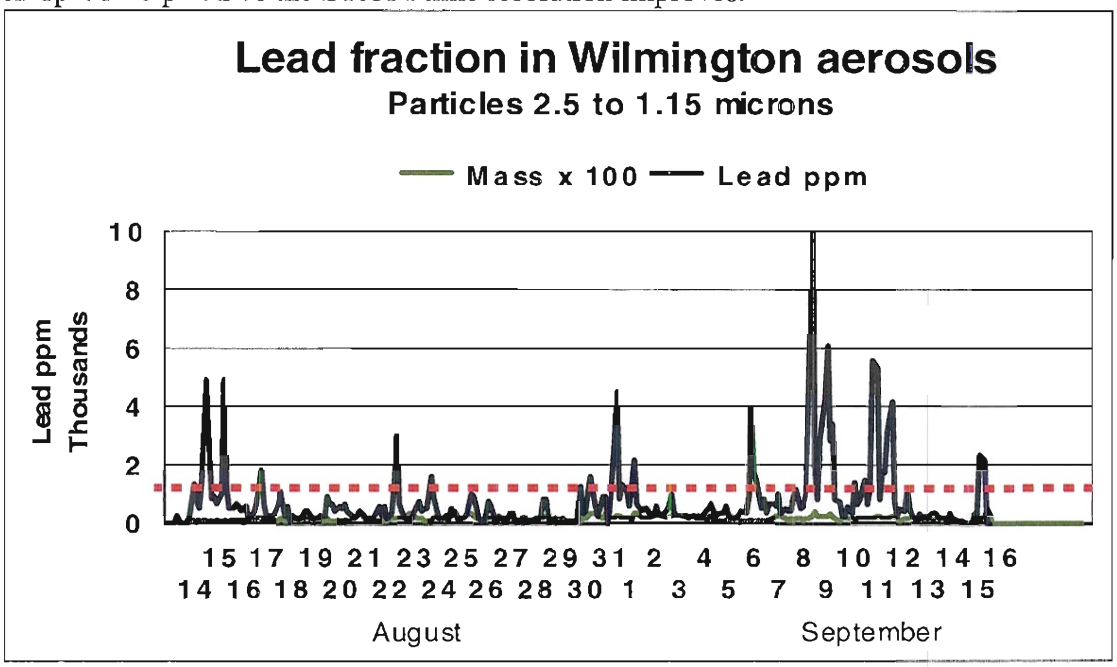


Figure 26 DRUM mass and elemental data –2.5 to 1.15 µm lead (ppm)

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.

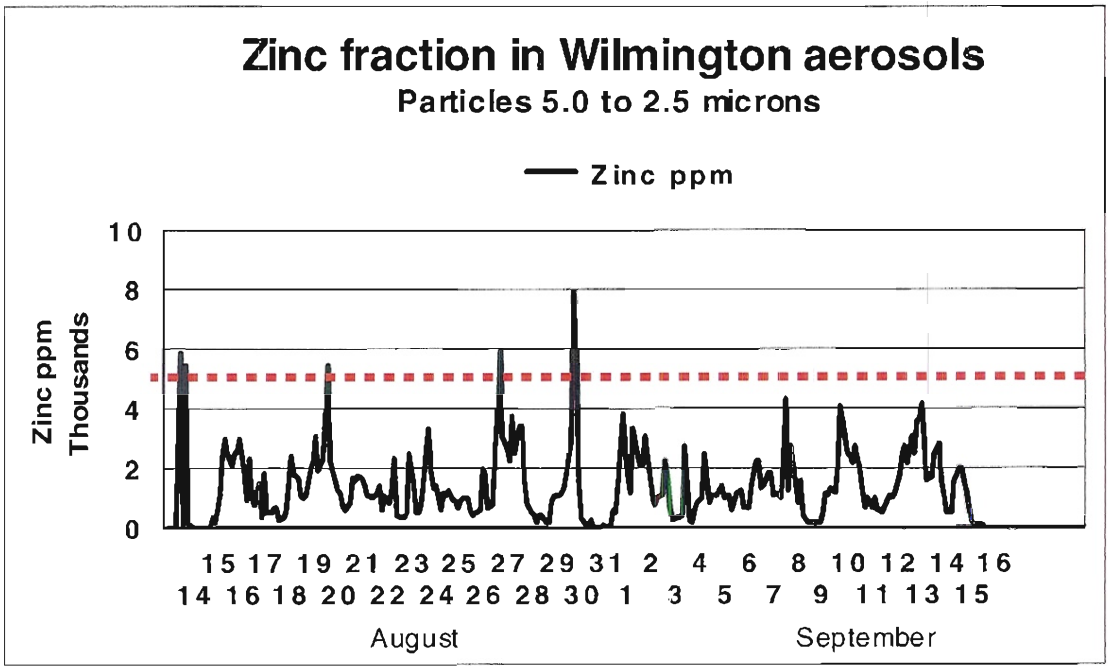


Figure 27 DRUM mass and elemental data –5.0 to 2.5 µm zinc (ppm)

Zinc also shows the potential to violate 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 concentrations versus date.

Date - August (based on very fine iron tracer)	Lead (ng/m^3) 10 to 1.0 μm	Lead ppm 10 to 5.0 μm	**Lead ppm Weighted for deposition (10 to 1.0 μm)**
15	103	8,180	**8,598**
16	123	9,612	**10,136**
18	46	5,477	**5,962**
21	42	3,439	**3,700**
23	123	4,442	**3,774**
24	99	5,279	**5,831**
25	115	5,229	**5,737**
26	121	4,082	**4,442**
29	47	1,691	**2,003**
31	80	3,325	**3,789**
September			
2	50	1,280	**1,553**
6	36	1,285	**1,652**
8	173	1,356	**2,902**
9	93	2,802	**3,158**
11	127	2,541	**3,354**
15	118	2,399	**3,713**

Table 2 Lead concentrations dominating lead deposition – 16 episodes identified as coming from the shredder by the unique very fine iron signature. On average, 83% of all lead is in particle sizes between 1.0 and 10 μm, but no data were available over 10 μm.

The amount of deposited particles was calculated by introducing the settling velocity (Sehmel, 1981, Seinfeld and Pandis 1997). DTSC's regulatory thresholds only apply to deposited particles, not aerosols, so the deposition-weighted values are the only relevant ones to compare with DTSC's hazardous waste threshold for lead of 1,000 ppm. We note that over all hours during the 6 week study the coarse (10 to 2.5 μm) lead values were 2,369 ppm, dominated by the episodes coming from the Terminal Island shredder, which averaged 4,446 ppm Pb.

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

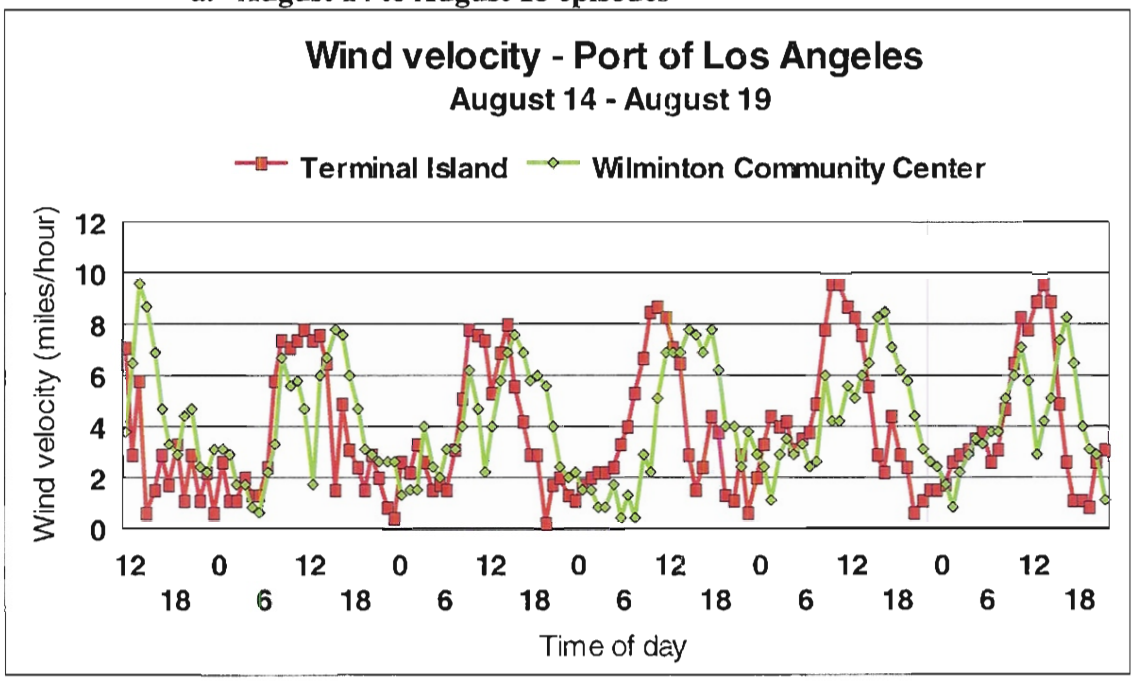


Figure 28 Local wind velocity – August 14 to August 18

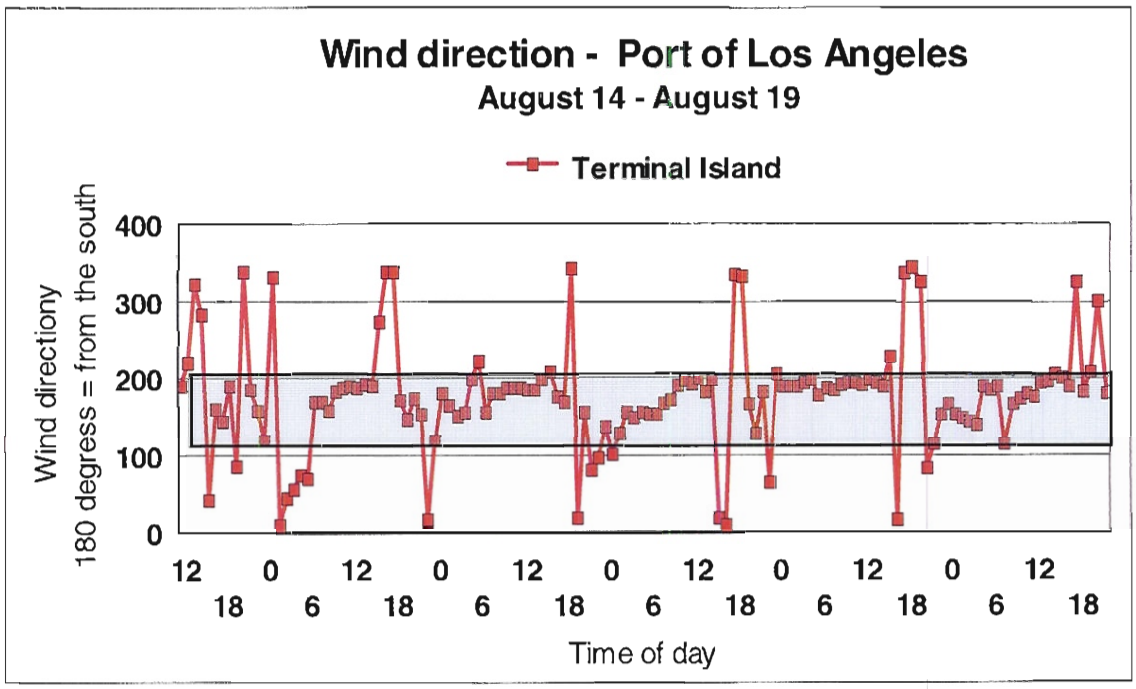


Figure 29 Local wind direction – August 14 to August 18. The shaded area is ± 45° from the direction of the shredder.

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

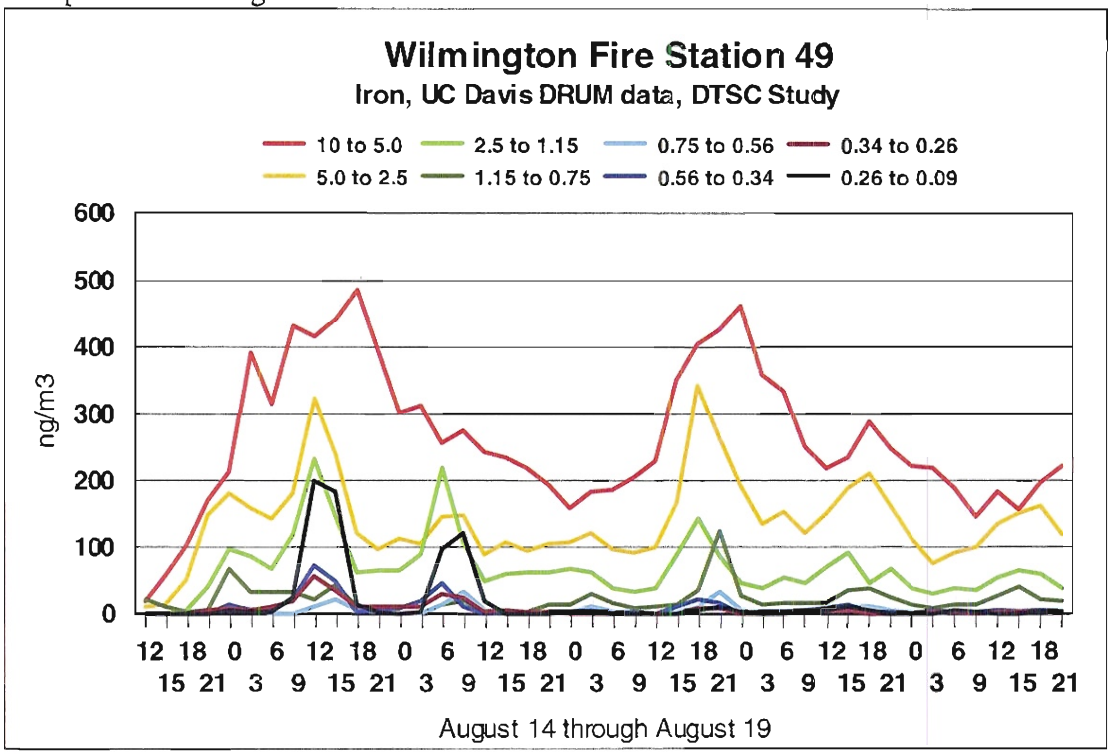


Figure 30 DRUM/S-XRF elemental data, iron, August 14 to August 18

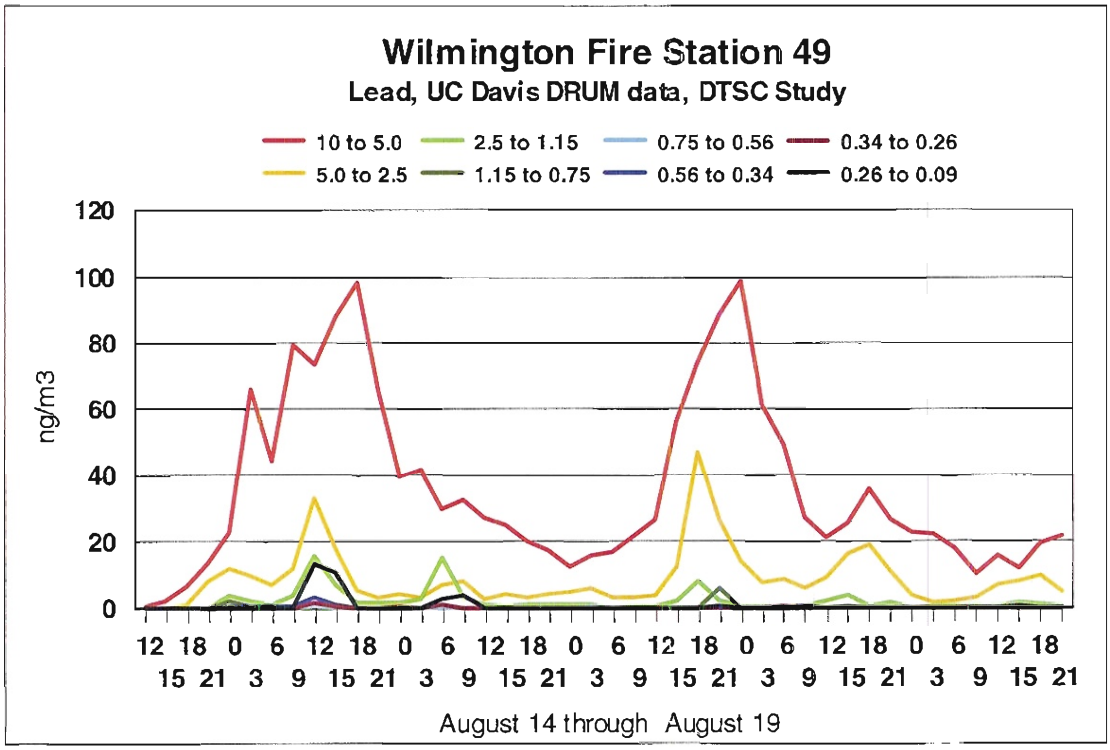


Figure 31 DRUM/S-XRF elemental data, lead, August 14 to August 18

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.

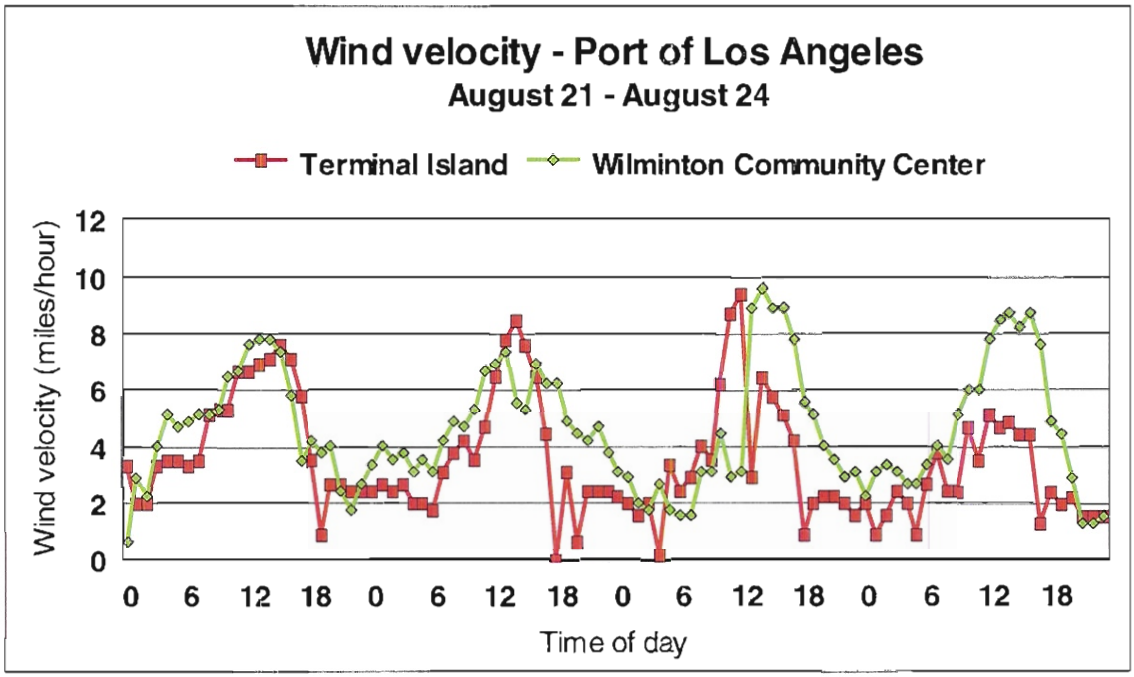


Figure 32 Local wind velocity – August 21 to August 24

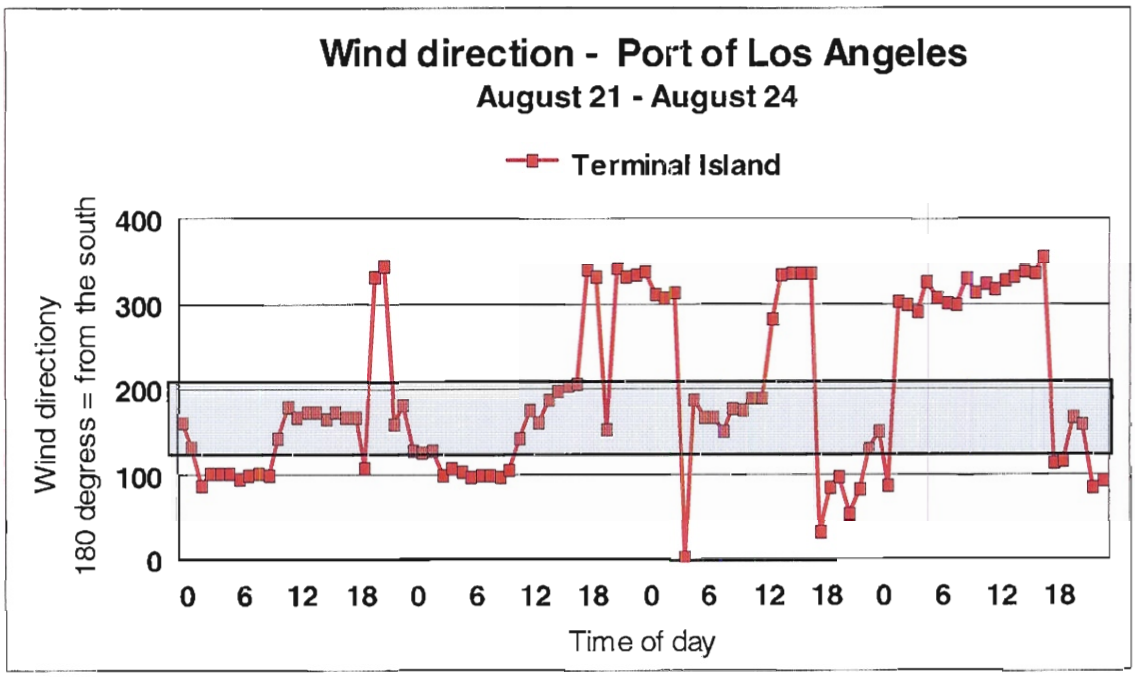


Figure 33 Local wind direction – August 21 to August 24

The first element is chlorine from sea salt.

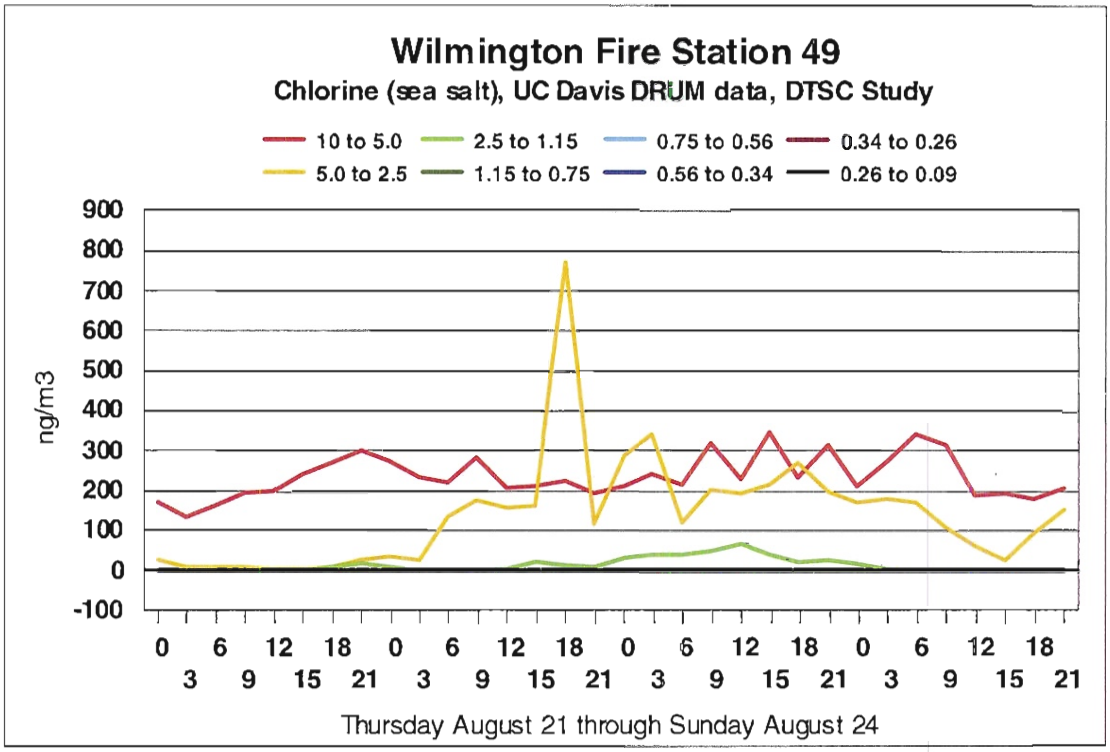


Figure 34 DRUM/S-XRF elemental data – chlorine

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

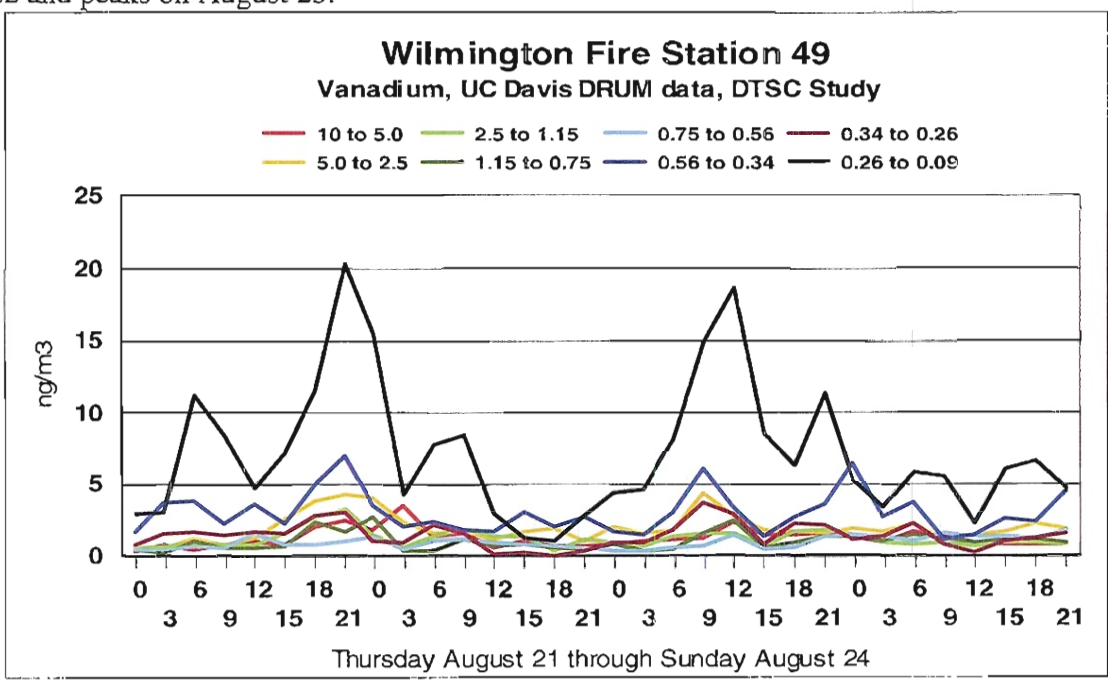


Figure 35 DRUM/S-XRF elemental data – vanadium

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.

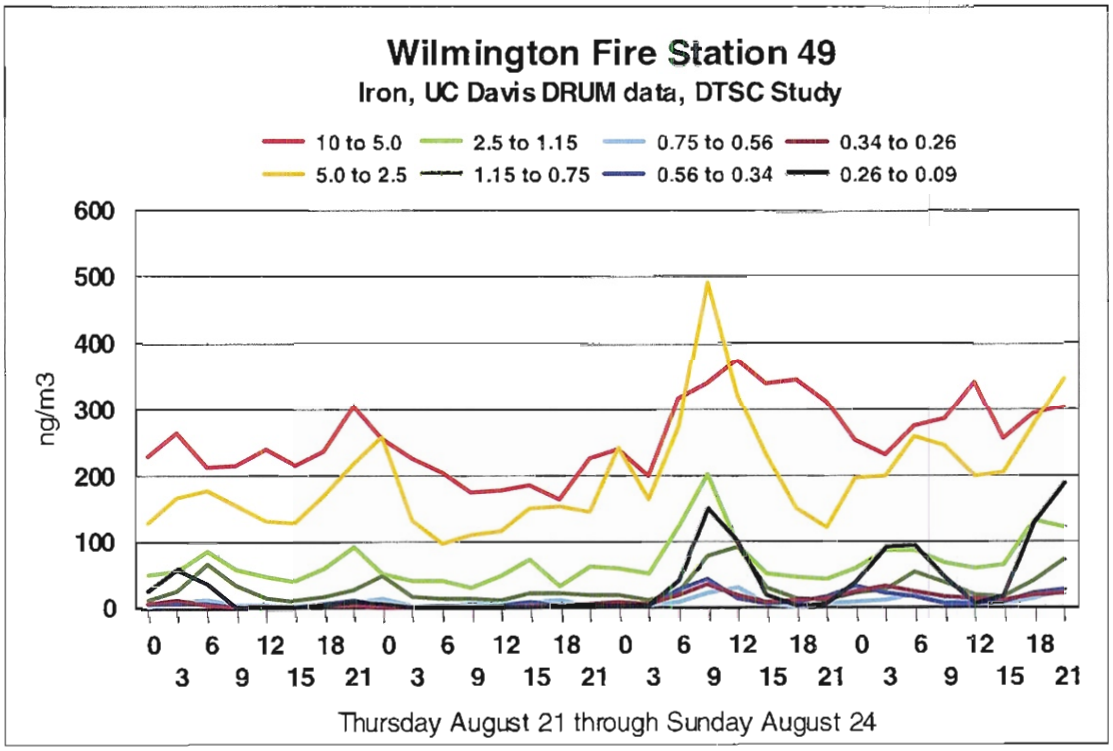


Figure 36 DRUM/S-XRF elemental data – iron

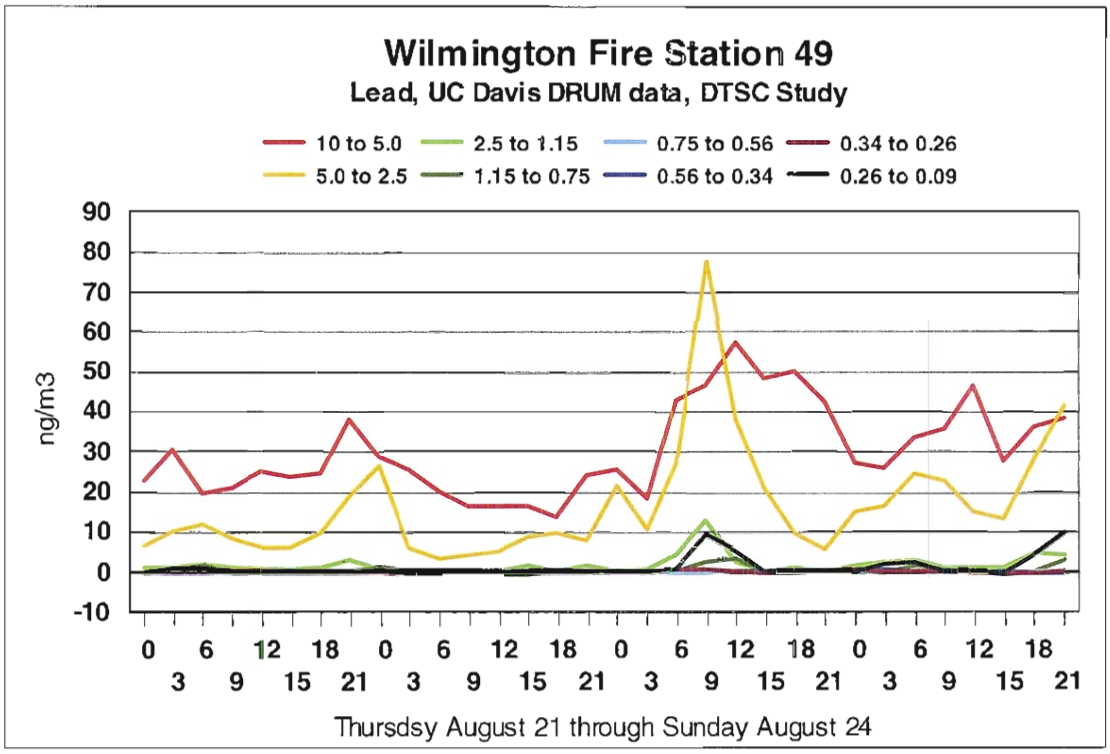


Figure 37 DRUM/S-XRF elemental data – lead

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.

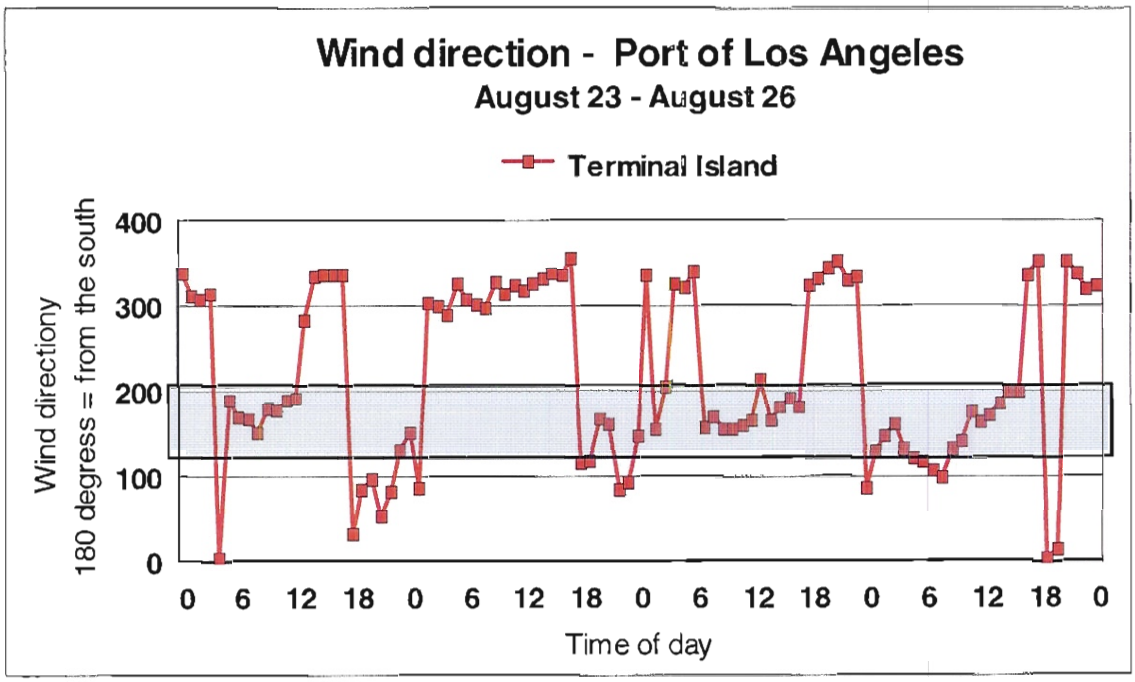


Figure 38 Wind direction data with shredder direction overlay

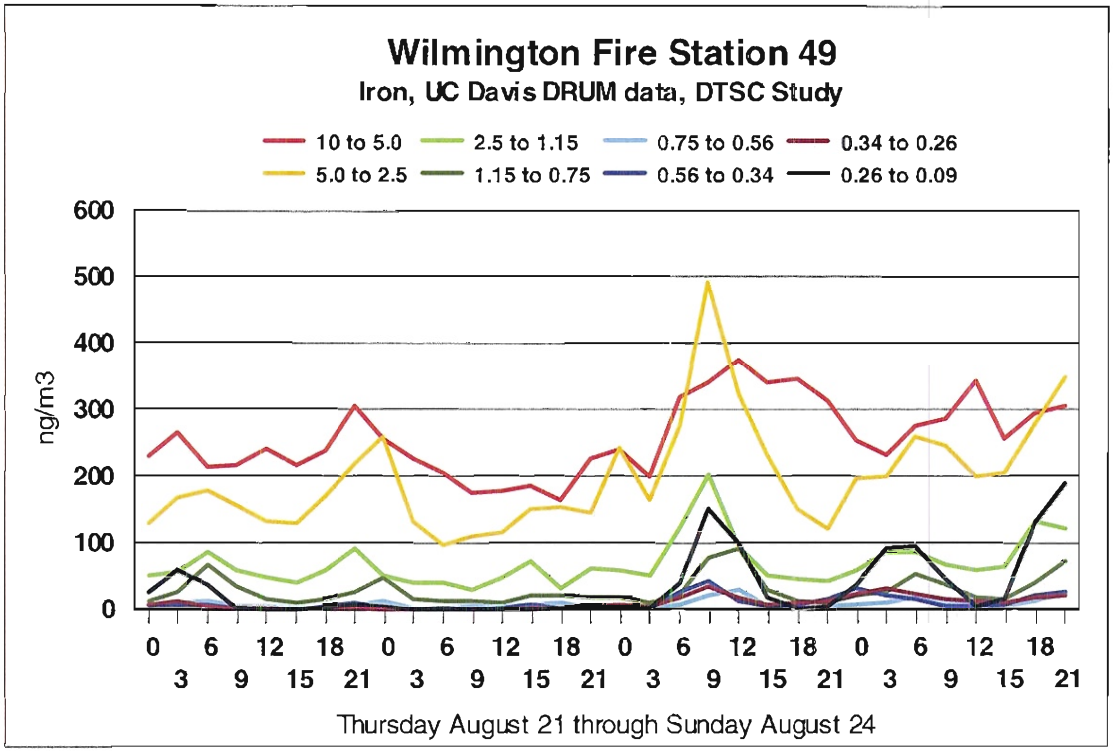


Figure 39 DRUM/S-XRF elemental data – fine iron

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**

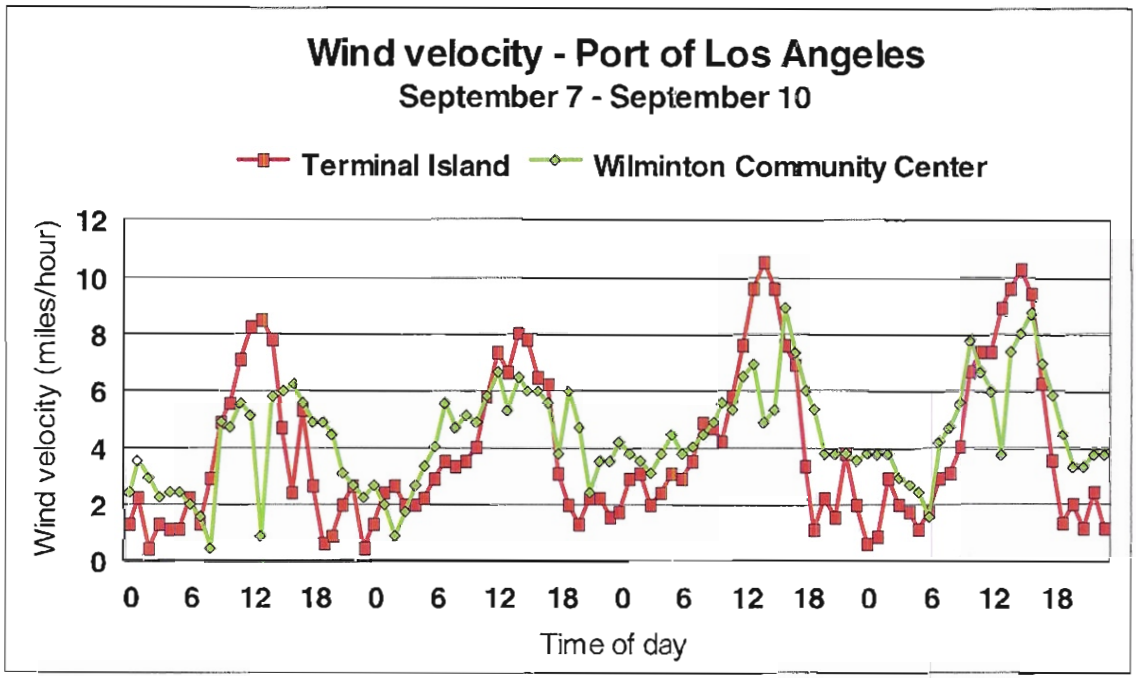


Figure 40 Local wind velocity – September 7 through September 10

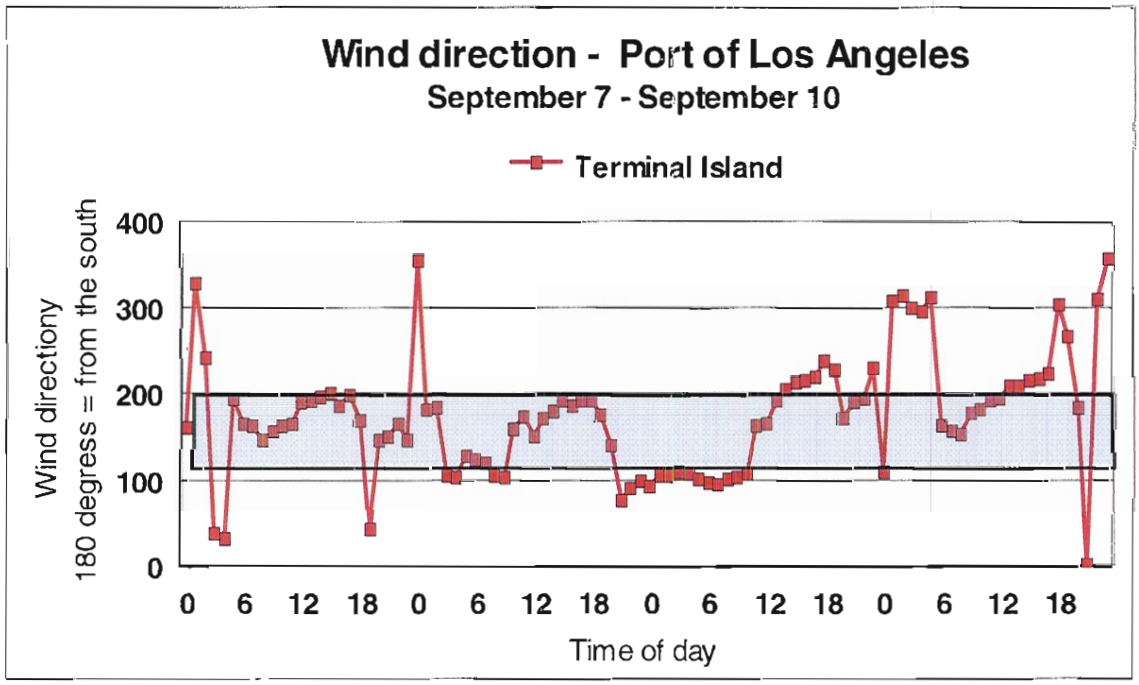


Figure 41 Local wind velocity – September 7 through September 10

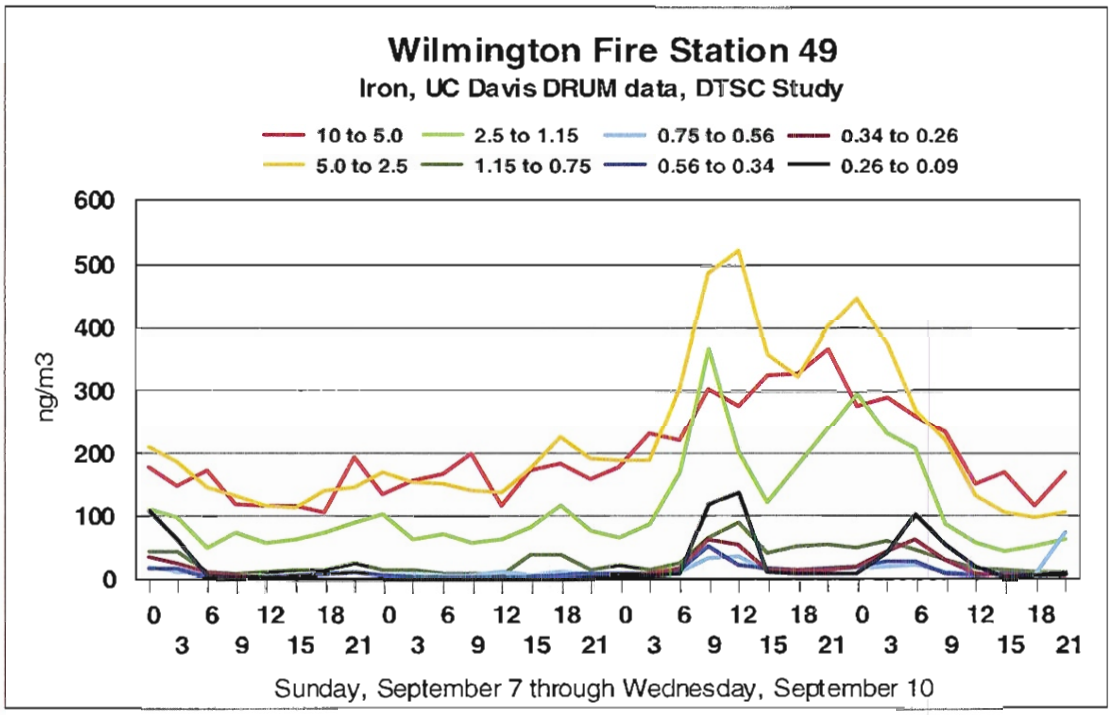


Figure 42 DRUM/S-XRF elemental data – iron

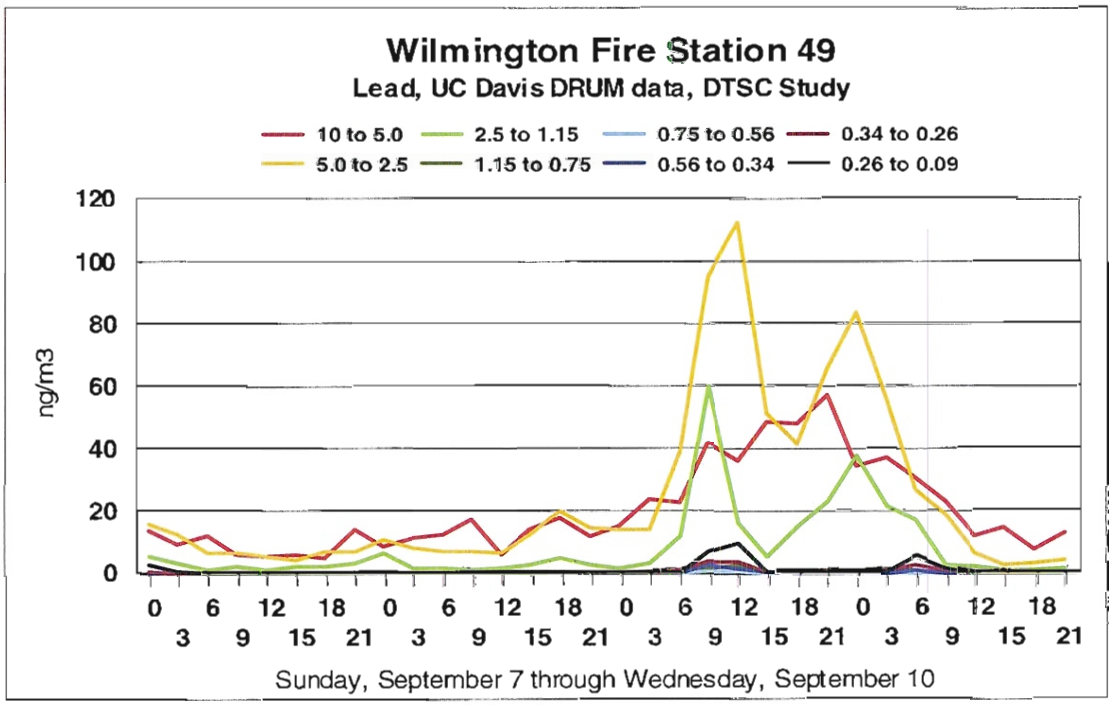


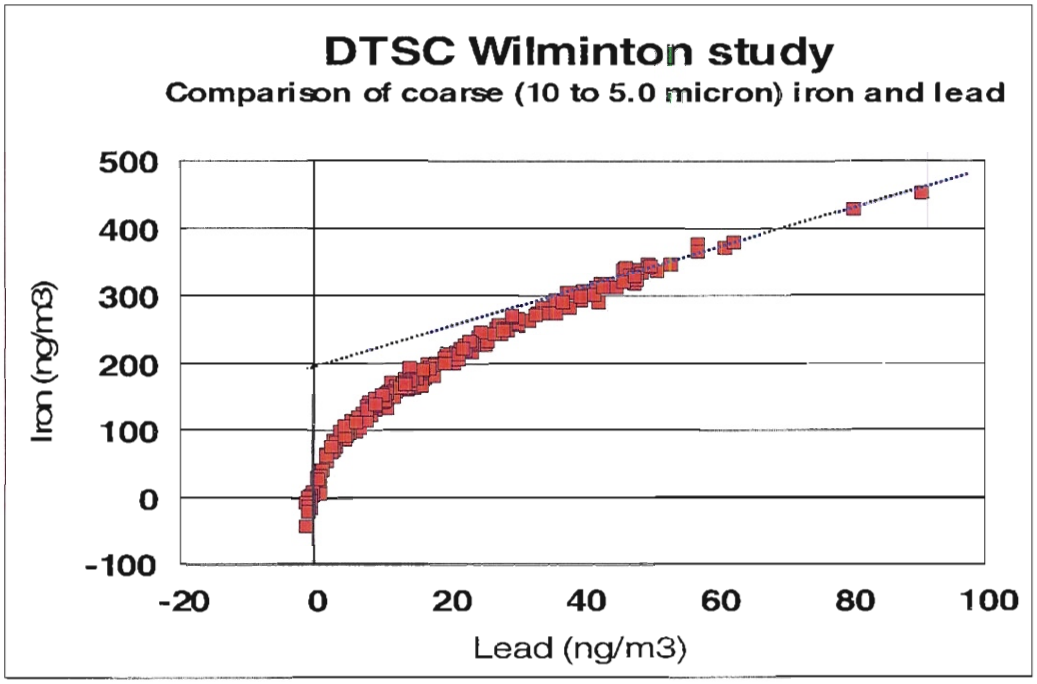
Figure 43 DRUM/S-XRF elemental data – iron

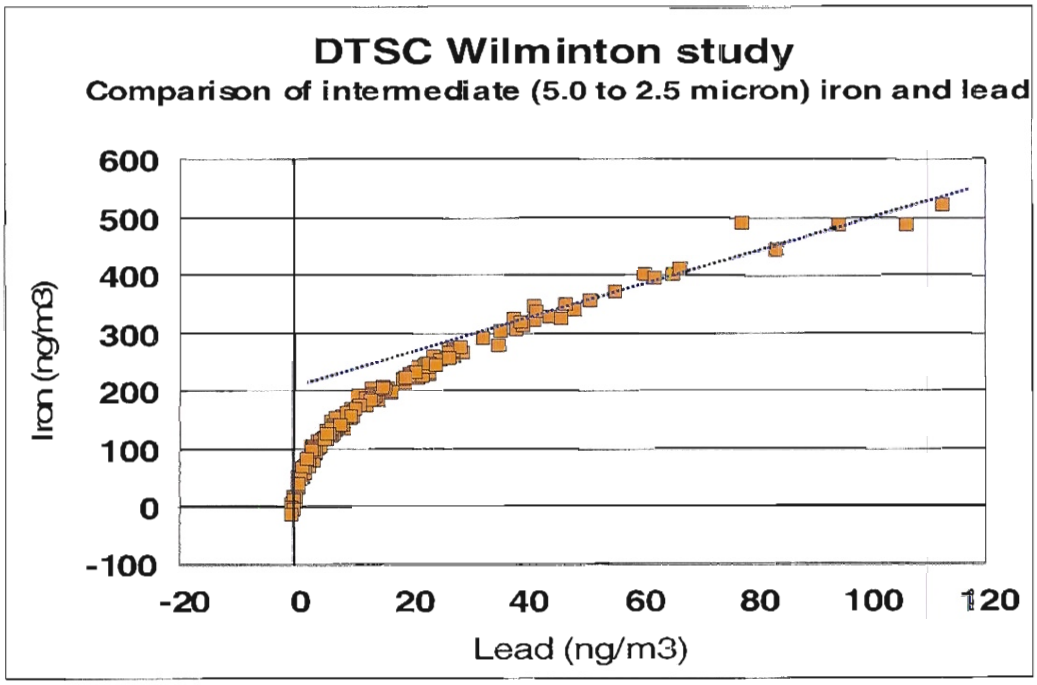
This period is interesting because despite favorable meteorology, there was minimal shredder source impact on Sunday and Monday. Clearly, details of shredder operations and feed stock are key to further analysis.

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 total threshold limit concentrations and DELTA detectable limits for regulated 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

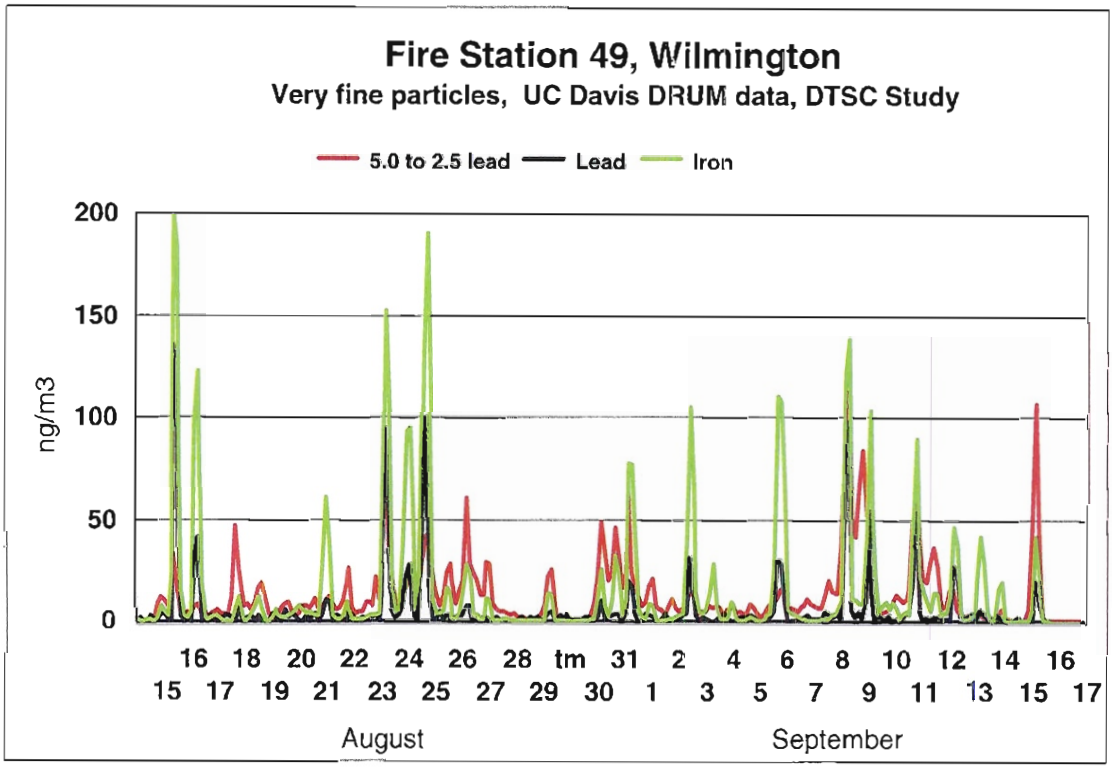
Fenton reaction $FeO_2 + H_2O_2 \Rightarrow Fe_2O_3 + OH^-$ (free radical)

Free radicals react causing tissue damage and also producing a free radical continuing this reaction again and again…the result is decreased Lung function due to the cascade of reactions producing damaging free radicals until free radicals find an anti-oxidant, eg. Vitamin E.

Kent Pinkerton, Professor, Dir., Center for Health and The Environment, Expert regarding health effects on Lungs. Specific research shows correlation between elevated levels of fine Fe in the Lungs of rats

Toxicologist to determine relation of fine Fe to known health impacts.

We are seeing 100 – 200 ng/m^3 of Fe in air this would normally be approx. 1 ng/m^3.



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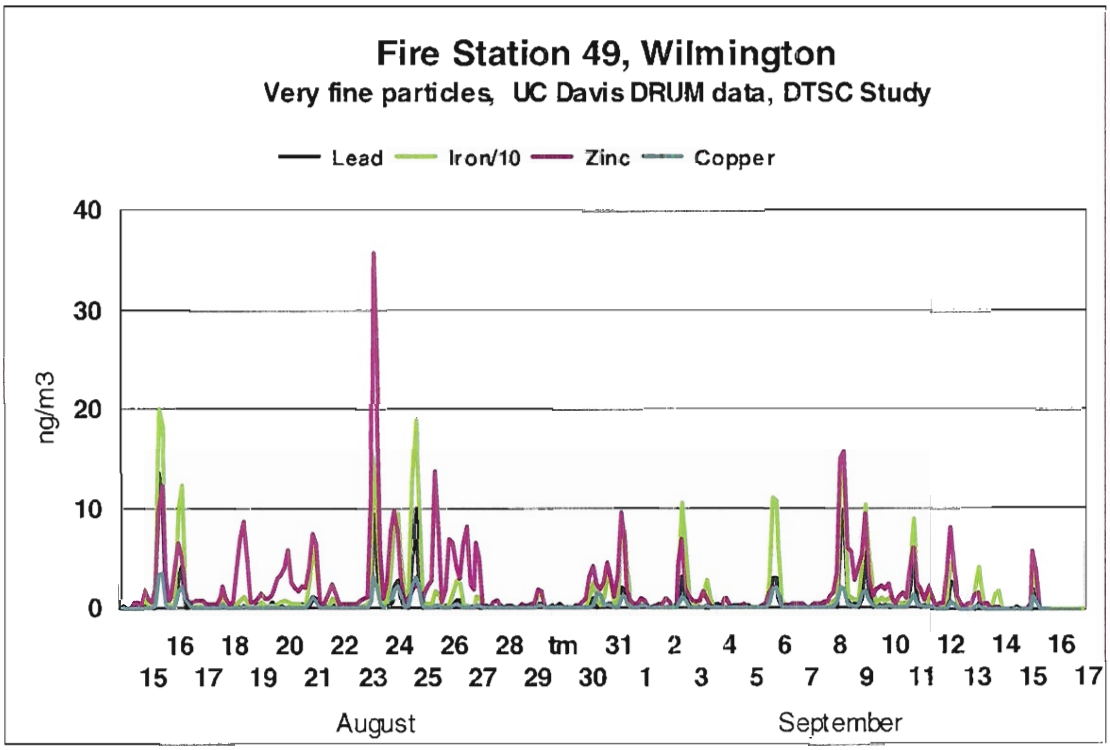
4. Can we distinguish diesel and auto emissions from Shredder emissions?

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?

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

The species that we have measured to date include about a dozen PAHs (including specifically benzo[a]pyrene), n-alkanes (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 4 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)?

Hg

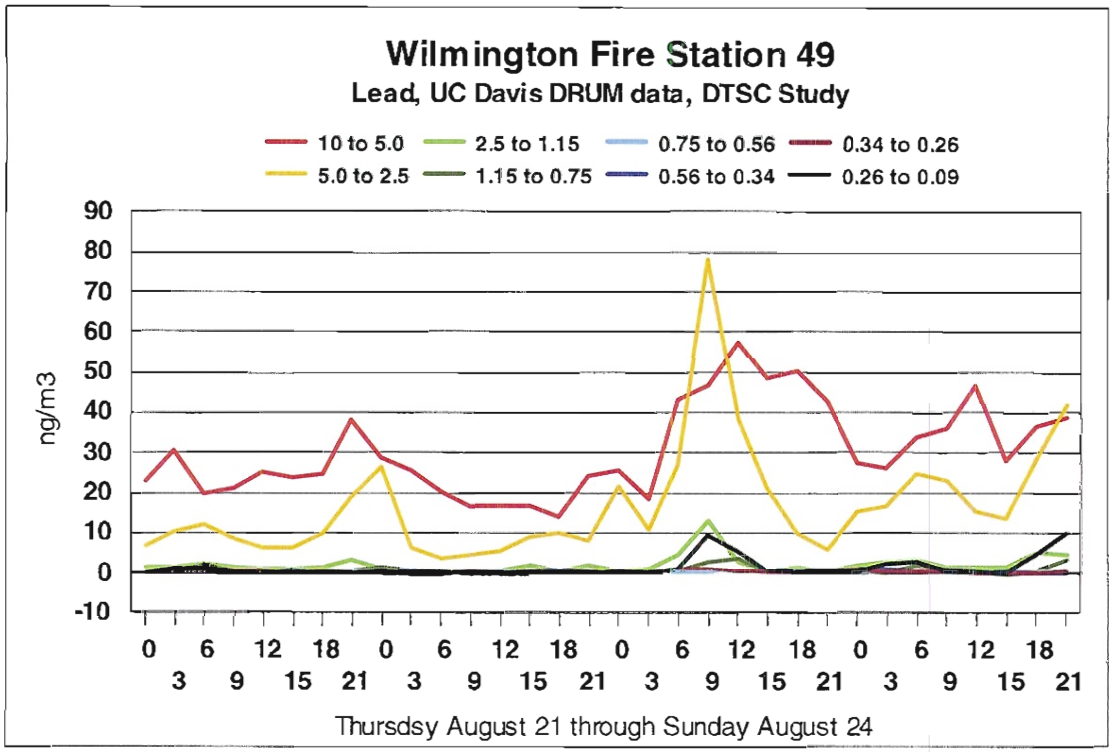
Because Mercury readily moves between the vapor, liquid, and solid state; we can provide a lower limit only, due to potential evaporation in analysis chamber, (we must ask for analysis, Hg is not included in standard analyses).

Cd

Elemental interference due to domination by 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?

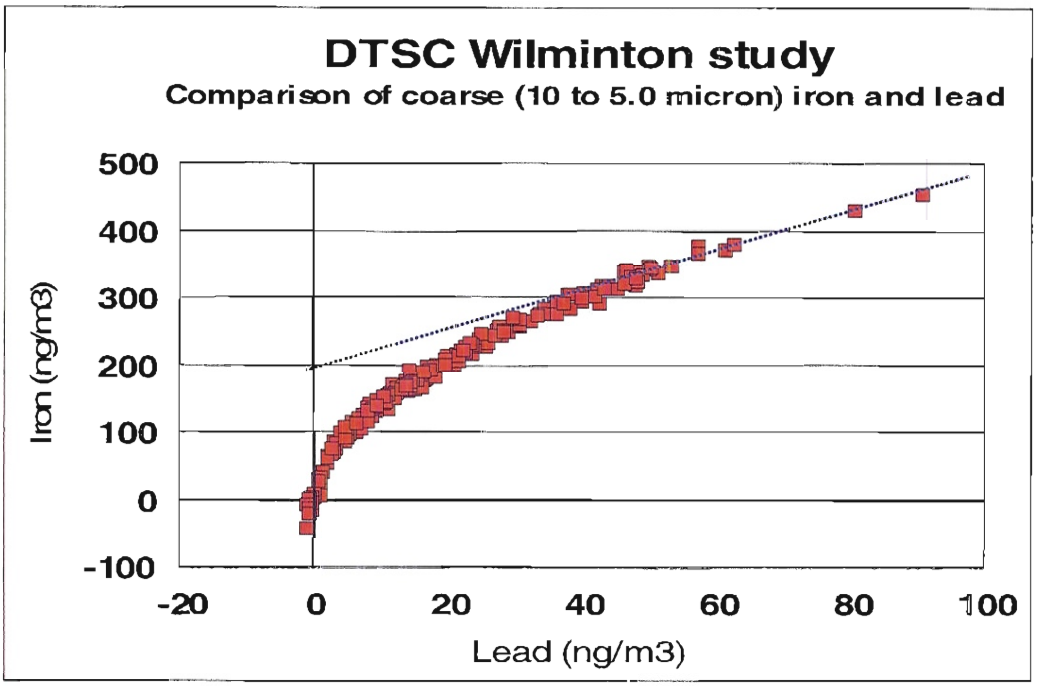
(See Progress report #2, page 19)

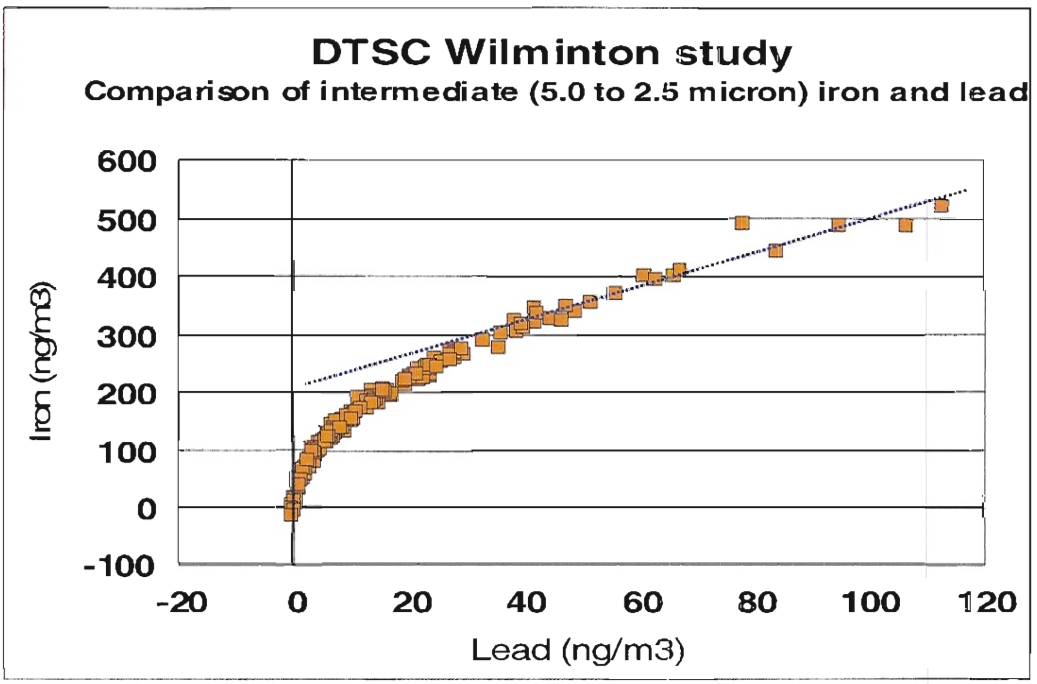


The shredder operating information allows us to identify 3 sources of lead in this one episode. However, every episode must be analyzed independently.

1. "Background" source – about 15 to 20 ng/m^3 in 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 dust 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 separate this from the shredder product pile fugitive dust, especially in the largest size mode, with out more detailed wind data. It 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 2 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. Boberg, 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?

Peter Wood did a calculation based on the following:
At 80% efficiency = 68.87 tons/year controlled (from New Terminal Island Emission Calculator with MegaShredder.xls, "shredder" estimate). At 100% efficiency = 86.08 tons/year, or this is equal to amount released with no air pollution control system

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 readily settle to the ground.

Part 2: Spring, 2009

Deposition of coarse toxic particles in Wilmington, CA for the Department of Toxic Substances Control (DTSC) May – June, 2009

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

Executive Summary – spring, 2009:

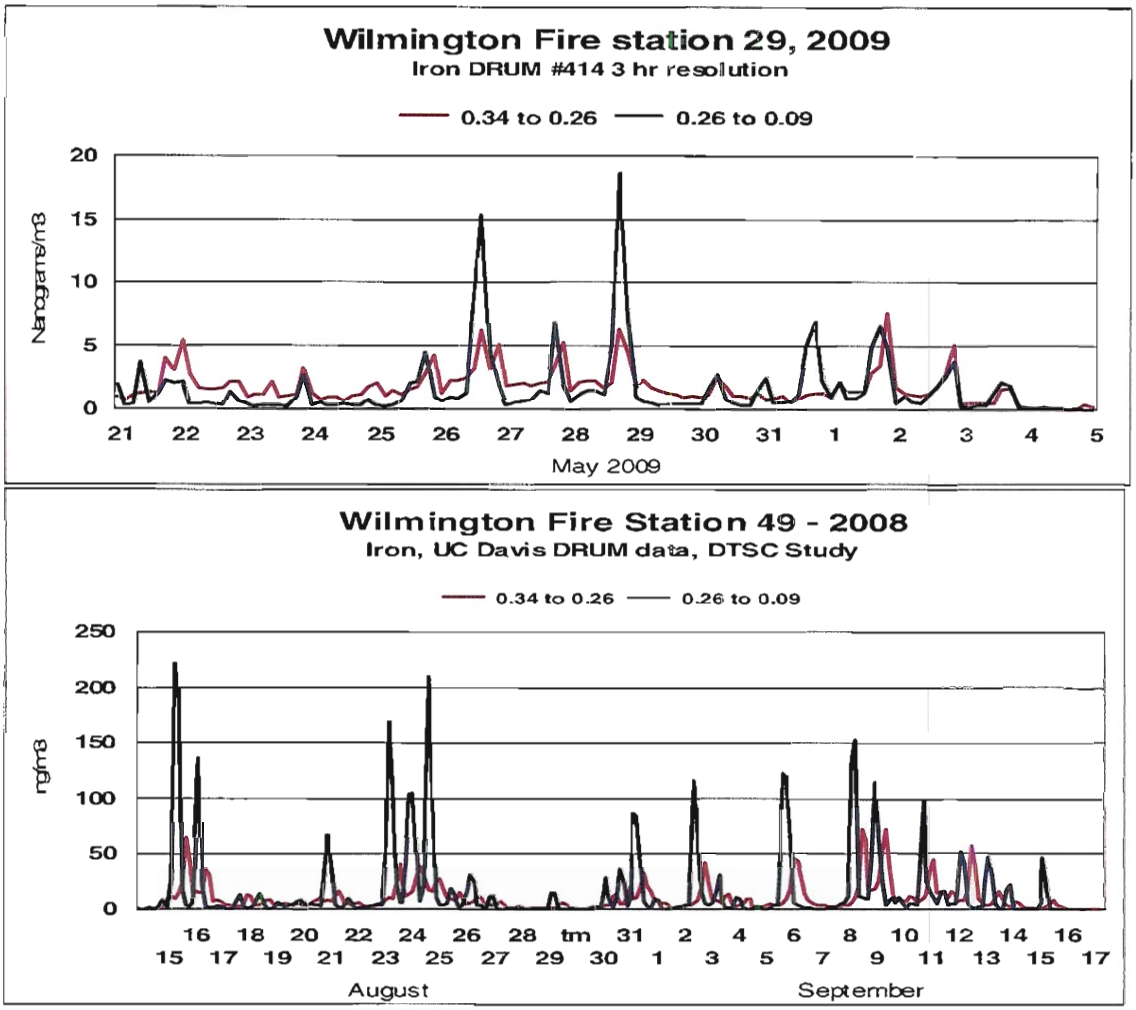
Aerosols were measured in May and June, 2009, at the same site used in the August – September, 2008 study, Fire Station #49 of the City of Wilmington. Guided by the results of the summer, 2008 study, a number of changes were made to reduce uncertainties and better establish rates of deposition of toxic particles:

1) Video monitoring was used to study shredder operations, day and night, with 1 hr time resolution,
2) Aerosol samples were collected from the pollution control system of the shredder to establish potential sources,
3) Aerosol measurements were made at FS #49 with two DRUM samplers.
   a. One was identical to the DRUM used in summer, 2008, with a PM_{10} inlet, and analysis for mass and S-XRF elements, (Mg to Mo, plus Pb, Appendix C), but with time resolution changed from 3 hr. to 1 hr. (a field problem yields an actual resolution of 2 hr.)
   b. The second had a 35 μm inlet and a continuous ultra fine stage, $0.09 > D_p > 0.0$ μm stage, with 1 hr. resolution, with mass and S-XRF elements,
4. A third DRUM sampler was established in downtown Wilmington, with a 35 μm inlet, 1 hr. time resolution, mass, and S-XRF elements,
5. Deposition foils were placed from the port to downtown Wilmington to directly measure deposition onto S-XRF analyzable filters,
6. Wipe samples from surfaces and water were taken on S-XRF analyzable Teflon filters at sites near the port to downtown Wilmington to examine deposition to impervious surfaces.

Aerosol pollution from ships in the harbor burning bunker oil, traced by vanadium and nickel in the very fine mode, were reduced to 71% of the summer, 2008 values, with possible decreased port operations and/or improved regulations. Very fine sulfur aerosols, with the same ship sources plus diesels, were reduced to only 31% of the 2008 values.

The aerosol results showed that the same aerosols were seen as were observed in summer, 2008, coming from the shredder, confirming the previous association with the shredder but with important differences. The 2009 fine iron and lead were generally associated with smoke observed coming from shredder operations.

Very fine aerosols measured in Spring, 2009, measured much less than in summer, 2008. Specifically, very fine iron was reduced to only 9% of its 2008 value, and lead was reduced to 40% of its 2008 value.



Coarse particles, however, were roughly the same or even slightly higher than in 2008. This is interpreted as a successful reduction of prompt shredder very fine emissions, but continuing problems with mechanical mode particles mixed with soil disturbed land surfaces, exposed piles, shredder operations, etc.

The behavior of the wipe samples shows a progression from high levels for deposited lead and zinc at or near the port, and a fall off by about a factor of 2 as one moves deeper into the community. Other species such as iron show no such variation. All samples were above 1000 ppm for lead and 5,000 ppm for zinc. The E Street School site wipe was taken at the boundary fence of a pre-school play ground.

The deposition samples had a relatively high failure rate, with filters lost to winds, samplers missing, etc, but the method shows promise. The results of the deposition samples show clear input of non-soil iron, plus titanium, vanadium, manganese, and zinc, along with a modest increase in lead.

Field Experiment

Aerosol sampling commenced on May 21, 2009 to June 4, 2009 at two sites, the prior site at Fire Station 49 (picture 1), and a site in Central Wilmington (picture 2).

Several innovations were added to the program, including high time resolution sampling at both sites, and a continuous afterfilter to evaluate the very fine/ultra fine aerosols, and a new PM_{35} inlet to the DRUM that was designed to match the old TSP filter samplers with their 35 micron cut.

Wipe test samples were collected on a trajectory from the Central Wilmington site to the marina across from the shredder, as well as prior samples taken during a criminal search warrant executed by DTSC staff at the site. Only part of the data has been reduced to date, partially because the non-standard samples required modifications of the ALS/LBNL analysis system.

Port activity was greatly reduced in this period, as compared to summer, 2008, and we were told that only 2 ships were berthed on May 21 when we started sampling.

Figure 44 Station 49. Note the inverted sampler with the 35 micron inlet.

Figure 45 Downtown Wilmington.

Results

Comparison will be made first to the DRUM sampler that ran with the same parameters as in summer, 2008.

Aerosols associated with ships burning residual oil were very evident on south winds from the port. The magnitude of the signal was on the average about ½ of what it had been summer 2008.

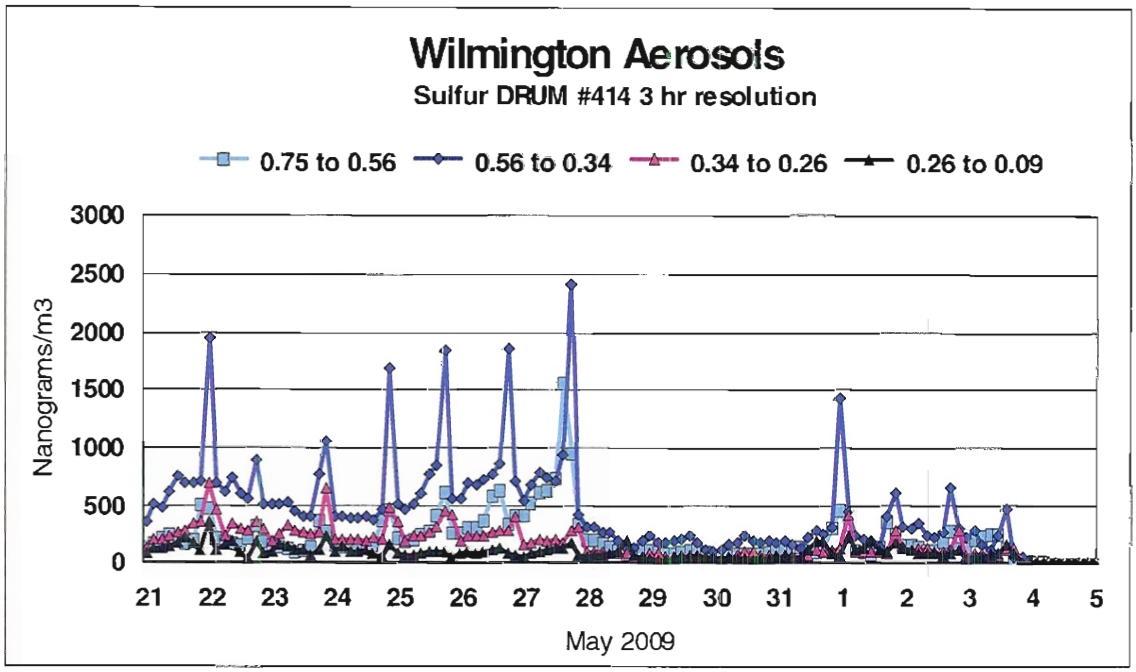


Figure 46 Sulfur at Fire Station 49 site

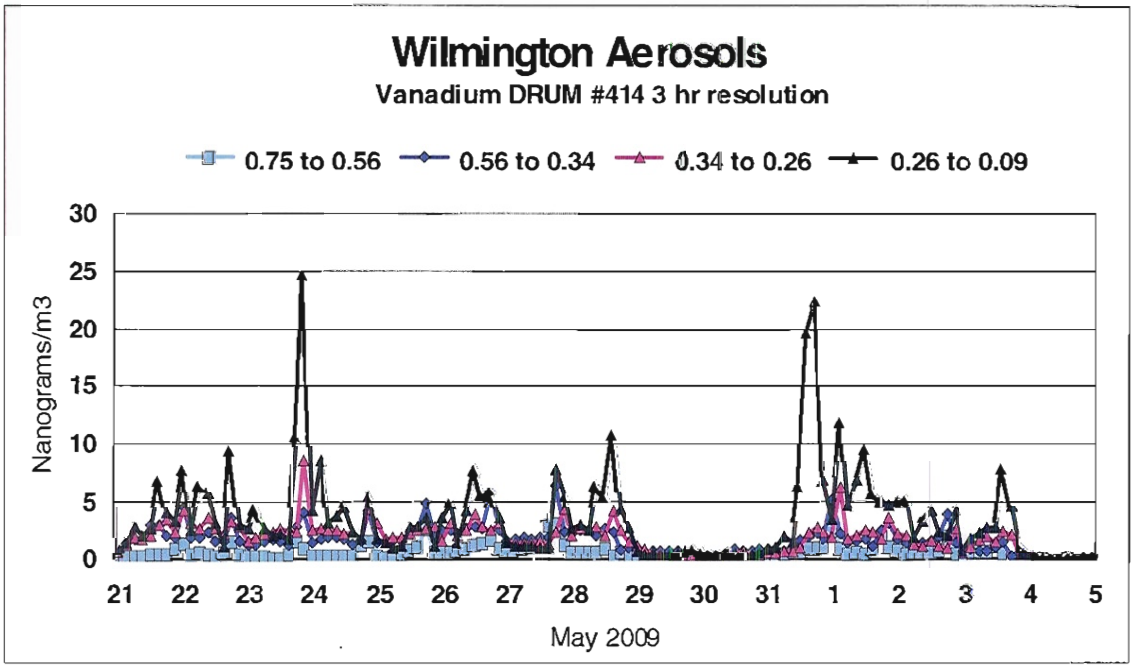


Figure 47 Vanadium at Fire Station 49 site

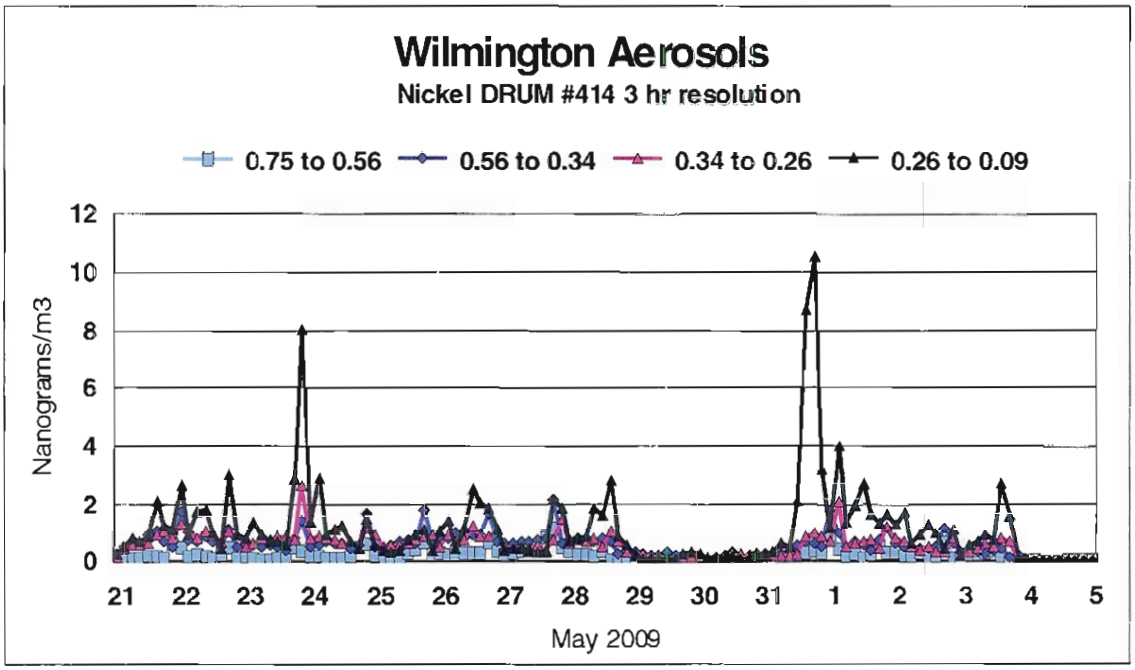


Figure 48 Nickel at Fire Station 49 site

The anomalous fine iron was still present, but the magnitude of the signal was sharply less than in 2008, by about a factor of 8 (compare to Figure 12, Final Report).

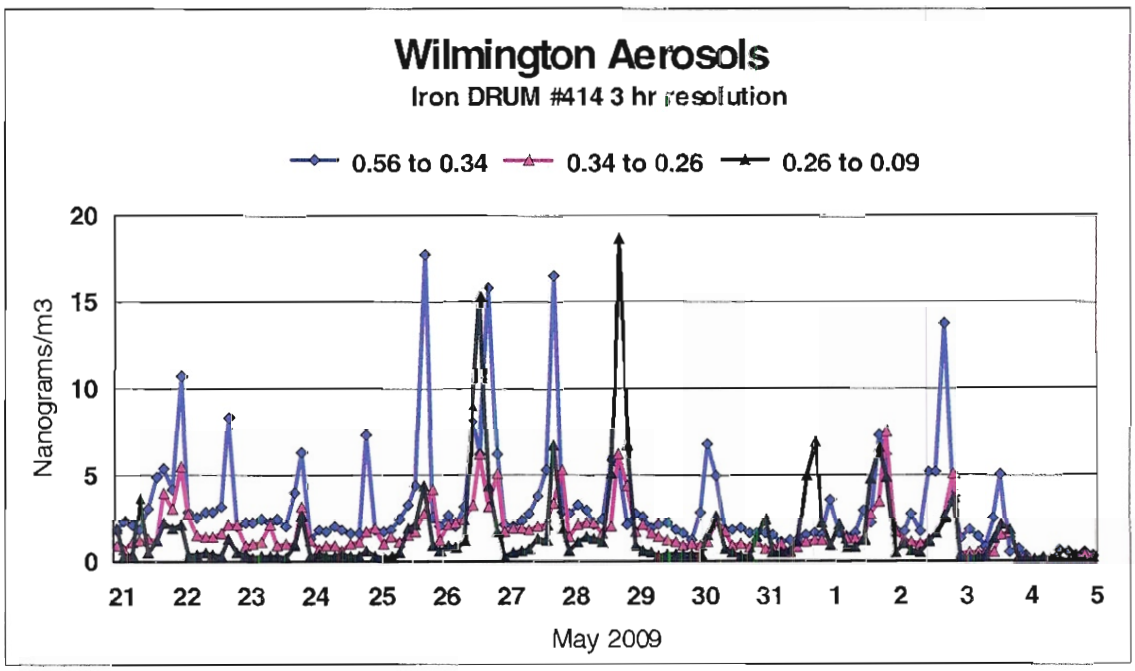


Figure 49 Iron at Fire Station 49 site

Likewise, lead levels were sharply reduced, again by roughly a factor of 8, although we still have to analyze the coarse fraction that included most of the lead in summer, 2008 (July, 2010 run).

Ultra fine measurements

Very little ultra fine iron was present except for one period of about 2 hrs, when it reached 200 ng/m^3. This period occurred at a time of visible shredder smoke emissions.

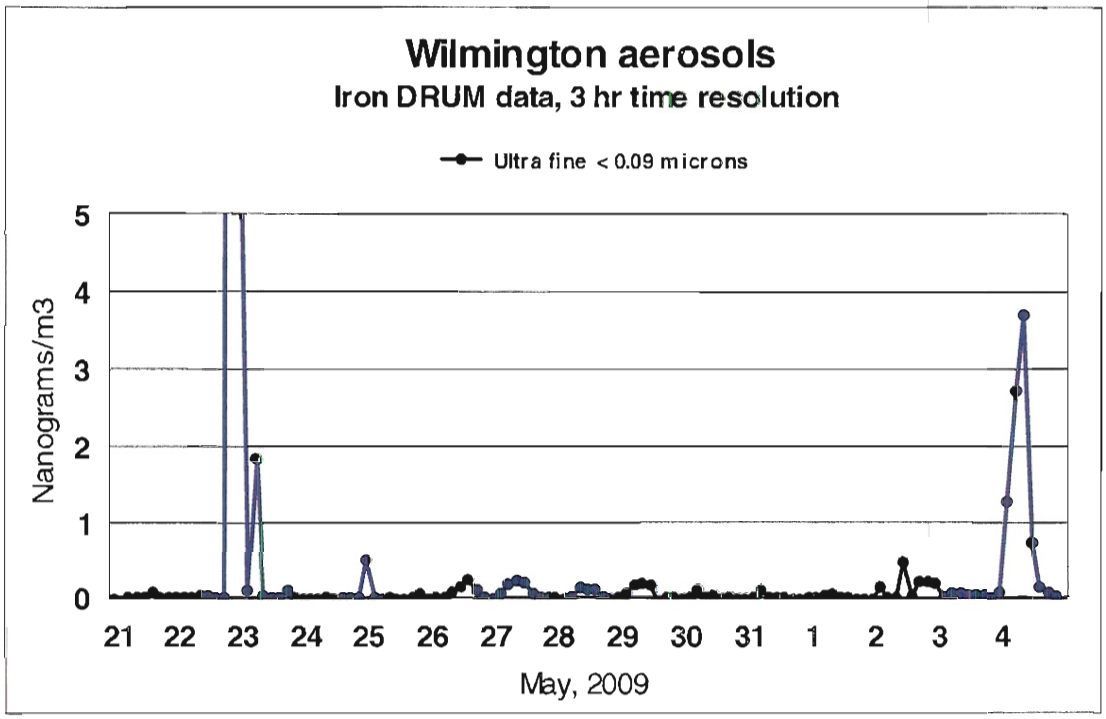


Figure 50 Ultra fine iron at Fire Station 49 site

High time resolution runs

In order to more closely identify wind directions, 2 DRUMS operated at higher rotation rates yielding samples with 1 hr. resolution. An example is shown below.

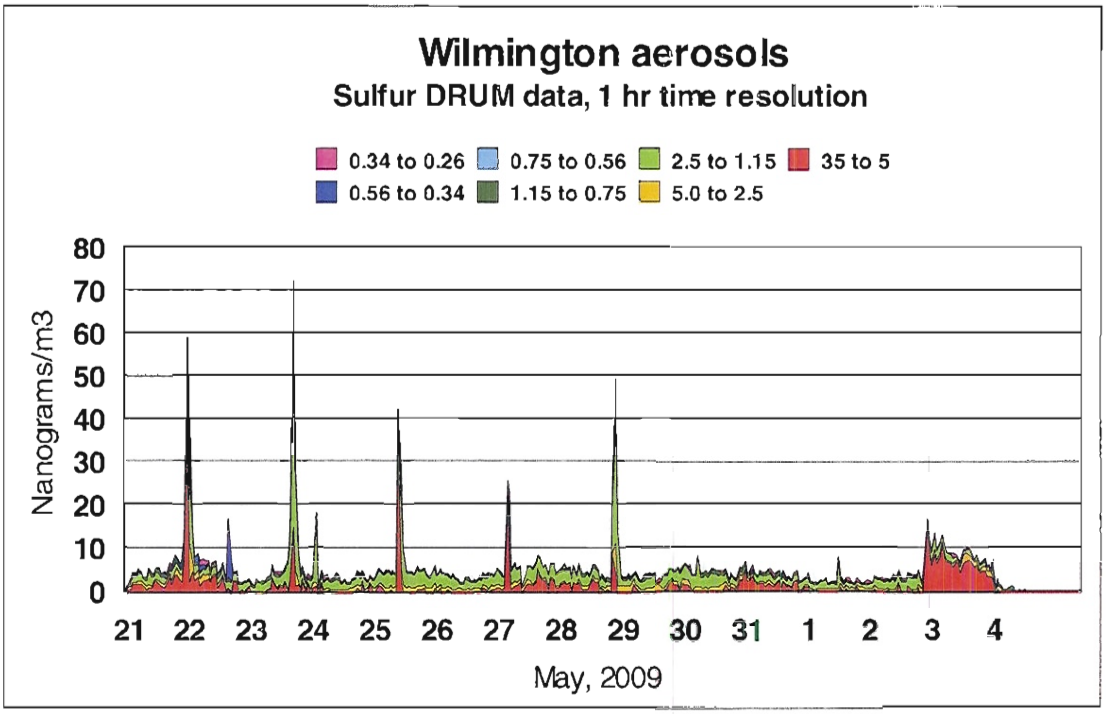


Figure 51 High time resolution sulfur at Fire Station 49 site

Ultra Coarse aerosols, 35 micron

The DRUM sampler was modified to measure particles as large as 35 µm in diameter, matching the upper cut point of the old TSP Hi-Vols. Such particles have a very rapid settling velocity and deposit locally near the source.

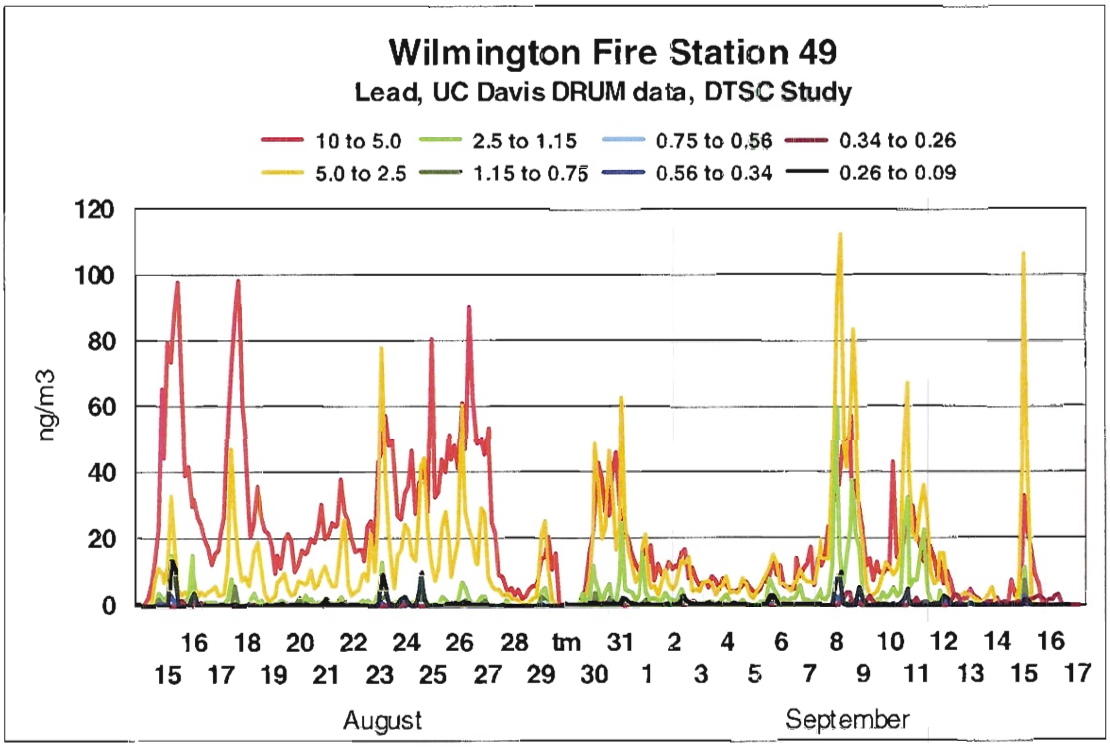


Figure 52 Lead at Fire Station 49 site, 2008

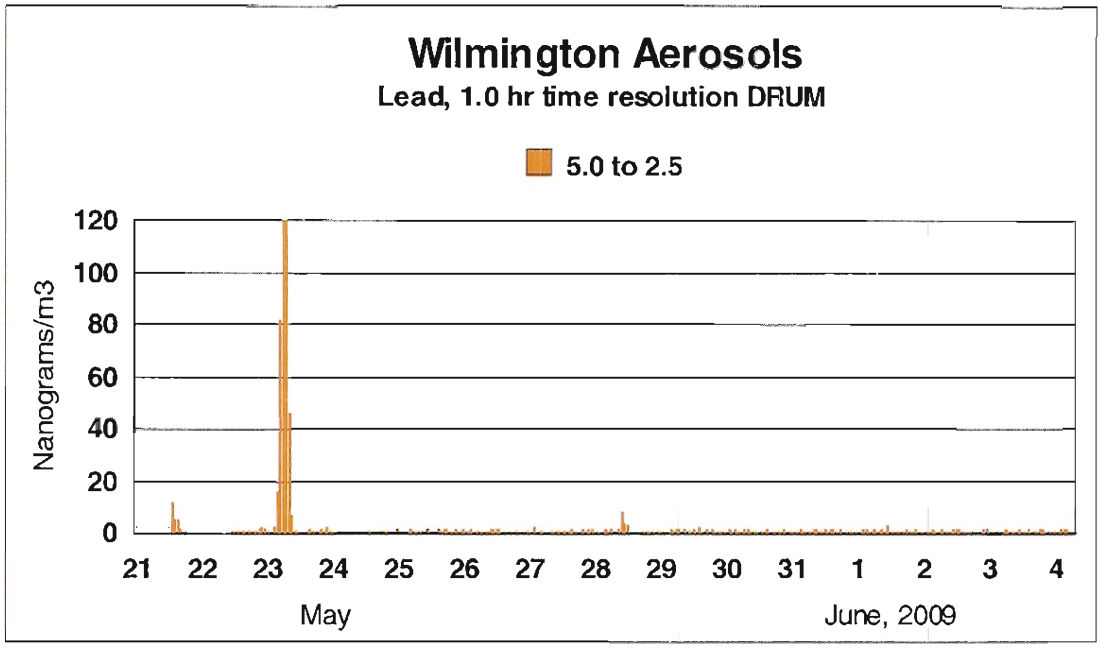


Figure 53 High time resolution lead at Fire Station 49 site, 2009

The pattern seen is very different than summer, 2008, with only a few episodes of lead emissions whereby previously lead was seen on almost all days.

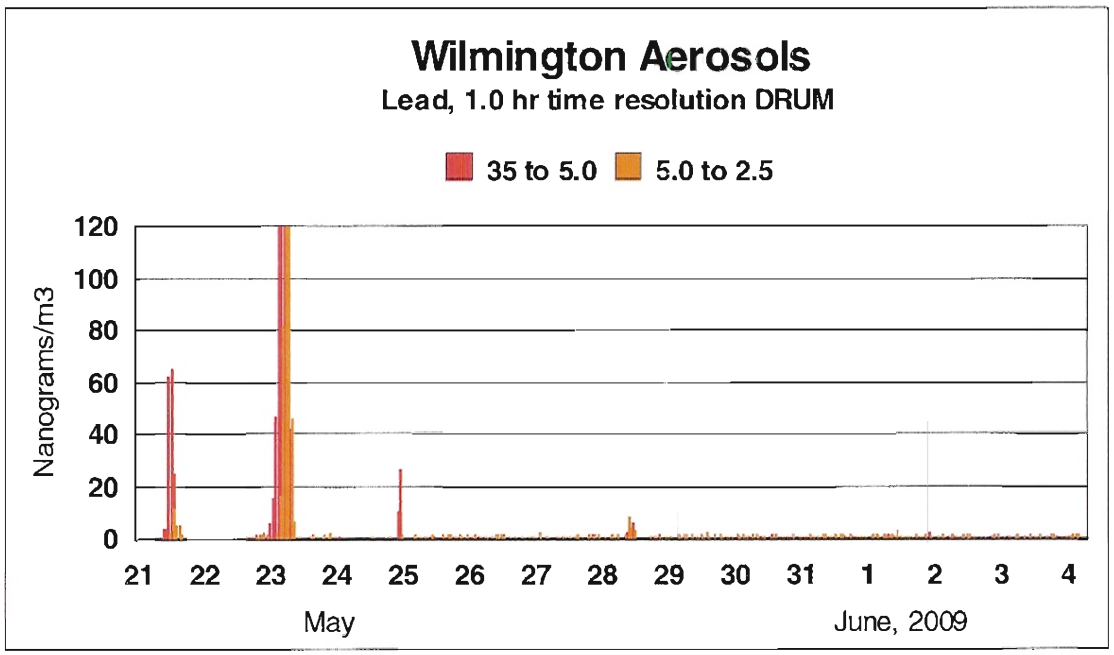


Figure 54 High time resolution coarse lead at Fire Station 49 site

If we add the new data to 35 μm, we see that a large fraction of the lead in the relatively few events occurs in the largest sizes. Thus, reliance on PM_{10} sampling will miss a good fraction of the total lead and especially underestimate the rate of deposition.

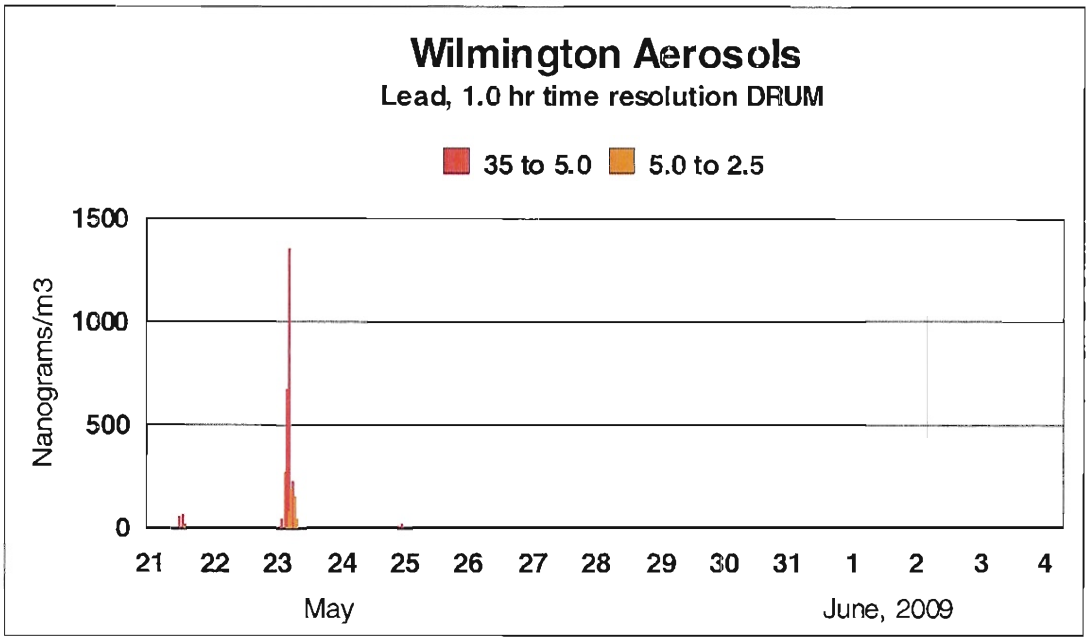


Figure 55 High time resolution coarse lead at Fire Station 49 site, larger scale

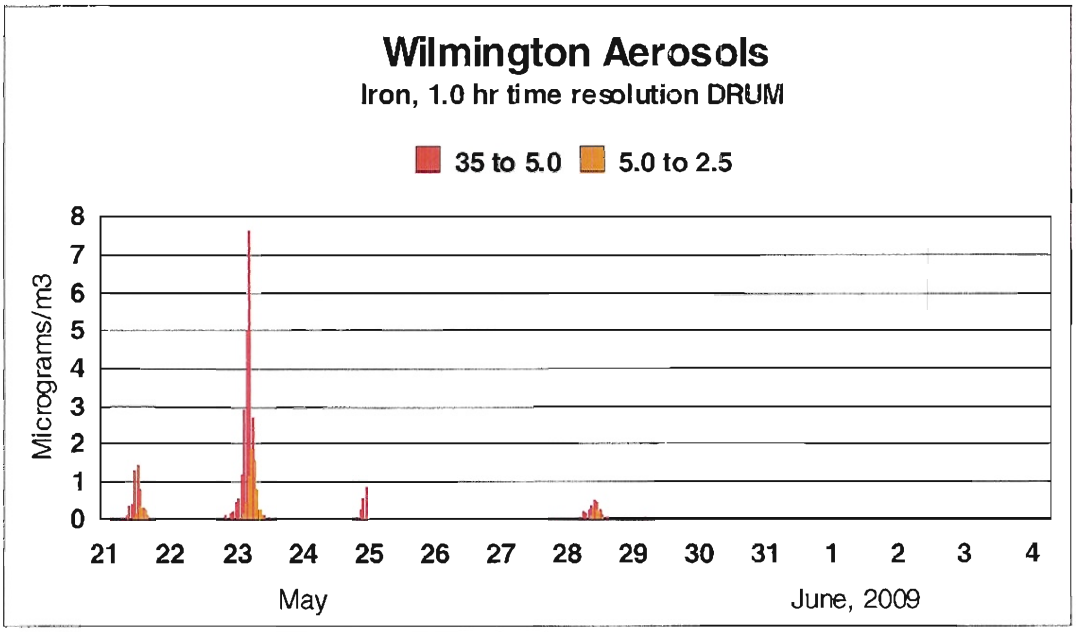


Figure 56 High time resolution coarse iron at Fire Station 49 site

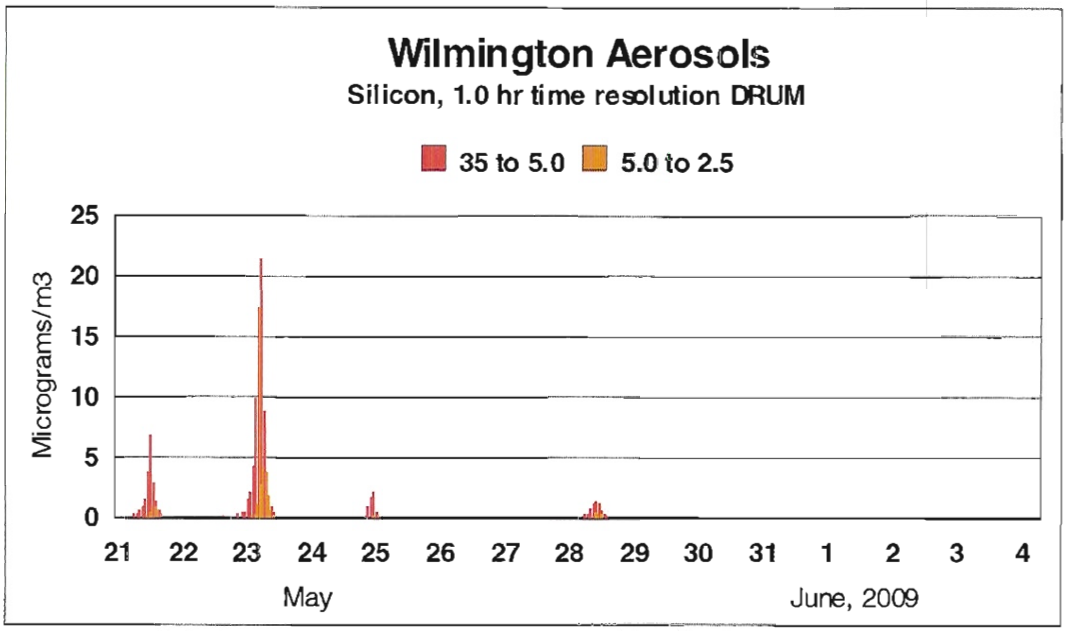


Figure 57 High time resolution coarse silicon at Fire Station 49 site

The iron to silicon ratio is approximately that of soil, so that a hypothesis can be made that the lead episodes are connected with resuspension of contaminated soil. A result supported by other trace metals.

Analysis of grab and deposition samples

Summary: The grab samples from the Los Angeles port study collected by Kristen, Dave, and Tom have now been analyzed by synchrotron-induced x-ray fluorescence (S-XRF) by Dr. Zhao, the x-ray spectra reduced by Prof. Perry, and the results reduced by Tom Cahill. There were technical problems on all three parts of the study, including heavily loaded samples, non-uniform deposits, and difficult to mount fluid extractions. The top AXIL spectra shows a saturated x-ray detector and the results are deleted. The bottom is a typical spectrum, Note the tight log scale.

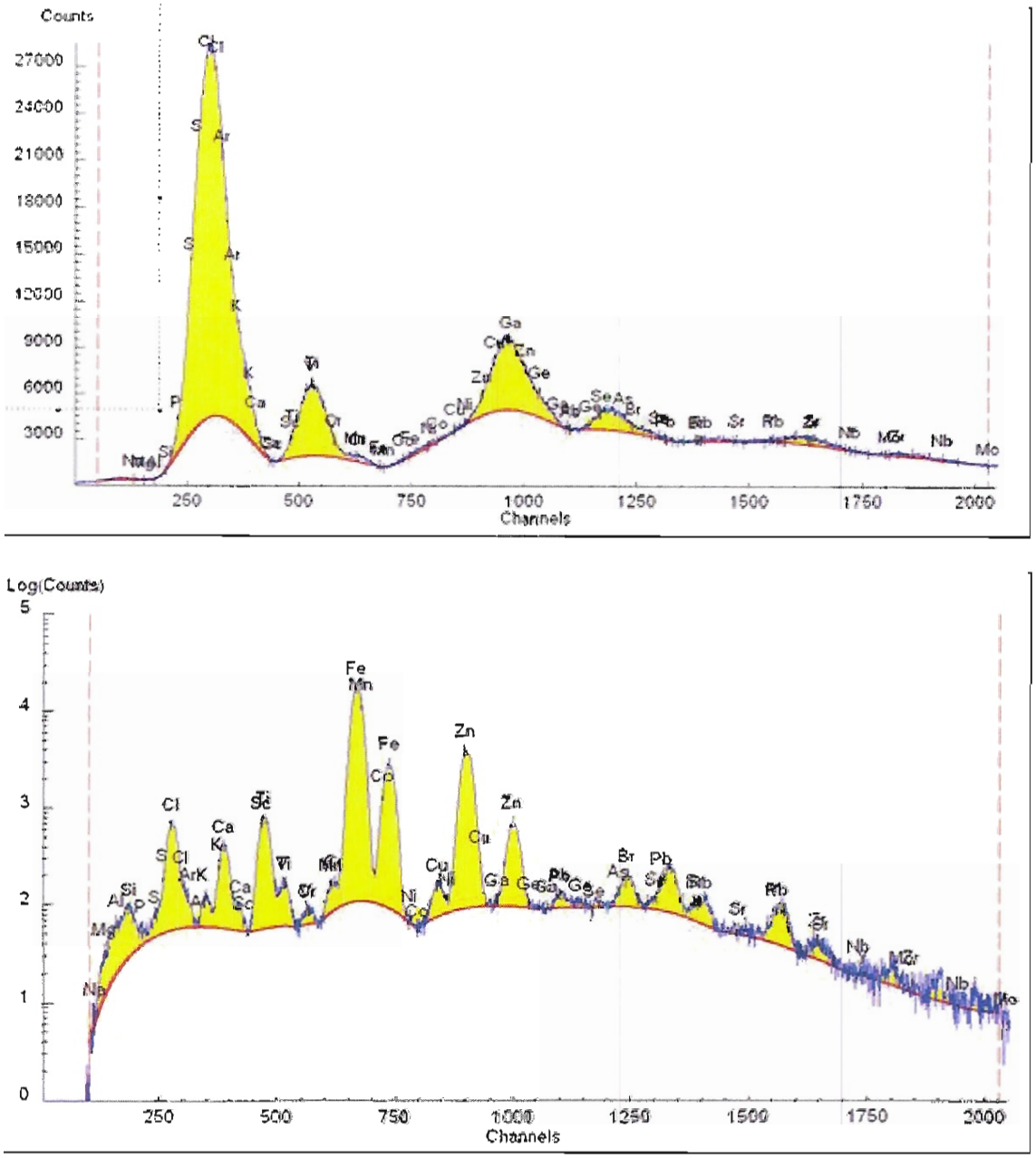


Figure 58 a,b Examples of S-XRF spectrum of grab samples

Field sampling

Samples were taken from the air pollution control filters at the site, collection foils left out face up for deposition, wipe samples from surfaces open to the sky, and water.

The samples include:

1. DTSC Jars – 6 samples
2. DTSC Tom's small filters – 4 samples

3. DTSC Wipes – 1 strip, 9 samples
4. DTSC Foils – 8 samples plus a field blank
5. DTSC Frames – 6 samples

The results support the aerosol ambient data and confirm the impact of the car/appliance shredder on the environment from samples at the plant and materials deposited in the downwind area, including DTSC regulated toxic elements lead and zinc.

Results

1. Aerosol deposition (est. without 10 to 35 μm mode)

These data are from summer, 2008. The largest 3 stages were weighted to roughly match deposition velocity, 2 x Stage 2, (2.5 to 5.0 μm), 4 x Stage 1 (5.0 to 10 μm). The May, 2009 data show that the 5.0 to 35 μm aerosols as typically 4 x the 2.15 to 2.5 μm aerosols.

Sample_ID	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr
	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
1.15 to 2.5	60.98	104.32	7.36	209.10	75.26	28.19	61.24	4.71	1.64	0.04
2.5 to 5.0	165.97	301.12	7.38	195.98	255.85	51.14	128.29	11.67	1.84	0.10
5.0 to 10	244.43	427.06	7.03	140.62	283.09	54.85	167.89	13.79	1.24	0.18
wtd	1371	2415	50	1164	1719	350	989	83.20	10.26	0.97
Ratio to soil 6339.92	21.6	38.1	0.8	18.4	27.1	5.5	15.6	1.3	0.2	0.0

	Mn	Fe	Ni	Cu	Zn	As	Se	Br	Sr	Pb
	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
1.15 to 2.5	0.77	73.97	0.39	1.59	3.31	-0.05	0.02	0.57	0.35	3.45
2.5 to 5.0	1.81	167.05	0.26	2.57	6.56	-0.03	-0.05	0.79	0.43	13.92
5.0 to 10	2.43	198.26	0.17	2.01	9.69	-0.01	-0.04	0.92	0.36	22.23
wtd	14.12	1201	1.57	14.76	55.21	-0.02	-0.05	5.84	2.66	120.2
Ratio to soil 6339.92	0.22	18.95	0.02	0.23	0.87	-0.00	-0.00	0.09	0.04	1.90

Table 5 Results of aerosol deposition foils, 2008

2. Samples collected at the shredder

a. DTSC frames

These samples were taken from an entire large metallic filter frame in plastic bagging.

1. Orange deposit from plastic bagging, inlet side
2. Black deposit from plastic bagging, inlet side
3. Smear from filter face
4. Smear from plastic bag 2

5. Cut fabric from SPUCO 2A
6. Fabric surface SPUCO 3A

Average	8054.5	4255.8	860.3	1189.3	2422.8	706.9	700.1	5631.7	90.9	302.0	
	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	
	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	
	7219.1	5826.4	78.6	6409.2	8324.9	276.7	672.1	1407.8	6544.1	5819.2	2946.3
	Mn	Fe	Ni	Cu	Zn	As	Se	Br	Sr	Zr	Pb
	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2

Table 6 Results of samples from the metallic frames of the TI shredder

These samples were wiped from the filter frame itself. As such, it represents particles as they would have been presented to the air pollution removal system.

b. JAR samples

The JAR samples represent materials collected at the shredder from the air pollution control filters. The samples were very oily.

1. ANUCO1 A filter pressed on sample, wet
2. Fibers from ANUCO1A
3. ANUCO3A sample is drier, filter pressed on sample
4. Fibers from sample ANUCO3A
5. ANUCO2A
6. Extracted from liquid ANUCO2A, fibrous

Average values are –

Average - 2 soil		Average - 1 soil		Average soil	
6531	ratios to soil	5784	ratios to soil	7937	ratios to soil
0.25	**Pb**	**0.46**	**Pb**	**0.33**	**Pb**
0.06	V	0.05	V	0.03	V
0.01	Mn	0.01	Mn	0.27	Mn
0.11	**Fe**	**0.49**	**Fe**	**0.45**	**Fe**
0.00	Ni	0.00	Ni	0.01	Ni
0.01	Cu	0.02	Cu	0.23	Cu
0.03	**Zn**	**0.90**	**Zn**	**0.66**	**Zn**

Table 7 Average values from the Jar samples from the TI shredder

Note that at this point (in the air pollution control system) there is relatively little soil present based on the lack of calcium. Also, note the other three largest non-soil constituent elements not shown are Phosphorus, Sulfur, and Chlorine, which in soils are roughly the same percentage as iron. The high levels of lead are seen in all samples; manganese, iron copper, and zinc are also enhanced based on ratios to the other typical soil elements as silicon.

c. Extracted small filters

These 4 samples were taken from the shredder filter and placed onto Teflon filters.

1. ANUC13A fabric filter, back side
2. ANUC13 A fabric filter middle
3. ANUC13A fabric filter front 1
4. ANUCi3A fabric filer front 2

Soil was the major component of the mass, and will act as above as the surrogate since the nature of the filters did not allow weighing for mass.

Soil 19.5 $\mu g/cm^2$

Pb	26.8 %
V	0.0 %
Mn	44.4 %
Fe	91.7 %
Ni	0.1 %
Cu	4.7 %
Zn	34.4 %

Thus, we are dealing with a soil dust from the shredder operations heavily contaminated with manganese, non-soil iron, zinc, and lead.

3. DTSC wipes

The wipes were samples taken from exposed surfaces that would not donate elements into the wipe (stainless steel, plastic, water ...). They were all located on the exposed up-facing surface and any with evidence of bird droppings were rejected. The assumption is that these surfaces would be washed by rain every winter, and thus represents recent deposition. The largest component was again soil, so it is used as the surrogate for mass. The major elements were typically soil, with the iron/soil ratio about correct for normal dirt. In addition to the elements shown were chlorine and potassium as major constituents, with relatively little manganese.

Figure 59 Location of wiped samples

Sample #	Iron %	Lead %	Zinc %	Chromium %
9 – water scum in Marina	23.4	0.15	26.2	0.24
6 – boat	20.6	0.61	1.32	1.23
7 – boat	24.6	0.78	0.70	1.89
8 - boat	8.3	0.51	4.40	0.49
1 FS 49	17.9	0.92	0.97	0.20
4 Com. center	12.1	0.24	0.24	0.36
5 Marina	17.1	0.36	0.80	0.42
2 E St site	**14.1**	**0.31**	**0.61**	**0.09**
3 E St school	**12.8**	**0.25**	**0.67**	**1.47**

Table 8 Results of the surface depositions from samples wiped onto Teflon filters from the Marina to Wilmington

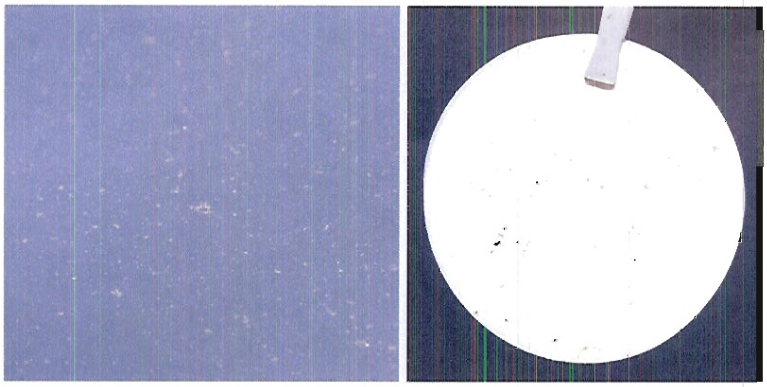


Figure 60 a,b Water surface and wipe sample # 9 taken from the water in the Wilmington marina

The behavior of the wipe samples shows a progression from high levels for lead and zinc at or near the port, and a fall off by about a factor of 2 as one moves deeper into the community (sites in bold). Other species such as iron show no such variation. All samples were above 1,000 ppm for lead and 5,000 ppm for zinc. The E Street School site wipe was taken at the boundary fence of a pre-school play ground.

4. DTSC Deposition Foils

The foils were open faced filters used as deposition monitors. As such, they collected all depositing particles, including soil. The foils were measured precisely, and were very similar to the Field Blank. Average values are given below.

Average	412.17	127.97	18.48	37.10	32.40	9.37	37.39	124.96	5.76	10.41	
Field Bl	328.96	49.45	20.07	32.40	26.47	0.82	2.00	52.96	1.70	13.61	
	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	
	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	
Average	5.02	171.84	1.84	15.87	13.60	2.16	4.80	144.01	14.85	24.08	12.74
Field Bl	0.00	9.26	2.04	17.41	6.10	1.48	1.47	143.74	8.67	17.72	11.03
	Mn	Fe	Ni	Cu	Zn	As	Se	Br	Sr	Zr	Pb
	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2	ng/cm^2

Table 9 Results of DTSC deposition foils

The deposition samples show clear input of non-soil iron, plus titanium vanadium, manganese, and zinc, along with a modest increase in lead. The method shows promise, but samples must be left out longer and protected against losing the foil to wind.

The detailed analysis sample by sample is proceeding with the input of location. The status of samples at the time of substrate collection from field were:

1.	A	No
2.	B	Petri empty
3.	C	Good
4.	D	Good
5.	E	Good
6.	Field blank	
7.	G	Petri empty
8.	H	Petri empty
9.	I	Good
10.	J	Visible deposit
11.	K	Good

Part 3: Comparison, August, 2008 to May, 2009

Comparisons between August – September, 2008 and May – June 2009 must take into account changes in the activity levels at the Port of Los Angeles, activities at the shredder, and changes in meteorology. Port activities can be evaluated by changes in the pollution from ocean going ships, tracked by the very fine sulfur, vanadium, and nickel pollution from the combustion of heavy bunker fuel oil. Meteorology should be similar, since the summer pattern of on shore winds is well established by May.

Activities at the shredder were directly evaluated in Spring, 2009, by video of shredder activities hourly, day and night, no similar data or record is available in Summer 2008. In addition, characteristic effluents of the shredder operations, especially the almost unique very fine iron signatures, plus lead, zinc, and other species, can be directly compared with identical air sampling instrumentation and mass/elemental analysis at the Fire Station #49 site in Wilmington.

Port activity evaluated by ship pollution was reduced in May, 2009, with the three key species all reduced: vanadium, 64% of 2008, nickel, 79% of 2008, and sulfur, which has both diesel and ship sources, 31% of 2008.

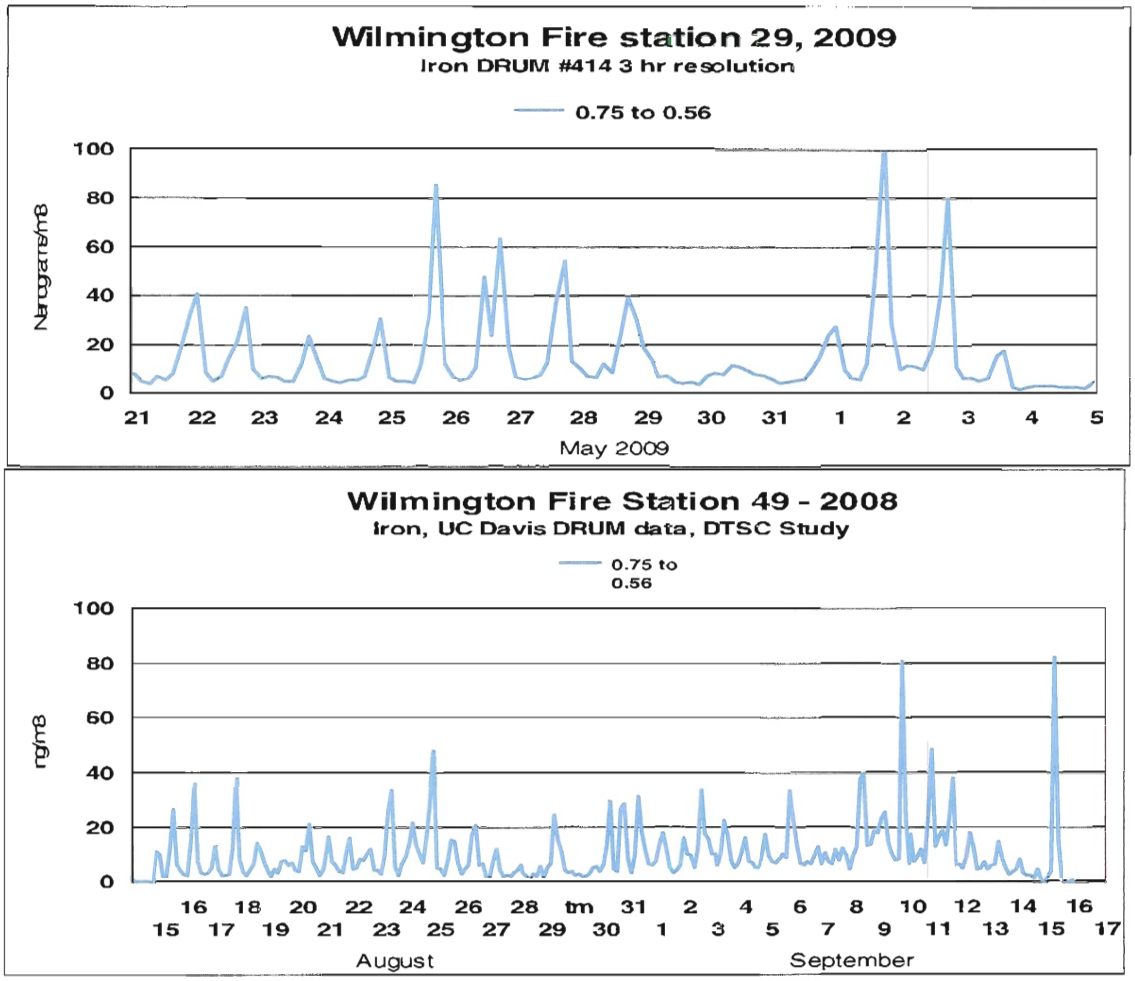
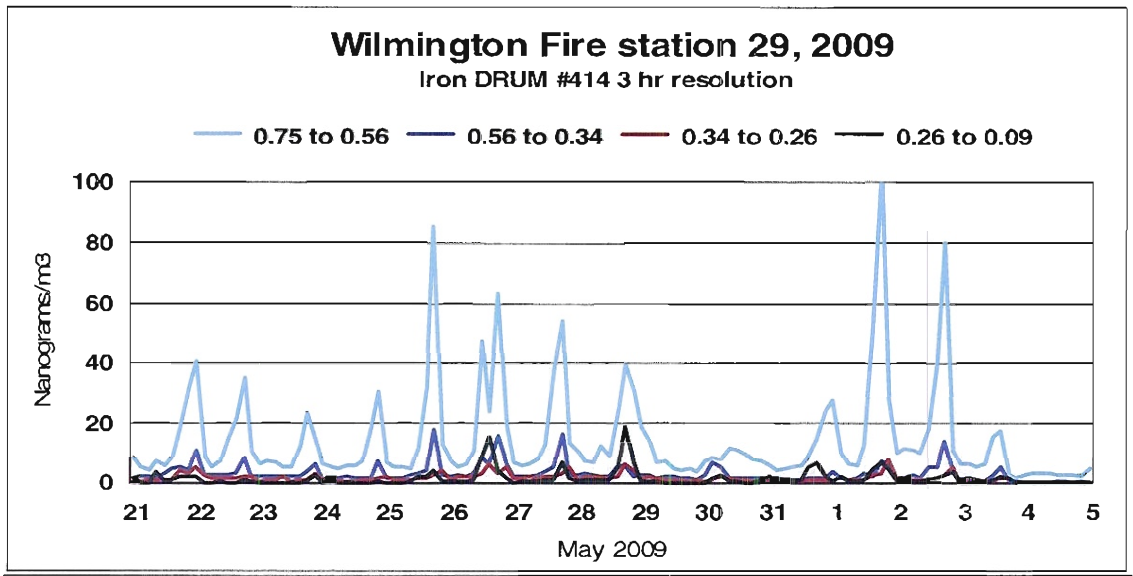


Figure 61 Fine iron, which in this size mode is from industrial or vehicular sources, and not a soil component.

Looking at characteristic shredder effluents, we can compare the coarser components of iron, from roadway activities and other sources, 2008 versus 2009. Thus the average coarse soil components, marked by elements silicon and aluminum, were about the same, 2008 versus 2009, 1.03 ± 0.23. These species in this size mode are often associated with soil ground fine by traffic and then resuspended. This is also roughly true for iron, which is 63% greater in 2008 than 2009.

However, when examining the very fine iron, that pattern is dramatically different.



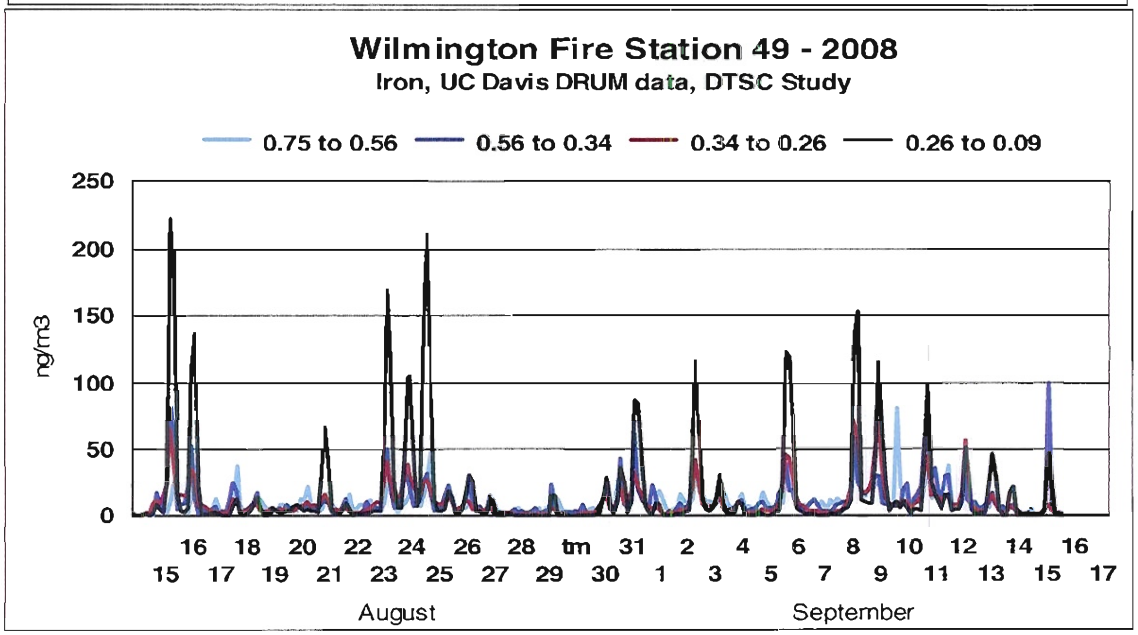


Figure 62 Fine and very fine iron, 2008 versus 2009. Note the scale change.

Fine iron values in 2009 are only 30% (0.56 to 0.34), 15% (0.34 to 0.26) and 9 % (0.26 to 0.09 µm diameter), of the 2008 values. While some of this change may be due to the operational work level at the shredder, 2008 versus 2009, the best explanation of this difference is greatly enhanced efficiency in pollution control at the shredder.

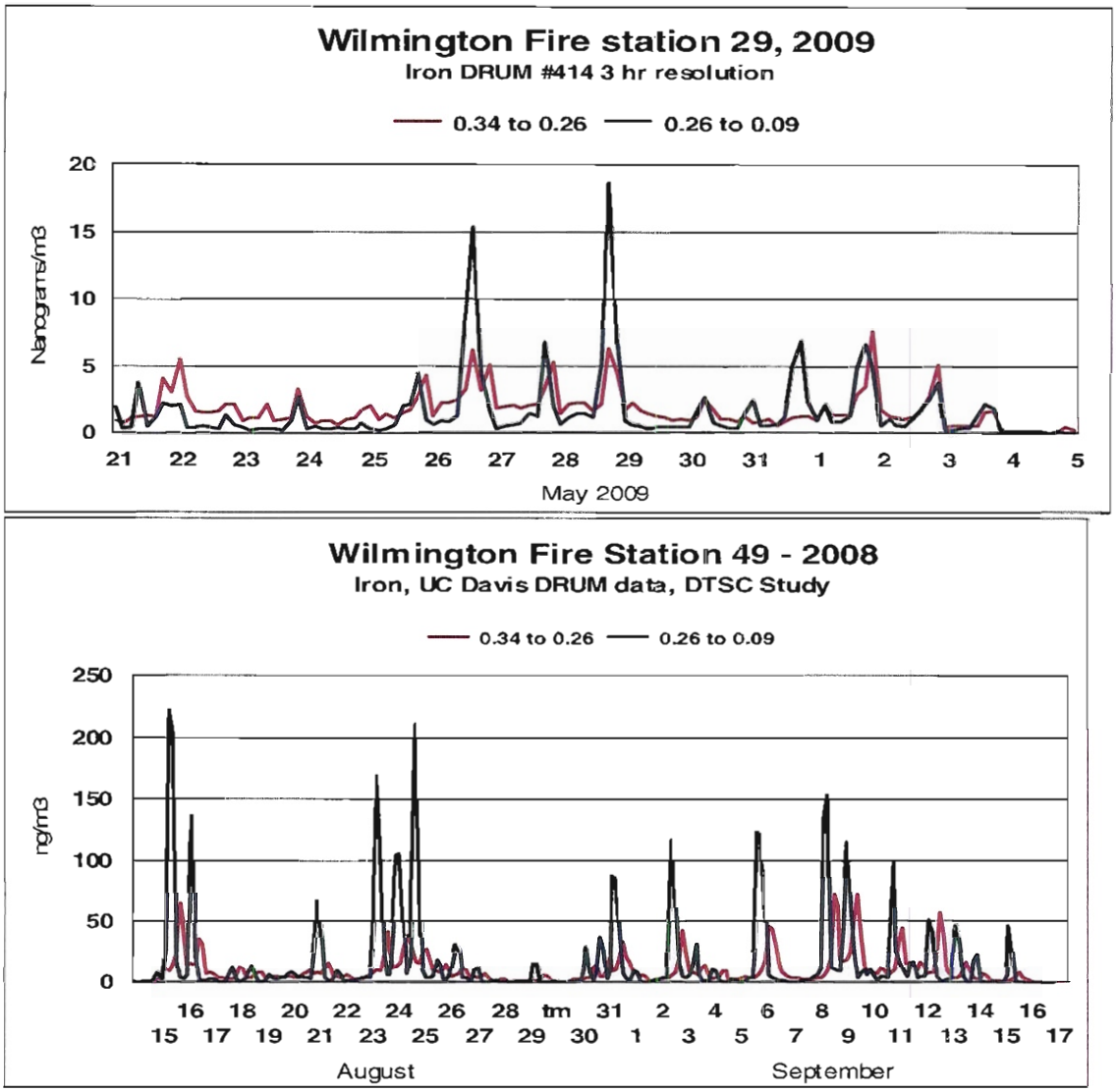


Figure 63 Fine and very fine iron at Wilmington Fire Station 49, 2008 versus 2009

However, anomalously fine soil-like aerosols, silicon and iron, continue to be seen from the direction of the Terminal Island shredder. Normally, very little soil is generated by natural processes in the sub-micron size range, so an industrial or transportation-derived source is indicated.

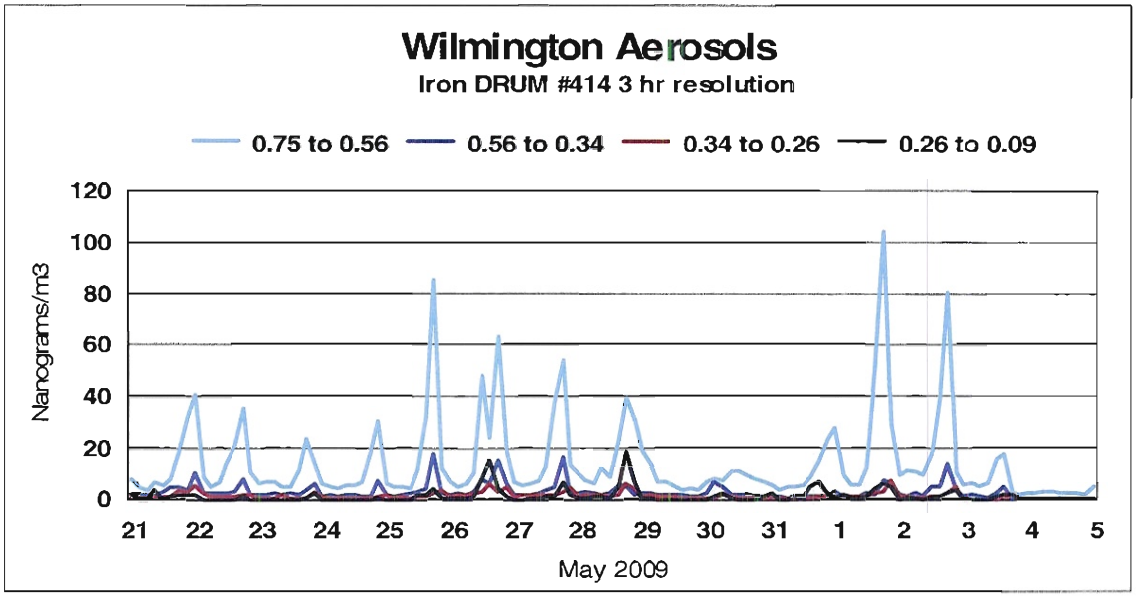


Figure 64 Sub micron iron, May, 2009

The very fine iron peaks in Spring, 2009, almost all occur in the period from about noon to 2 AM when meteorology is favorable for transport into Wilmington. Further, the major very fine modes correlate with specific activities at the shredder, notably the presence of visible smoke.

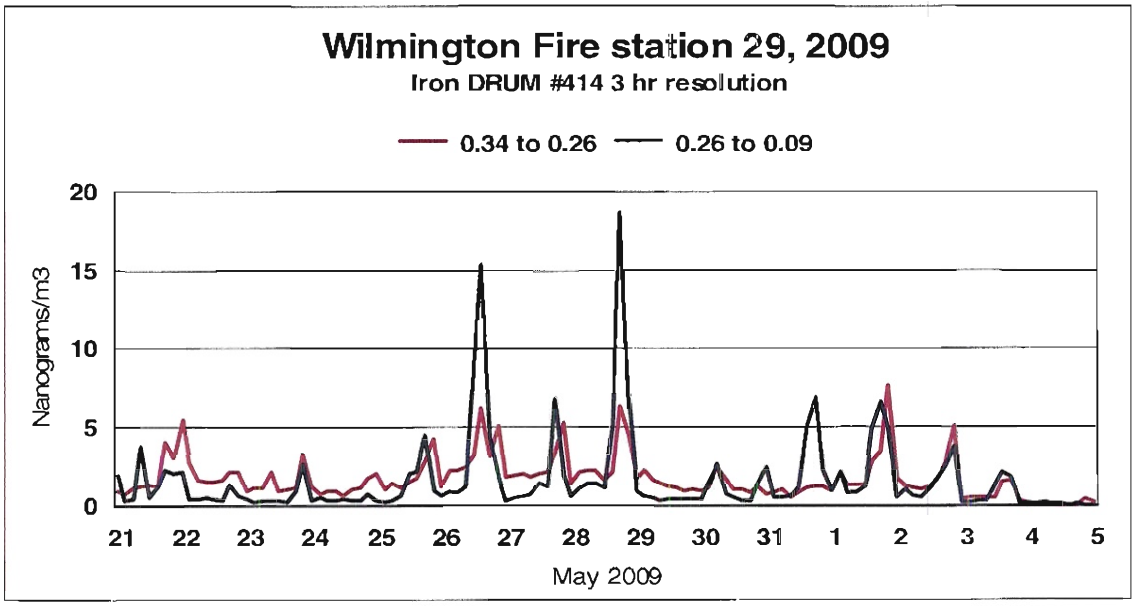


Figure 65 Very fine iron, May, 2009

Specifically, May 22, 26 and 28 all recorded visible smoke from shredder operations, while on May 28, a ship docked at the site, with heavy equipment working on site. Likewise, activity and visible smoke were seen on May 1 and 2.

With the confirmation of shredder activities, and the small amount of ultra fine iron seen, only 9% of August, 2008 values, we have confirmation that the much lower levels in spring, 2009, are a reflection of important improvements in the pollution control systems at the Terminal Island shredder.

Other elements of concern show reductions, too. The very fine component of lead, representing prompt emissions, was reduced to only 40% of the 2008 value, and zinc was slightly reduced in the very fine modes, reduced to roughly 80% of the 2008 values.

On the other hand, the coarser component of lead was slightly greater than 2008, increased by 23%, and the coarser components of zinc, were, like lead, also increased, by 46%.

The interpretation of the aerosol data indicate that the prompt emissions of very fine lead and iron were greatly reduced in 2009, by a factor of 3 to 10, but that coarse modes were essentially unchanged. Coarse iron, lead, and zinc can be associated with mechanical processes and soil, mechanical operations, and fugitive dust from piles.

This conclusion is supported by the continuing presence of iron, zinc, and lead in deposition samples and wipes taken in the city of Wilmington, showing a reduction of these materials as one moves away from the Terminal island shredder in a downwind direction.

Acknowledgements

The authors gratefully acknowledge the personnel of Fire Station #49 for access and support of these activities, The DELTA Group wished to recognize Dr. Yongjing Zhao, Prof, Steve Cliff, and Prof Kevin Perry (U. Utah) for the S-XRF analysis.

References

Seinfeld, J.H, and Pandis, S.N., Atmospheric Chemistry and Physics, Wiley Interscience (1998)

DELTA Group references on DRUM sampling and analyses – see complete list in Appendix D.

Appendix A

Terminal Island Annual Emission Summary - Stationary Sources Based on Throughput at Equipment

Pollutant	Source	Annual Throughput (Tons/Year)	Annual Emissions (Tons/Year)
PM10	Shredder	734,570	3.78
	Non-Ferrous (including CKD & R2)	189,017 23,470	1.06
	Shear	135,604	1.00
	Shiploading	1,129,470	0.02
	Stockpiling	1,864,040	0.03
	Storage Piles (acres of piles)	5	1.09
	Combustion Processes	Gas, Diesel & Nat Gas	0.00
	Mobile Equipment (gals/yr)	0	0.00
		PM10 Total:	**6.98**
ROG	Diesel Tank (gals/yr)	717,800	0.1
	Gasoline Tank (gals/yr)	11,768	0.01
	Pressure Washer (gals/yr)	74	0.00
	Emergency Generator (gals/yr)	90	0.00
	Hot Water Heater (mmscf)	0.072	0.00
	Facilities Maint. (painting, gals/yr)	129	0.14
	Mobile Equipment (gals/yr)	0	0.00
		ROG Total:	**0.21**
NOx	Pressure Washer (gals/yr)	74	0.001
	Emergency Generator (gals/yr)	90	0.021
	Hot Water Heater (mmscf)	0.072	0.005
	Mobile Equipment (gals/yr)	0	0.00
		NOx Total:	**0.03**
CO	Pressure Washer (gals/yr)	74	0.000
	Emergency Generator (gals/yr)	90	0.005
	Hot Water Heater (mmscf)	0.072	0.001
	Mobile Equipment (gals/yr)	0	0.00
		CO Total:	**0.01**

Basis:

1 - Uncontrolled PM10 Emission Factors from AP-42 Table 11.19.2-2

2 - Water Provides Minimum of 80% Dust Control

3 - Annual Throughput Based on 2006 AER

AB2588 Toxics Analysis

Basis:

1 - See Toxics Calculations Worksheet for Discussion

Compound	Ratio to Total PM10	Source	Annual Emissions (lbs/yr)	Rule 1401 Screen at 100 Meters (lbs/yr)
Cadmium	0.000084	Shredder	0.63	
		Non-Ferrous Separator	0.18	
		Shear	0.17	
		Shiploading	0.00	
		Stockpiling	0.00	
		Storage Piles	0.18	
		Generator	0.00	
		Pressure Washer	0.00	
		Mobile Equipment	0.00	
		Cadmium Total:	**1.17**	0.06
Copper Non-cancer	0.001736	Shredder	13.12	
		Non-Ferrous Separator	3.69	
		Shear	3.46	
		Shiploading	0.06	
		Stockpiling	0.10	
		Storage Piles	3.79	
		Copper Total:	**24.22**	7,200
Lead	0.009062	Shredder	68.51	
		Non-Ferrous Separator	19.25	
		Shear	18.04	
		Shiploading	0.33	
		Stockpiling	0.54	
		Storage Piles	19.80	
		Generator	0.00	
		Pressure Washer	0.00	
		Mobile Equipment	0.00	
		Lead Total:	**126.47**	5.07
Mercury	0.000029	Shredder	0.22	
		Non-Ferrous Separator	0.06	
		Shear	0.06	
		Shiploading	0.00	
		Stockpiling	0.00	
		Storage Piles	0.06	
		Mercury Total:	**0.40**	2.31

Nickel	0.000336	Shredder	2.54	
		Non-Ferrous Separator	0.71	
		Shear	0.67	
		Shiploading	0.01	
		Stockpiling	0.02	
		Storage Piles	0.73	
		Generator	0.00	
		Pressure Washer	0.00	
		Mobile Equipment	0.00	
		Nickel Total:	**4.69**	0.98
Benzene		Mobile Equipment	0.00	
		Generator	0.02	
		Pressure Washer	0.00	
		Benzene Total:	**0.02**	8.92
1,3-Butadiene		Mobile Equipment	0.00	
		Generator	0.02	
		Pressure Washer	0.00	
		1,3 Butadiene Total:	**0.02**	1.4
Formaldehyde		Mobile Equipment	0.00	
		Generator	0.16	
		Pressure Washer	0.03	
		Formaldehyde Total:	**0.18**	42.5
Hexavalent Chromium		Mobile Equipment	0.00	
		Generator	0.00	
		Pressure Washer	0.00	
		Hex Chromium Total:	**0.00**	0.00175
Arsenic		Mobiel Equipment	0.00	
		Generator	0.00	
		Pressure Washer	0.00	
		Arsenic Total:	**0.00**	0.0155
PAHs		Mobile Equipment	0.00	
		Generator	0.01	
		Pressure Washer	0.00	
		PAHs Total:	**0.01**	0.00769
Ammonia		Mobile Equipment	0.00	
		Generator	0.26	
		Pressure Washer	0.21	
		Ammonia Total:	**0.48**	51,700

Appendix B

Responses to SCAQMD letter of May 28, 2009

Tom Cahill, DELTA Group tacahill@ucdavis.edu

DTSC is pleased to respond to the specific requests for additional information, since we realize that while deposition onto surfaces is DTSC's responsibility, contaminants in the air are the purview of SCAQMD. We hope that by sharing these data, both agencies will benefit.

In terms of specific questions:

1. The data have been profiled into units of ng/m^3 and a CD written to provide this information in Excel spread sheets. These data are accompanied by the quality assurance report, DRUM Quality Assurance Protocols ver. 1/09, which explains the inherent differences between filter based aerosol data and continuous size and time resolved data.
2. and 3. These data are included in the discussion of the weather data, request #3, and are being provided on the same CD.
4. All data were plotted.
5. In a study just completed, (May, 2009), we utilized the continuous quasi-TSP DRUM sampler, developed by the UC Davis DELTA Group for road sanding work for CalTrans at Lake Tahoe, at Fire Station # 49 in Wilmington. These additional data should be available by early fall. A standard DRUM was used in central Wilmington at the same time.

I must mention that the Davis scientists are disturbed by what appears to be the presence of FeO from the shredder in very fine particles, < 0.26 μm, as this compound has serious impact on lung tissue via the Fenton reaction and free radical generation. These are by far the highest levels they have ever seen in ambient conditions.

Please feel free to contact me for further information.

Additional information, Dec. 12, 2009

The thrust of DTSC is not ambient aerosols but deposition of toxics onto surfaces, including children's play structures and other surfaces that have easy hand to mouth transfer potential.

Thus, in the Final Report, we calculated fractional toxic concentrations of aerosols by taking the concentration of toxics in ng/m^3, obtained by S-XRF analysis, and dividing by the total mass of aerosols in that size regime, obtained by soft beta ray transmission, also in ng/m^3. The latter measurement was key to the excellent agreement we achieved in side by side tests with RB FRMs at 13th and T Street, as calculated by the ARB and exhibited in the figure (page 2).

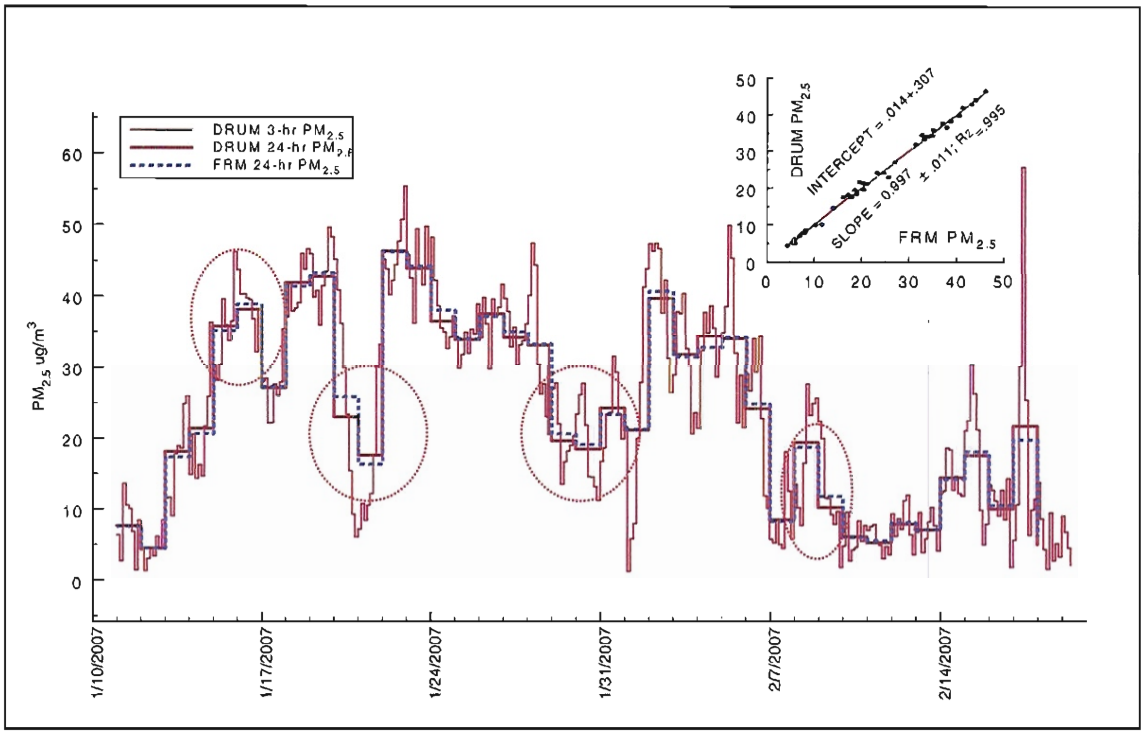
Once calculated, we can obtain the amount deposited to the surface per hour, or 8 hr business day, by settling velocities for coarse particles and removal rate by diffusion for fine particles, using the relationships of Seinfeld and Pandis. Assumptions must be

made for particle density. This was the reason we extended the size regime up to 35 μm for the DRUM since the settling velocities are so high in this range.
Table 1 S-XRF comparison, all blind tests since 1999

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**	**0.984**	**0.15**	**0.977**	**0.115**

The S-XRF system has been tested in blind inter-comparisons since 1999, and all of these are shown above. Typically 32 elements are recorded for each analysis, all of which can be traced back to NIST primary (SRM # 1832, SRM # 1833) or secondary (Micromatter thin film) standards. Over 500,000 S-XRF analyses have been done by the DELTA Group since completion of the system in 1999.

Figure 1 Report of the staff, ARB Research Division, on the 2007 full year inter-comparison, DELTA Group 8 DRUM and standard FRM. Note that it takes 49 individual soft beta mass measurements for the DRUM to match a single 24 hr FRM mass.


DRUM 3-hr PM2.5
DRUM 24-hr PM2.5
FRM 24-hr PM2.5
PM2.5 ug/m3
0
10
20
30
40
50
60
1/10/2007
1/17/2007
1/24/2007
1/31/2007
2/7/2007
2/14/2007
DRUM PM2.5
FRM PM2.5
INTERCEPT = .014+-.307
SLOPE = 0.997 +- .011; R2 = .995
0
10
20
30
40
50

Appendix C

Short summary from **DRUM Quality Assurance Protocols**

DELTA* Group DRUM samplers
Original Version 8/02. (DQAP 8/02)
Current version January, 2009 (DQAP 1/09)

Tom Cahill and DELTA* Group staff

Dr. Steve S. Cliff, Prof. Kevin D. Perry (Meteorology, U. Utah), Dr. David E. Barnes, Lee Portnoff (DRUMAir)

*Detection and Evaluation of Long-range Transport of Aerosols

Newest information

Three new studies have enhanced our understanding of continuous sampling by size, time, and composition with DRUM impactors:

1. Final report to the California Air Resources Board, **Comparison of Fine Mass, UC Davis DRUM versus FRM, at the ARB 13th and T Street Site**, Thomas A. Cahill and David E. Barnes, UC Davis DELTA Group, and the Breathe California of Sacramento/Emigrant Trails Health Effects Task Force, April 25, 2009

2. Final Report, **Drum Sampler Demonstration of PM Mass and XRF Elements** Final Report to the US EPA ORD, , March 14, 2009, Thomas A. Cahill, David E. Barnes and Jonathan Lawton, University of California, Davis, with Thomas M. Cahill, Arizona State University, May, 2009,

and a third that emphasized the size resolved DRUM organics (including ultrafine) with comparison to DRUM S-XRF and mass (including ultrafine),

3. Organic and Elemental Aerosols near Watt Avenue, Late Winter – Spring, 2007, Draft prepared for The Health Effects Task Force, Breathe California of Sacramento-Emigrants Trails and the Sacramento Metropolitan Air Quality Management District, June 26, 2009.

The first two are available electronically from BC/SET and the UC Davis DELTA Group.

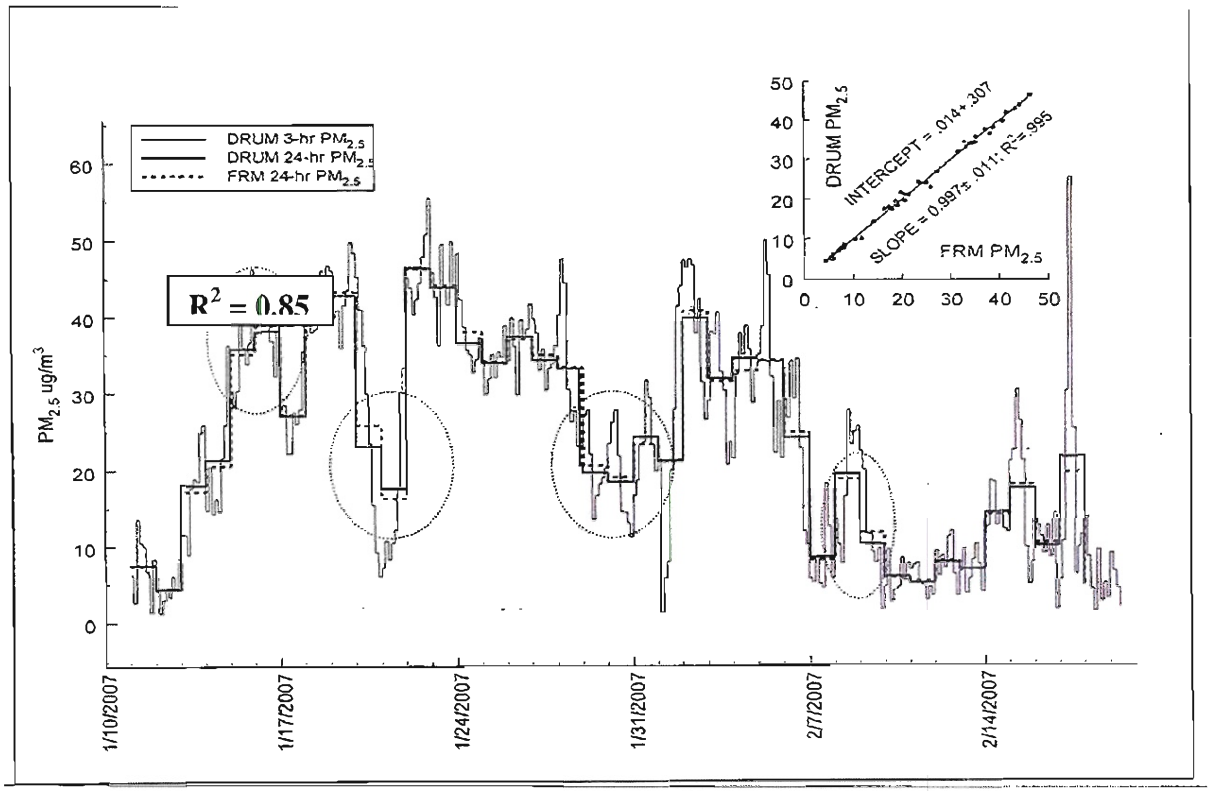
1 New data on DRUM to FRM mass comparisons from the ARB comparisons.

A side by side comparison is made between a DELTA Group 8 DRUM with integrating afterfilter and ARB FRM $PM_{2.5}$ 24 hr filters for 6 months in 2007. The mass was measured by soft beta ray transmission, so the test involved both the accuracy and precision of the DRUM sampler and soft beta ray mass analysis.

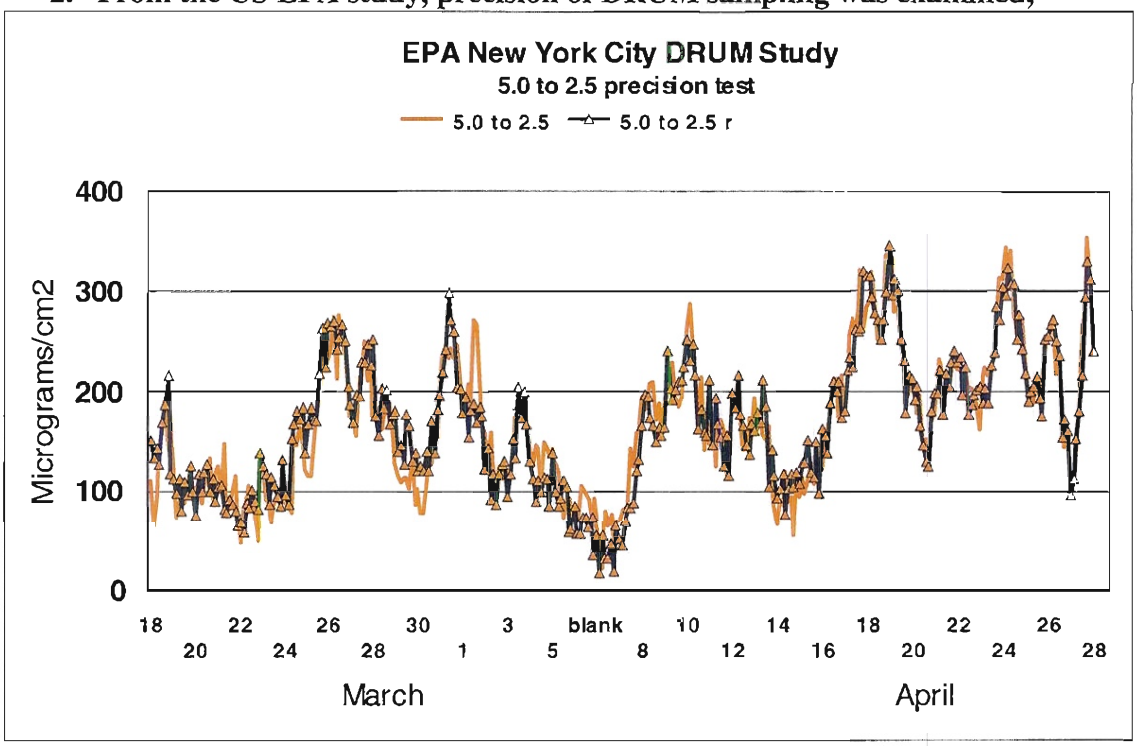
In summary, for Period I, January 12 – February 20, 2007, good agreement between ARB 24 hr filters and the sum of 49 individual DRUM stages and ultra fine after filter, 23.2 ± 1.0 μg/m^3 DRUM, 22.1 μg/m^3 ARB. For the entire 6 months, the ratio, DRUM/FRM, was 1.01 ± 0.21, with the uncertainty dominated by the need to take 49 individual DRUM mass measurements to equal one 24 hr filter.

The data were transmitted to the ARB and ARB staff, aided by their access to short-time aerosol data unavailable to UC Davis, re-did the analysis making a slight (3 hr) adjustment in the DELTA Group's estimated start time. The results were sharply better agreement with the FRM (below) with slope = 0.99 and $r^2 = 0.99$.

Based upon these efforts, time accuracy can be improved by deploying in parallel a high time resolution sampler, such as a Dust Trak nephelometer, at the start of every field campaign, to allow an accurate start time adjustment of the DRUM data.



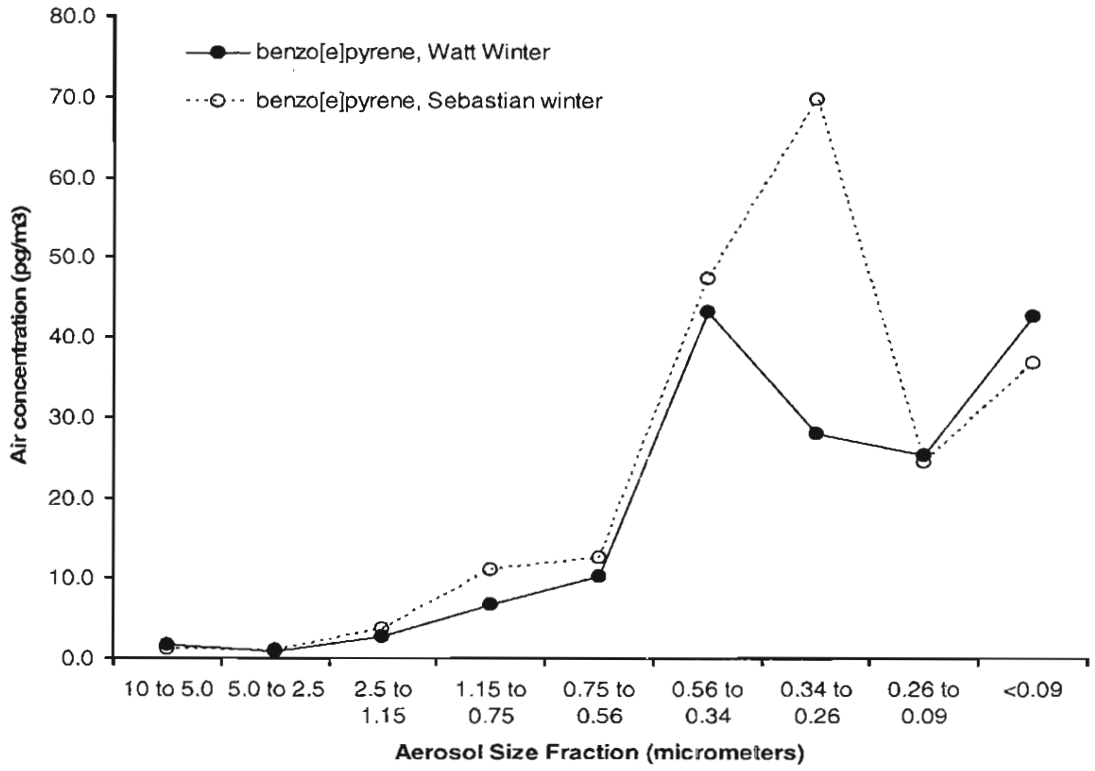
2. From the US EPA study, precision of DRUM sampling was examined,



This work also showed mass balance on the ultra fine filters, the "Gold Standard" for QA.

Major components	ug/m3 filter	ug/m3 cont.		Minor components	ng/m3 filter	ug/m3 cont.
Mass (gravimetric)	2.04	2.9		Phosphorus	2.4	0.7
Mass (reconstructed)	2.15	na		Vanadium	0.15	0.3
				Chromium	0.45	< 0.1
Organic	1.72	na		Nickel	3.5	0.2
Diesel PM (est.)	na	1.3		Copper	8.3	0.2
Ammonium Sulfates	0.34	0.03		Zinc	11.5	0.7
Salt	0.04	0.01		Arsenic	0.6	0.1
Soil	0.048	0.06		Selenium	0.3	0.2
K non	0.053	0.04		Bromine	3.7	5.7
Metals	0.035	0.011		Lead	4	1.1

3. From the Watt Avenue studies, the precision and accuracy of the organic data are shown by the agreement at 2 sites 500 m apart.



4. Summary comparison, all DELTA S-XRF double blind experiments

Below we summarize all DELTA Group S-XRF inter-comparisons in the past 5 years. Note that there were problems with the ARB RAAS analyses since the two internal ARB X-RF to ARB RAAS comparisons agreed only at the level 1.29 ± 0.63 for all co-measured elements(DQAP v. 8.02, pg 32). We also give averages below without the ARB RAAS data. A comparison was also done with IMPROVE in the Yosemite study

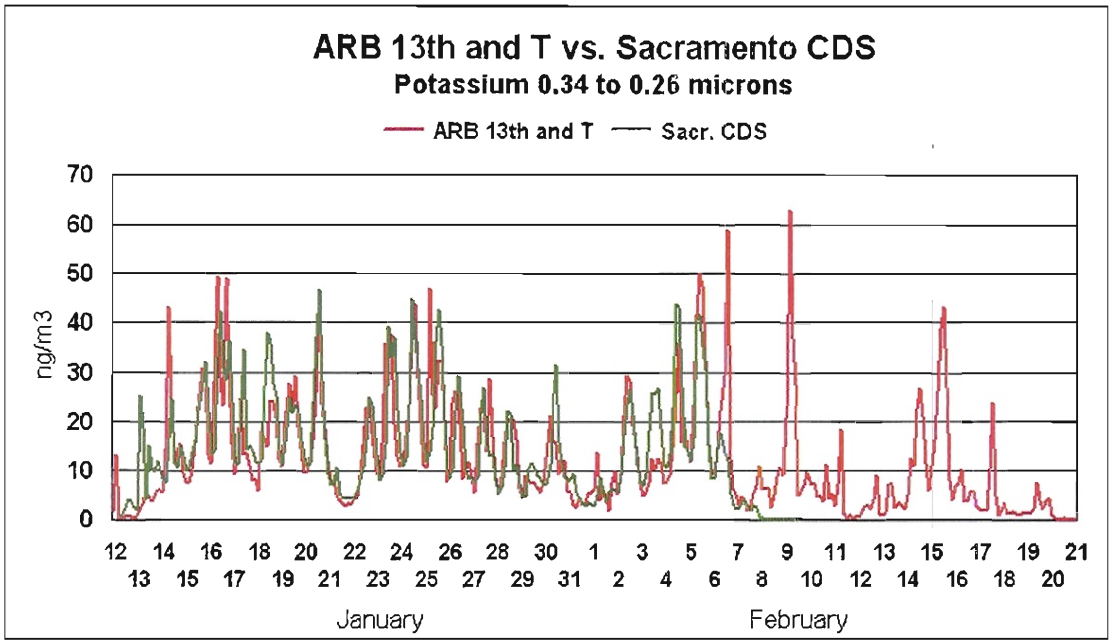
(2002) but this comparison is not included since IMPROVE has also since identified serious deficiencies in data from that period (White et al, AAAR 2004).

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 (alt) 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** (wo ARB alt)	**0.984**	**0.15**	**0.977**	**0.115**

A. DRUM to DRUM comparison, 0.26 to 0.09 potassium data, BC/SET HETF ARB study

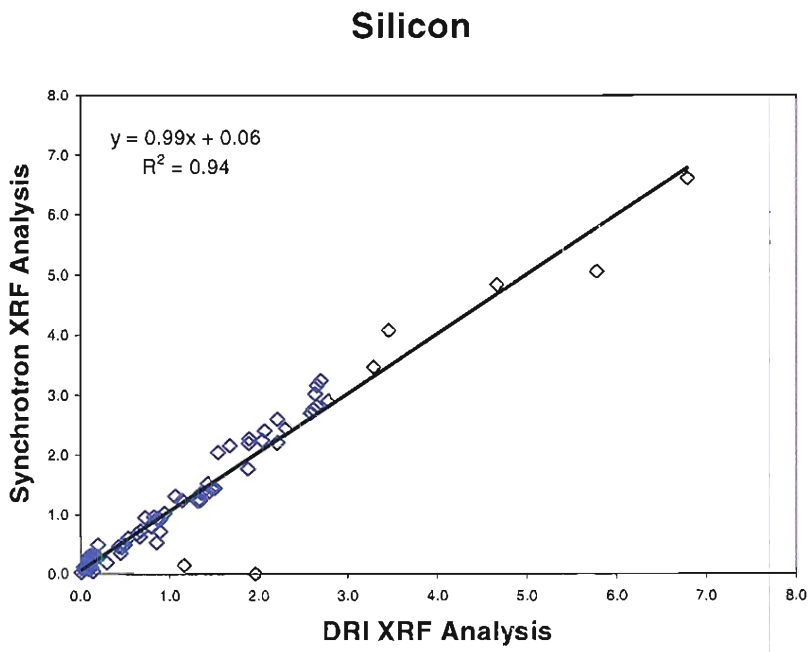
The comparisons of DRUM to DRUM including all aspects of air flow, particle sizing, and S-XRF analyses can result in a serious propagation of error uncertainties. Nevertheless, below we show two DRUM samplers, one of the older design running at 16.7 L/min, one of the newest design running at 10 L/min. The sites were roughly 8 km apart in Sacramento.

Very fine potassium shows remarkable agreement week after week as the inversion caps the entire city.



B. DELTA Group S-XRF versus DRI XRF, ARB Lake Tahoe Atmospheric Deposition (LTAD) study, (2005)

This comparison for silicon in very lightly loaded samples (a few $\mu g/m^3$), was typical of major elements. For many minor elements, S-XRF had much higher sensitivities and MDL limitations with the DRI data made comparisons impossible. Specifically, the very important element for lake clarity, phosphorus, was seen above MDL in only about 1% of analyses by DRI, while phosphorus was seen in over 80% of DELTA Group S-XRF analyses. All these data are in the comparison table (above).



Appendix D

DELTA GROUP DRUM PUBLICATIONS

Thomas A. Cahill
September 10, 2008

History: The Air Quality Group (AQG, 1971 – 1997) and the Detection and Evaluation in Long-range Transport of Aerosols (DELTA Group, 1997 – present) have always preferred on fundamental and scientific grounds to perform experiments with continuous sampling of size and compositionally resolved aerosols. The samplers used have varied in time (typical time resolutions have and can be varied at will): **The sampler types in bold are covered by the current DRUM Quality Assurance Protocol (DQAP), which is updated annually (latest version 1/08 (2008)**

1. Lundgren sampler 1972-1974 , thereafter 5 stages, slots, 4 hr resolution, 160 L/min
2. Multiday sampler 1973 – 1981 3 stages, slots, 24 hr resolution 35 L/min
3. DRUM samplers
    a. Jetted 8 DRUM 1985 – 1995 8 stages, jets, 3 hr resolution, 1.0 L/min
    b. DELTA 8 DRUM 1996 – 10.0 L/min **8 stages, slots, 3 hr resolution**
    c. DELTA 8 DRUM, 2001 – 16.7 L/min **8 stages, slots, 3 hr resolution**
    d. DELTA 3 DRUM, 2001 – 22.5 L/min **3 stages, slots, 3 hr resolution**
    e. 8 DRUM upgrade, 2005 – 16.7 L/min **8 stages, slots, 3 hr resolution**

The publications below are from the slotted DRUM set in bold (above). The remaining publications are on the DELTA Group web site http://delta.ucdavis.edu. The numbers are the identifiers in the Master AQG/DELTA master publication list.

Publications from DRUM samplers (slotted, 3 and 8 stage, types b through e)

08 - 1 Emma Pere-Trepat, Eugene Kim, Pentti Taatero, and Philp k. Hopke, **Source Apportionment of time and size resolved ambient particulate matter measured with a rotating DRUM impactor**, Atm. Env. (September, 2008)

06 - 1 Alan W. Gertler, Andrzej Bytnerowicsz, Thomas A. Cahill, Michael Arbaugh, Steven Cliff, Jülide Kahyaoğlu-Koračin, Leland Tarney, Rocio Alonso, Witold Fraczek. **Local Air Pollutants Threaten Lake Tahoes Clarity**. *California Agriculture, Vol. 60 Num. 2, 49-58, 2006.*

05-1 Perry, Kevin; Cliff, Steven S.; Jimenez-Cruz, Michael P.; **Evidence for hygroscopic mineral dust particles from the Intercontinental Transport and**

Chemical Transformation Experiment. *Journal of Geophysical Research, Vol. 109, 2004.*

04-4 Cahill, T. A., Cliff, S.S., Shackelford, J.F., Meier, M., Dunlap, M., Perry, K.D., Bench, G., and Leifer, R. **Very fine aerosols from the World Trace Center collapse piles: Anaerobic incineration?** ACS Symposium Series 919, 152-163 (2005)

04-3 Seinfeld, J.H., Carmichael, G.R., Arimoto, R, Conant, W. C., Brechtel, F. J., Bates, T. S., Cahill, T. A., Clarke, A.D., Flatau, B.J., Huebert, B.J., Kim, J., Markowicx, K.M., Masonis, S.J., Quinn, P.K., Russell, L.M., Russell, P.B., Shimizu, A., Shinozuka, Y., Song, C.H., Tang, Y., Uno, I., Vogelmann, A.M., Weber, R.J., Woo, J-H., Zhang, Y. **ACE-Asia: Regional Climatic and Atmospheric Chemical Effects of Asian Dust and Pollution,** *Bulletin American Meteorological Society* 85 (3): 367+ MARCH 2004

04-2 Han, J.S, K.J. Moon, J.Y. Ahn, Y.D. Hong, Y.J Kim, S. Y. Rhu, Steven S. Cliff, and Thomas A. Cahill, **Characteristics of Ion Components and Trace Elements of Fine Particles at Gosan, Korea in Spring Time from 2001 to 2002,** *Environmental Monitoring and Assessment* 00: 1-21, 2003

04-1 Thomas A. Cahill, Steven S. Cliff, Michael Jimenez-Cruz, James F. Shackelford, Michael Dunlap, Michael Meier, Peter B. Kelly, Sarah Riddle, Jodye Selco, Graham Bench, Patrick Grant, Dawn Ueda, Kevin D. Perry, and Robert Leifer, **Analysis of Aerosols from the World Trade Center Collapse Site, New York, October 2 to October 30, 2001.** Aerosol Science and Technology 38; 165–183 (2004)

03-1 Cahill, C.F. **Asian Aerosol Transport to Alaska during ACE-Asia**. J. Geophys. Res. J. Geophys. Res., 108 (D23), 8664 (2003)

03-4 Reuter, John E., Cahill, Thomas A., Cliff, Steven S., Goldman, Charles R., Heyvaert, Alan C., Jassby, Alan D., Lindstrom, Susan, and Rizzo, Davis M., **An Integrated Watershed Approach to Studying Ecosystem health at Lake Tahoe, CA-NV**, in *Managing for Healthy Ecosystems* Rapport et al, ed., CRC Press, New York, 1283-1298 (2003)

01-1 V. Shutthanandan, S. Thevuthasan, R. Disselkamp, A. Stroud, A. Cavanaugh, E.M. Adams, D.R. Baer, L. Barrie, S.S. Cliff, T.A. Cahill. **Development of PIXE, PESA and transmission ion microscopy capability to measure aerosols by size and time**. 2001 *Nuclear Instruments and Methods in Physics Research B: Beam Interactions with Materials and Atoms*.

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00-1 Miller, Alan E. and Thomas A. Cahill. **Size and compositional analyses of biologically active aerosols from a CO_2 and diode laser plume**. 2000 *International Journal of PIXE*. Vol. 9, Nos. 3 & 4.

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