

# **Gulf Coast Aerosol Research and Characterization Program (Houston Supersite)**

## **PROGRESS REPORT**

**EPA Contract No. R-82806201**

between the Environmental Protection Agency and the  
University of Texas at Austin

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Quarterly progress report for April, 2001

Date of Report: **April 30, 2001**

EPA Agreement No.: **R-82806201**

Title: **Gulf Coast Aerosol Research and Characterization Study**

Investigators: **Dr. David Allen (PI) and Dr. Matthew Fraser (Co-PI)**

Institutions: **University of Texas and Rice University**

Research Category: **Air Quality/Fine Particulate Matter**

Project Period: **01/15/00-11/30/03**

Objective of Research: **Characterize fine particulate matter and fine particulate matter formation processes in Southeast Texas**

Progress Summary/Accomplishments:

**During the final quarter of 2000, the intensive sampling period for the Houston Supersite was conducted, in coordination with an air quality study focussed on gas phase chemistry (the Texas Air Quality Study).**

**Data analysis is ongoing and selected preliminary findings are presented in this report.**

During the final quarter of 2000, the intensive sampling period for the Houston Supersite was conducted, in coordination with an air quality study focussed on gas phase chemistry (the Texas Air Quality Study). Selected preliminary findings are presented in this report. Specifically, preliminary results of the infrared spectroscopy of size resolved ambient aerosol are presented.

## **I. Infrared spectroscopy of size resolved ambient aerosol,**

**University of Texas,**

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This progress report describes some of the sample collection and analysis activities performed during the six week Houston “Supersite” intensive study that occurred in August and September 2000. These samples were collected using a Low Pressure Impactor (LPI) and were analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The data and analyses will focus on the organonitrate fraction of the aerosol. Organonitrates are significant because they provide insight into chemical reaction processes occurring in the atmosphere. They are generally believed to be due to atmospheric reactions (rather than primary emissions), and their concentrations can lead to insights into whether NO<sub>x</sub> concentrations are high during reaction processes that lead to aerosol formation. Therefore, the concentrations, size distributions, and potential sources of these organonitrates will be examined and the results will be compared to similar analyses reported for Los Angeles (Mylonas, et al, 1991).

### ***Methods***

#### **Sampling Locations**

Extensive fine particulate matter sampling was performed at three locations during the Houston “Supersite” intensive sampling period (August 1-September 15, 2000). The three sampling sites are shown on the map in Figure 1, and are labeled as LaPorte, HRM3 (Houston Regional Monitoring Network Site 3), and Aldine. These three sites were chosen based on the most common wind directions observed in Houston during August and September. In August and September, winds generally flow from Galveston Bay and advect to the northwest. Thus, on many days during August and September, LaPorte sees relatively clean air from Galveston Bay. Point source emissions from the highly industrialized Ship Channel are added as the air parcel advects toward the HRM3 site. Data on the locations of point sources of particulate matter, nitrogen oxides, and other aerosol precursors are reported by Garnes (2001) and are available at ([http://www.utexas.edu/research/ceer/texaqs/participants/background\\_sci.html](http://www.utexas.edu/research/ceer/texaqs/participants/background_sci.html)). Finally, urban emissions are added as the air parcel advects toward the Aldine site. This type of

flow pattern, with winds off the bay advecting to the northwest, was observed during much of the intensive sampling period.

Figure 1. Map of southeast Texas showing the Houston metropolitan area (in white) and the sampling sites operated during the Houston Supersite intensive sampling period. The three core sampling sites, Aldine, HRM3, and LaPorte, were located along a southeast-northwest line originating at Galveston Bay.



### Sample Collection and Analysis

Fine particulate matter samples were collected using a Low Pressure Impactor (LPI) and analyzed using Fourier Transform Infrared spectroscopy (FTIR) (Allen, et al, 1994). The use of a Hering LPI and FTIR spectroscopy to analyze aerosol complements other methods commonly used to characterize the inorganic, and particularly the organic fraction of atmospheric aerosol. It is a nondestructive method of analysis, requiring no extraction. In addition, the method detects a large fraction of the organic and inorganic mass commonly encountered in atmospheric aerosol. Finally, for the carbonaceous fraction, the FTIR spectroscopy provides data on the compound classes, not just total carbon. The drawback to FTIR analysis is its inability to identify individual organic species, only compound classes. Regardless, FTIR analysis is a valuable tool that provides insight into the chemical composition of size segregated particles. Detailed descriptions of the method (Allen, et al, 1994) and its application in air quality field studies have been previously reported (Mylonas, et al, 1991; Pickle, et al, 1990, Blando, et al., 1998).

A Hering LPI (Hering, et al, 1978, 1979) was used to collect the aerosol samples. The LPI has eight stages that separate aerosol into size fractions with cutpoints at aerodynamic diameters of 4.0, 2.0, 1.0, 0.5, 0.26, 0.12, 0.075, and 0.05  $\mu\text{m}$ . Each stage contains a central orifice which produces a single, circular, 2-3 mm diameter aerosol sample on a ZnSe impaction surface. The ZnSe disks are transparent to infrared radiation in the range of 1-18  $\mu\text{m}$ , allowing for direct analysis using FTIR spectroscopy. Stage one contains a stainless steel disk which serves as a coarse particle precut and is not analyzed. The first four stages operate near atmospheric pressure whereas the final four stages operate at reduced pressure. A critical orifice is placed between stages four and five, which controls the volumetric flow rate through the impactor at 1.05 L/min. After the samples were deposited on ZnSe impaction disks, the disks were analyzed using FTIR spectroscopy. Each sampling event generated seven spectra, corresponding to stages two through eight in the Hering impactor. Sample spectra are shown in Figures 2-4. The spectra show a number of strong features, identified in Table 1, which can be used to characterize the composition of the aerosol. The focus in the remainder of this manuscript will be on the organonitrate peaks in the spectra. Analysis of other strong infrared absorption bands will be described in subsequent publications. As shown in Table 1, the organonitrate functionalities absorb at  $860\text{ cm}^{-1}$ ,  $1260\text{-}1280\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$ . The  $860\text{ cm}^{-1}$  and the  $1260\text{ cm}^{-1}$  absorbances were both typically observed in the spectra, however, in most of the samples, absorbances due to water obscured the peak at  $1630\text{ cm}^{-1}$ . Because the peak at  $1260\text{ cm}^{-1}$  was typically strong, sharp and isolated, this absorption band was used for quantification. It should be noted that the  $1260\text{ cm}^{-1}$  band was displaced slightly from the wavenumbers of the organonitrate absorbances observed in Los Angeles ( $1280\text{ cm}^{-1}$ ). It is not clear whether any structural implications can be associated with this shift, but the magnitude of the shift is within the bounds expected for the organonitrate functionality.

Table 1. Description of specific functionalities found in spectra.

Functionality		Absorbance Frequencies (cm <sup>-1</sup> )	Peak Description	Quantification
SO <sub>4</sub> <sup>-</sup> HSO <sub>4</sub> <sup>-</sup>	Sulfate ions	612-5, 1103-35	Discrete, sharp	580-635
	Bisulfate ions	580-90, 867, 1029, 1180	Discrete, sharp	1029, 1180
NO <sub>3</sub> <sup>-</sup>	Nitrate ions	830-4, 1318-35	Discrete, sharp	818-838
R-H	Aliphatic carbons	1452-5, 2800-3000	Non-discrete <sup>1</sup> , broad	2800-3000
Arom-H	Aromatic carbons	3000-3200	Non-discrete <sup>2</sup> , broad	2800-3000
R=O	Carbonyl carbons	1640-1850	Discrete, sharp	1640-1850
R-ONO <sub>2</sub>	Organonitrates	860, 1260-1280, 1630	Discrete, sharp	1255-1296
Arom-NO <sub>2</sub>	Nitroaromatics	1525-35	Discrete, sharp	1525-35
R-OH	Alcohols	3500-3750	Discrete, sharp	1255-1296
			Non-discrete <sup>3</sup> , broad	

<sup>1</sup> Absorbances due to aliphatic C-H bonds overlap absorbance peaks associated with hydrogen bonding and ammonium ions.

<sup>2</sup> Absorbances due to aromatic C-H bonds overlap absorbance peaks associated with hydrogen bonding and ammonium ions.

<sup>3</sup> Absorbances due to hydrogen bonding in alcohols (high frequency hydrogen bonding) overlap absorbance peaks associated with other hydrogen bonding and ammonium ion absorbances.

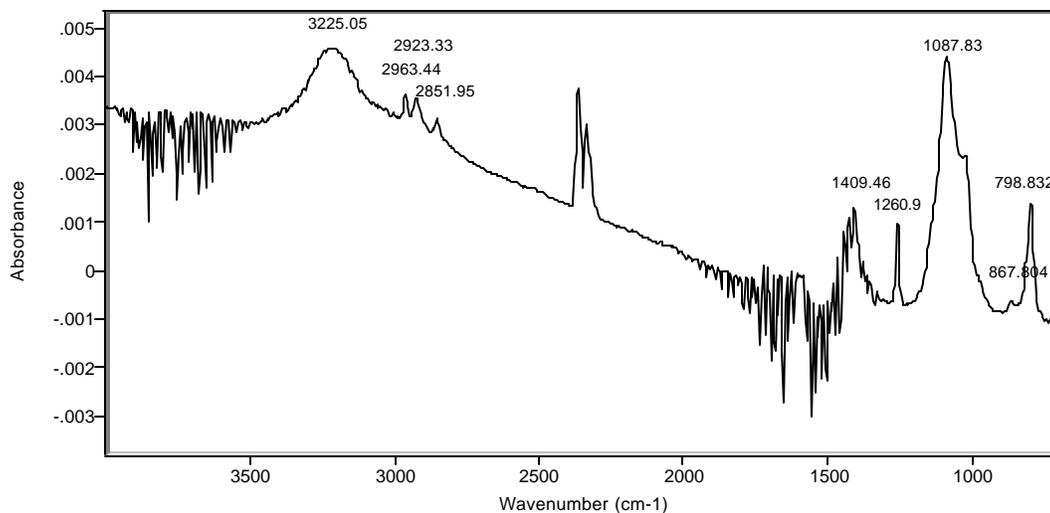


Figure 2. Representative spectra, collected at Aldine, with high organonitrate concentrations (August 5, 2000; <0.05 μm size fraction).

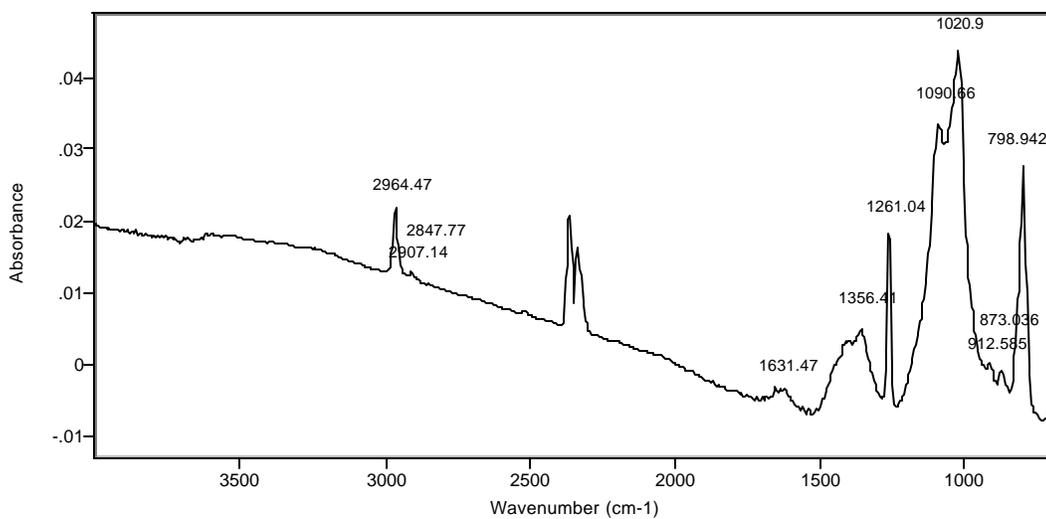


Figure 3. Representative spectra, collected at HRM3, with high organonitrate concentrations (August 6, 2000; <1-2 μm size fraction).

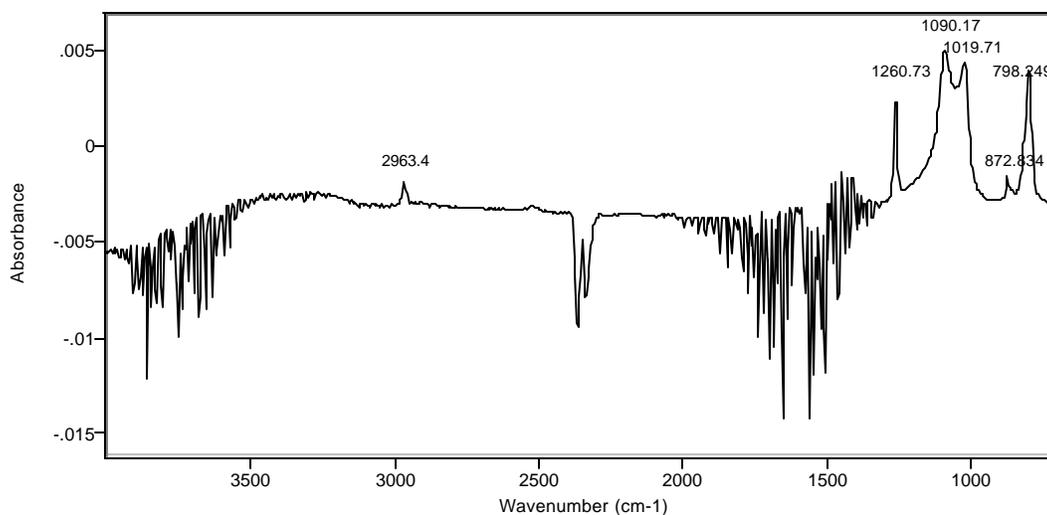


Figure 4. Representative spectra, collected at LaPorte, with high organonitrate concentrations (August 9, 2000; 0.05 – 0.075  $\mu$ m size fraction).

## Results and Discussion

Table 2 gives the sampling dates, start and stop times, total sampling time, and sampling locations for the intensive sampling period. Times are given in local time (CST). A typical set of infrared spectra is given in Figure 5 for LaPorte on August 8, 2000. For this set of spectra, the organonitrate peaks are prominent in stages 6 and 7 (0.05-0.12  $\mu$ m diameter). Absorbance intensities are approximately 0.001 and 0.002 absorbance units, respectively. In contrast, a more unusual set of infrared spectra is given in Figure 6 for HRM3 on August 6, 2000. This set of spectra is unusual because stages 2-8 all contain strong organonitrate peaks with stages 2, 3, and 8 having the largest organonitrate intensities. Further, the magnitude of the absorbances is much higher than in Figure 5, with absorbance intensities of approximately 0.022 absorbance units for stages 2 and 3 and 0.010 absorbance units for stage 8.

Four major patterns are observed in the size distributions of organonitrates in the spectra. The first is a maximum in absorbance intensity in the size range of 0.05-0.12  $\mu$ m (Figure 7). This occurs in 25% of all sampling events, 20% of events at Aldine, 26% of events at HRM3, and 28% of events at LaPorte. The second major pattern is a maximum in absorbance in the size range of 0.12-0.5  $\mu$ m (Figure 8). This occurs in 26% of all sampling events, 14% of events at Aldine, 16% of events at HRM3, and 41% of events at LaPorte. The third major pattern is a maximum in absorbance in the size range of 0.5-2.0  $\mu$ m (Figure 9). This occurs in 12% of all sampling events, 20% of events at Aldine, 13% of events at HRM3, and 6% of events at LaPorte. The fourth pattern is a maximum in absorbance in both the 0.1  $\mu$ m and 1  $\mu$ m size ranges (Figure 10). This occurs in 21% of

all sampling events, 20% of events at Aldine, 29% of events at HRM3, and 16% of events at LaPorte. The remaining samples have small absorbance areas through all size ranges, or have other size distributions. The samples collected at the Aldine (urban) site show all the patterns to roughly the same degree. Samples collected at LaPorte are dominated by the 0.05-0.12 μm and 0.12-0.5 μm modes while the HRM3 samples showed more variation

Table 2 also gives estimates of the concentrations of organonitrates and a characterization of the size distributions for each sampling event. The concentrations are reported as low (below the median value of absorbance per cubic meter of air sampled, over all samples at all sites), moderate (median value < absorbance area < 2\* median value), high (2\* median value < absorbance area < 5\* median value) and very high (5\*median value < absorbance area). These absorbance areas can be very approximately related to organonitrate concentrations by using calibration factors based on model compound spectra. Allen, et al, 1994, determined a calibration factor (molar absorptivity) for the organonitrate group using octyl nitrate as a model compound. Using this calibration factor, the mass concentration of R-ONO<sub>2</sub> in ambient air in each impactor size fraction can be estimated using the following equation:

$$\text{Loading} \left( \frac{\mu\text{g}}{\text{m}^3} \right) = \frac{A \cdot 1000 (\text{L} / \text{m}^3) \cdot \text{MW}}{F \cdot D \cdot C}$$

where A is the absorbance area of the peak produced from the spectrum in absorbance units, F is the flow rate in Liters/minute, D is the sampling duration in minutes, C is the molar absorptivity in absorbance units per μmole, and MW is the molecular weight of the organonitrate containing compounds. Total organonitrate concentrations were determined by taking the sum of the concentrations in each size fraction. The range of loading of organonitrate molecules with a molecular weight of 150 g/mole was 0 to 20 μg m<sup>-3</sup>. An average organonitrate loading for a molecule with a molecular weight of 150 g/mole was 1 μg m<sup>-3</sup> and the median value was 0.2 μg m<sup>-3</sup>. The maximum organonitrate loading at each site was 1.2 μg m<sup>-3</sup> (Aldine), 18 μg m<sup>-3</sup> (HRM3), and 20 μg m<sup>-3</sup> (LaPorte). The mean values for each site were 0.3 μg m<sup>-3</sup> (Aldine), 1.4 μg m<sup>-3</sup> (HRM3), and 1.0 μg m<sup>-3</sup> (LaPorte). The median values for each site are 0.2 μg m<sup>-3</sup> (Aldine), 0.2 μg m<sup>-3</sup> (HRM3), and 0.2 μg m<sup>-3</sup> (LaPorte). The median was approximately the same for every site. The sites differ by how much they diverge from this median with LaPorte diverging the most, closely followed by HRM3. This is due largely to a small number of samples that recorded very high concentrations. These samples will be described at more length below.

Table 2. Organonitrate concentrations and size distributions.

Start Date (CST)	Start Time (CST)	Duration (min.)	Site	Organonitrate Concentration	Mode of Size Distribution
2000/08/04	23:00:00	1440	Aldine	moderate	.1 µm and 1 µm
2000/08/06	11:00:00	360	Aldine	very high	.1 µm
2000/08/06	11:00:00	360	HRM3	very high	1 µm
2000/08/06	23:00:00	1440	Aldine	low	1 µm
2000/08/06	23:00:00	1440	HRM3	high	.1 µm
2000/08/08	00:00:00	1440	Aldine	low	ND
2000/08/08	11:00:00	360	HRM3	very high	1 µm
2000/08/08	11:00:00	360	LaPorte	very high	.1 µm
2000/08/08	23:00:00	1440	Aldine	low	.5 µm
2000/08/09	10:00:00	780	HRM3	high	.5 µm
2000/08/09	10:20:00	760	LaPorte	very high	.1 µm and 1 µm
2000/08/10	11:00:00	360	Aldine	low	.5 µm
2000/08/10	11:00:00	360	HRM3	very high	.1 µm and 1 µm
2000/08/10	11:00:00	360	LaPorte	very high	.1 µm and 1 µm
2000/08/10	23:00:00	1440	Aldine	moderate	.1 µm and .5 µm
2000/08/10	23:00:00	1440	HRM3	very high	.1 µm and 1 µm
2000/08/10	23:00:00	1440	LaPorte	moderate	.1 µm
2000/08/12	11:00:00	360	Aldine	moderate	.1 µm
2000/08/12	11:00:00	360	HRM3	very high	.1 µm and 1 µm
2000/08/12	11:00:00	360	LaPorte	high	1 µm
2000/08/12	23:00:00	1440	Aldine	low	.1 µm
2000/08/12	23:00:00	1440	HRM3	very high	.1 µm and 1 µm
2000/08/12	23:00:00	1440	LaPorte	high	1 µm
2000/08/14	11:00:00	360	Aldine	low	1 µm
2000/08/14	11:00:00	360	HRM3	high	.1 µm and 1 µm
2000/08/14	11:00:00	360	LaPorte	very high	.1 µm and 1 µm
2000/08/14	23:00:00	1440	LaPorte	moderate	.1 µm
2000/08/15	23:00:00	1440	LaPorte	high	.1 µm
2000/08/16	23:00:00	1410	Aldine	low	1 µm
2000/08/16	23:00:00	1440	LaPorte	low	.1 µm and .5 µm
2000/08/17	23:00:00	1480	HRM3	very high	.1 µm and 1 µm
2000/08/17	23:00:00	1440	LaPorte	moderate	.1 µm
2000/08/19	00:10:00	1400	HRM3	moderate	.5 µm
2000/08/18	23:00:00	1410	LaPorte	low	.1 µm
2000/08/19	23:45:00	1390	HRM3	low	1 µm
2000/08/19	23:00:00	1400	LaPorte	very high	.5 µm
2000/08/20	23:45:00	1330	HRM3	low	ND
2000/08/20	23:00:00	1510	LaPorte	low	.5 µm

ND = not detected

Table 2, cont'd. Organonitrate concentrations and size distributions.

Start Date (CST)	Start Time (CST)	Duration (min.)	Site	Organonitrate Concentration	Mode of Size Distribution
2000/08/21	22:55:00	1285	HRM3	low	.1 µm
2000/08/22	00:15:00	1400	LaPorte	low	.1 µm
2000/08/22	22:45:00	1440	HRM3	moderate	.1 µm and .5 µm
2000/08/22	23:35:00	1440	LaPorte	moderate	.5 µm
2000/08/24	11:00:00	360	Aldine	moderate	.1 µm and 1 µm
2000/08/23	23:00:00	1395	HRM3	low	.5 µm
2000/08/25	11:00:00	360	Aldine	high	.1 µm and 1 µm
2000/08/24	22:30:00	1425	HRM3	low	.1 µm
2000/08/25	00:40:00	1440	LaPorte	low	.1 µm and 1 µm
2000/08/26	11:00:00	360	Aldine	high	.1 µm, .5 µm and 1 µm
2000/08/25	22:30:00	1455	HRM3	low	.1 µm
2000/08/25	23:30:00	1410	LaPorte	moderate	.5 µm
2000/08/27	11:00:00	360	Aldine	high	.1 µm, .5 µm and 1 µm
2000/08/26	23:10:00	1415	HRM3	low	.1 µm and 1 µm
2000/08/27	00:00:00	1380	LaPorte	low	.1 µm and .5 µm
2000/08/27	23:00:00	1465	HRM3	high	1 µm
2000/08/28	00:15:00	1455	LaPorte	low	.5 µm
2000/09/01	22:45:00	1425	HRM3	low	.1 µm
2000/09/01	23:35:00	1434	LaPorte	high	.5 µm
2000/09/02	22:52:00	1473	HRM3	low	.1 µm and .5 µm
2000/09/03	00:05:00	1330	LaPorte	moderate	.5 µm
2000/09/03	23:40:00	1420	HRM3	moderate	.1 µm and 1 µm
2000/09/03	22:35:00	1432	LaPorte	low	.5 µm
2000/09/04	23:37:00	1423	HRM3	very high	.1 µm
2000/09/04	22:48:00	1411	LaPorte	very high	.5 µm
2000/09/05	23:36:00	1424	HRM3	low	.1 µm
2000/09/05	22:40:00	1410	LaPorte	high	.5 µm
2000/09/06	23:37:00	1431	HRM3	low	.1 µm and .5 µm
2000/09/06	22:31:00	1424	LaPorte	low	.5 µm
2000/09/07	23:42:00	1418	HRM3	low	.5 µm
2000/09/07	22:29:00	1416	LaPorte	low	.5 µm and 1 µm
2000/09/08	23:32:00	1453	HRM3	low	.1 µm and .5 µm
2000/09/08	22:20:00	1440	LaPorte	low	.5 µm
2000/09/09	23:00:00	1485	LaPorte	low	.1 µm and 1 µm
2000/09/10	23:10:00	1365	HRM3	low	.1 µm and .5 µm
2000/09/11	00:00:00	1365	LaPorte	low	.1 µm
2000/09/11	22:15:00	1480	HRM3	low	.1 µm
2000/09/11	23:00:00	1382	LaPorte	low	.5 µm
2000/09/12	23:10:00	1280	HRM3	low	.5 µm
2000/09/12	22:17:00	1377	LaPorte	low	.1 µm

ND = not detected

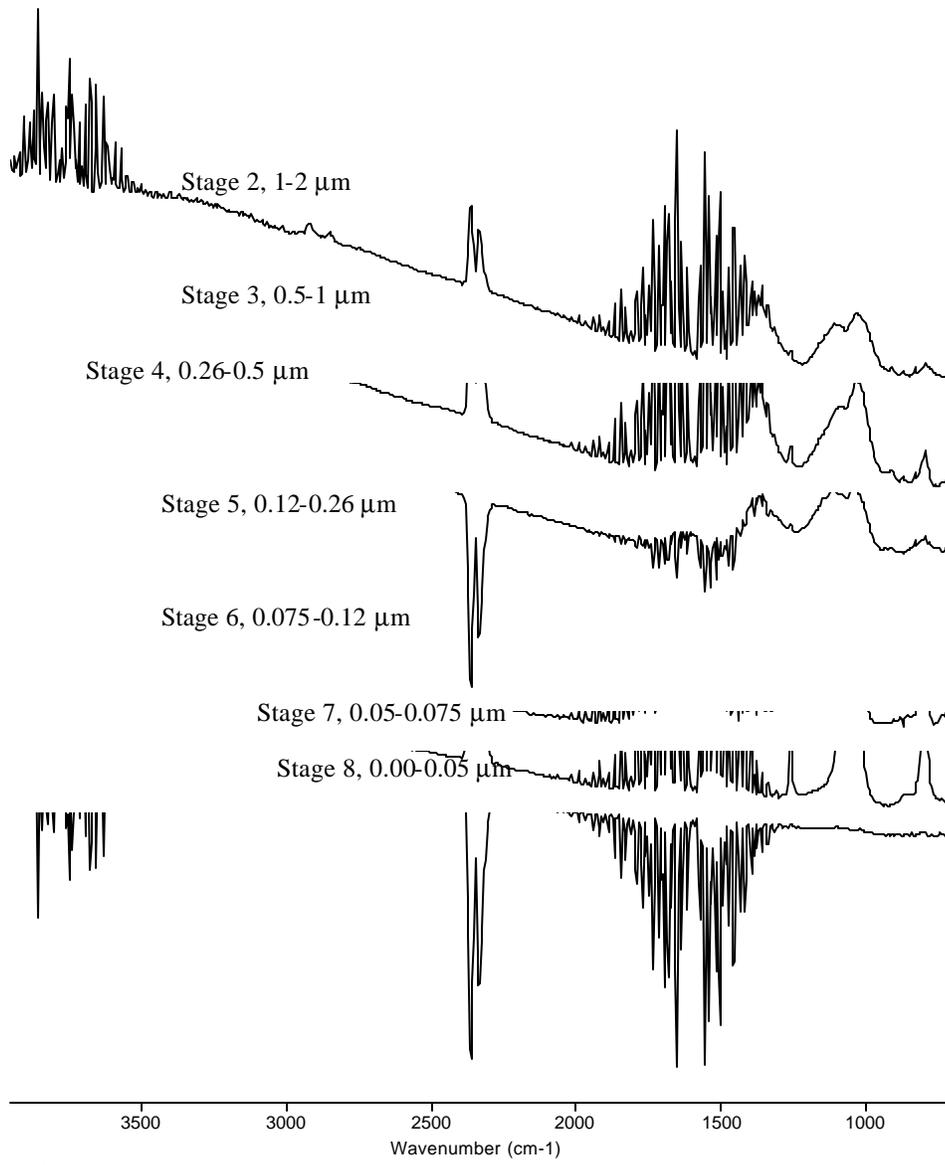


Figure 5. Set of infrared spectra for all seven stages at LaPorte on August 8, 2000.

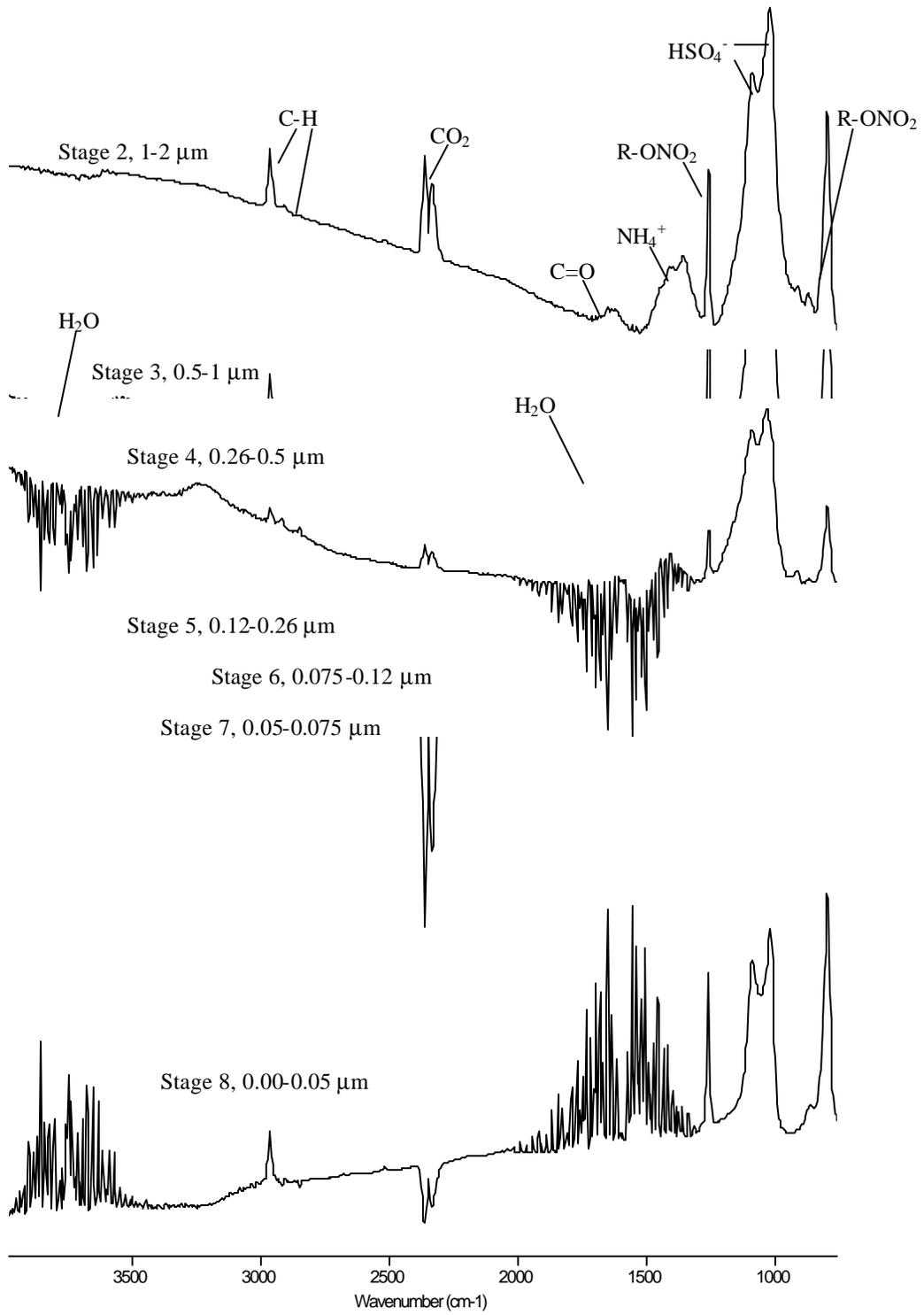


Figure 6. Set of infrared spectra for all seven stages at HRM3 site for August 6, 2000.

LaPorte 8/8/00, 360 Minute Duration

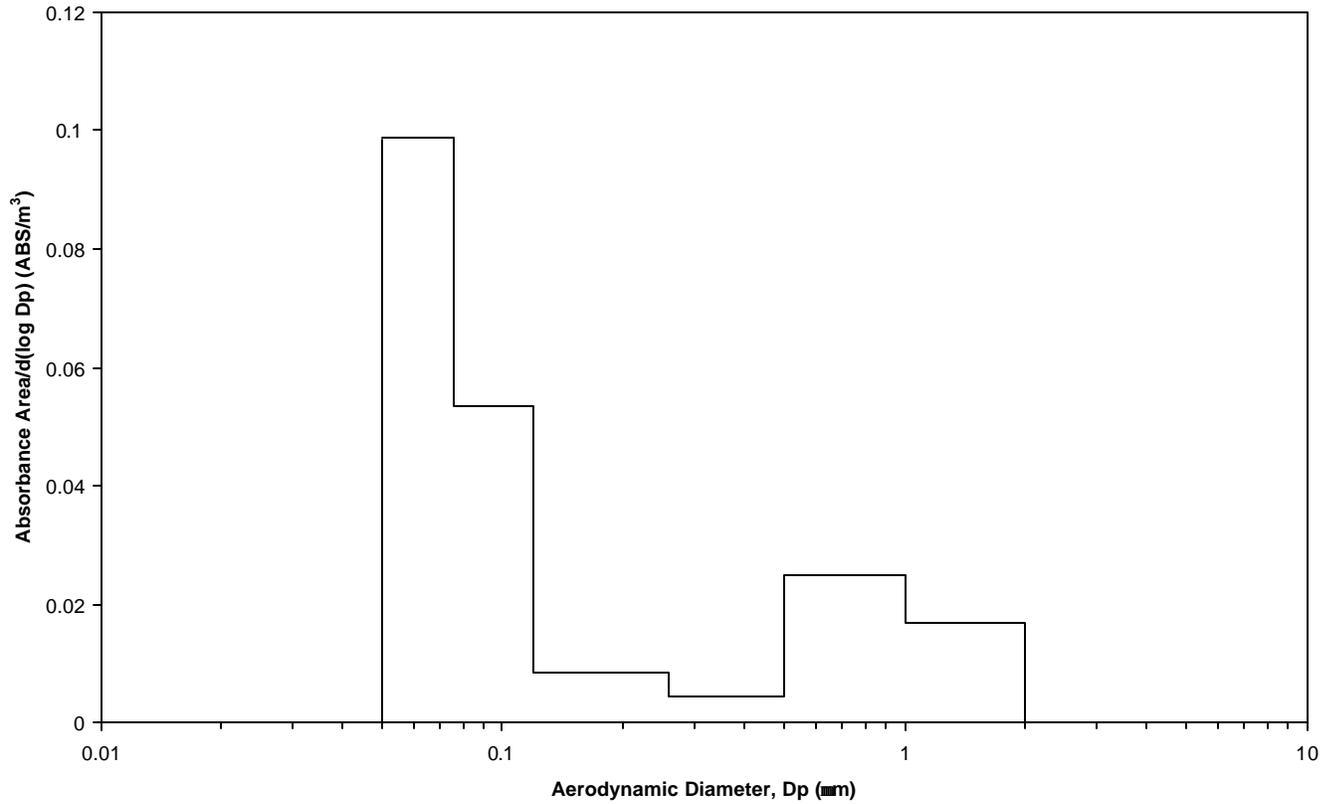


Figure 7. Size distribution of organic nitrates in the aerosol sample collected at LaPorte on August 8, 2000 in Houston. The 0.05-0.12 µm size fractions dominate this sample.

HRM 8/9/00, 780 Minute Duration

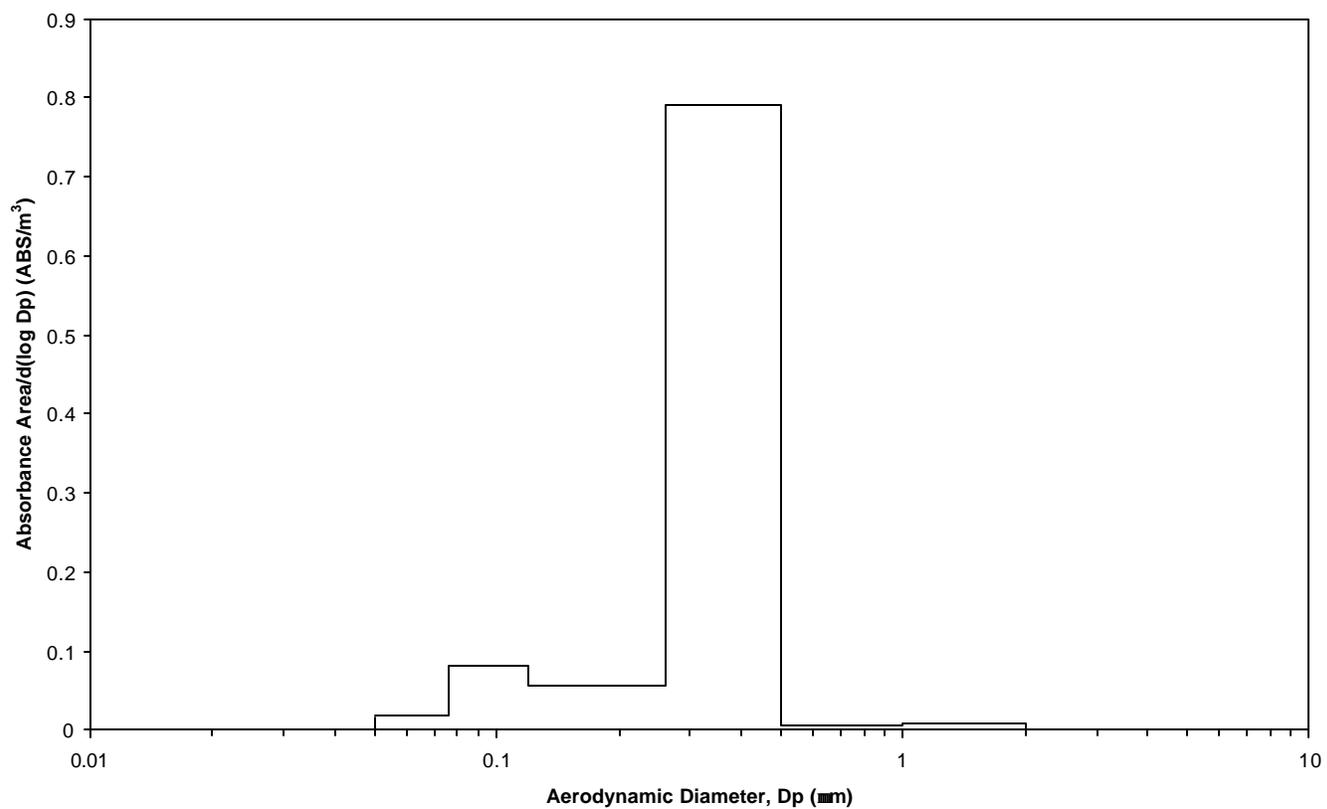


Figure 8. Size distribution of organic nitrates in the aerosol sample collected at HRM3 on August 9, 2000 in Houston. The 0.26-0.5 µm size fractions dominate this sample.

HRM 8/6/00, 360 Minute Duration

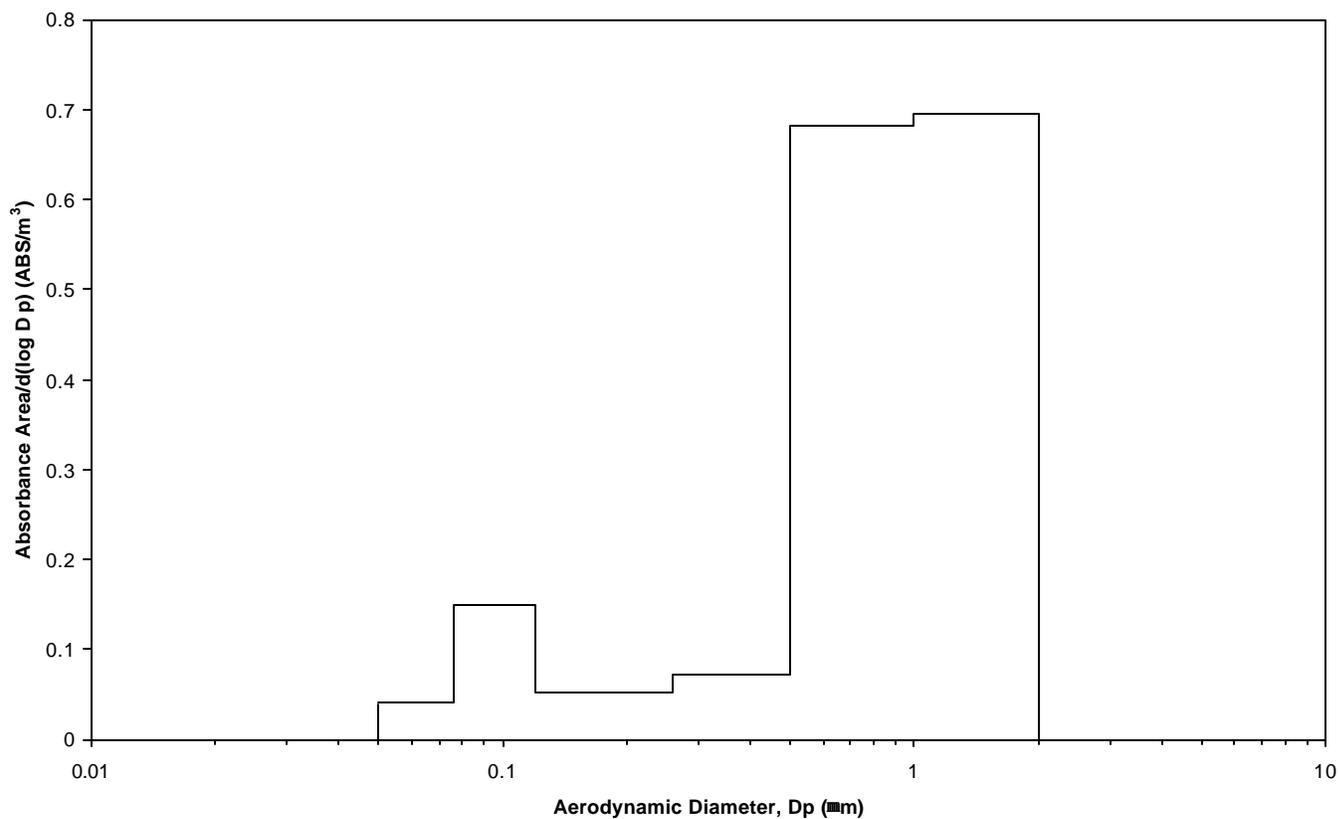
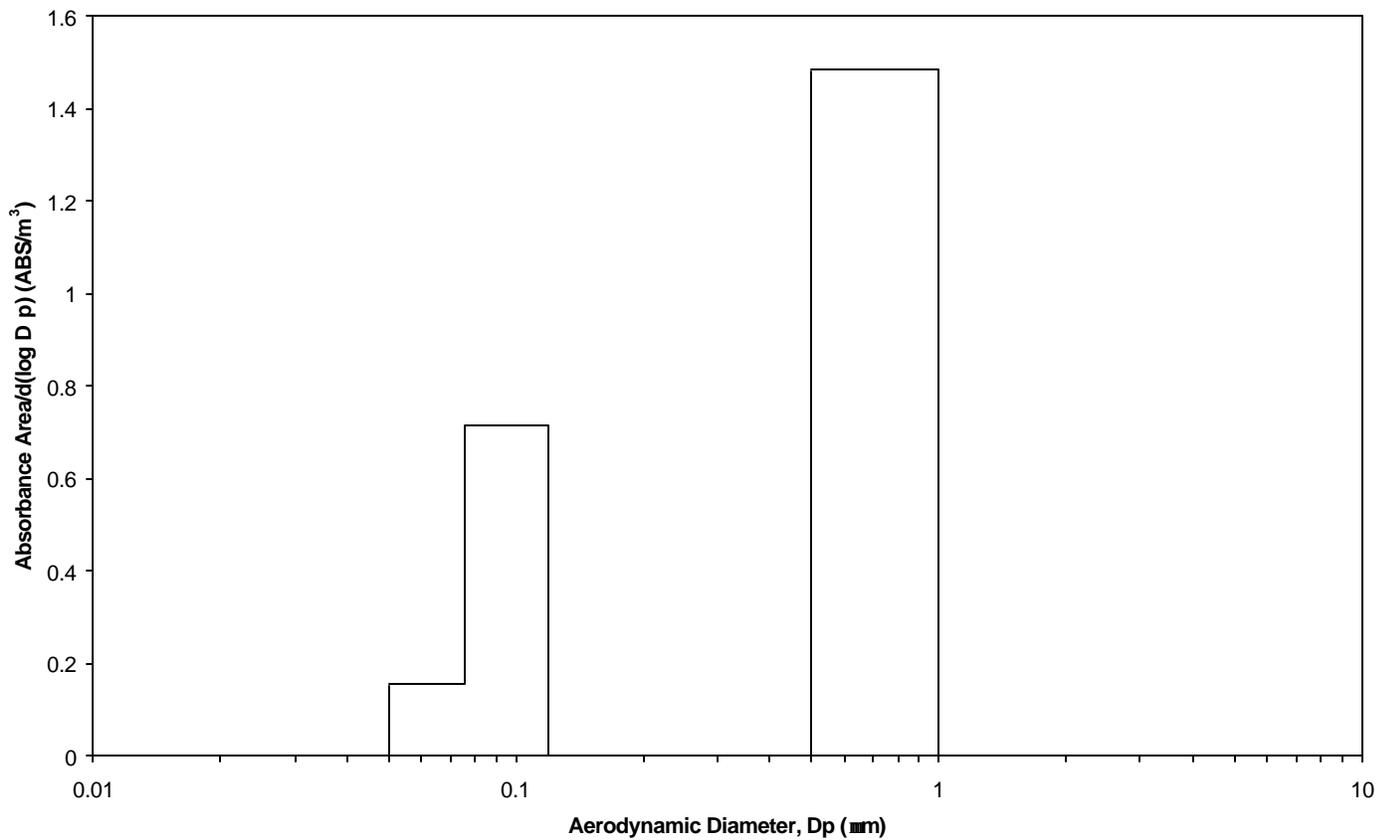


Figure 9. Size distribution of organic nitrates in the aerosol sample collected at HRM#3 on August 6, 2000 in Houston. The 0.5-2 µm size fractions dominate this sample.

Figure 10. Size distribution of organic nitrates in the aerosol sample collected at

**LaPorte 8/10/00, 360 Minute Duration**



LaPorte on August 10, 2000 in Houston. The 0.5-1.0 µm size fraction and the 0.05-0.26 µm size fraction dominate this sample.

The highest organonitrate group concentration at Aldine ( $0.6 \text{ } \mu\text{g}/\text{m}^3$ ) occurred on August 6, 2000 when HRM3 also had extremely high organonitrate group loadings ( $8.6 \text{ } \mu\text{g}/\text{m}^3$ ). LaPorte samples were not collected on this day. The average wind trajectory was  $180^\circ$  for Aldine (wind coming directly from the south) and the average wind trajectory was  $185^\circ$  for HRM3 (wind coming from the south-southeast). Therefore a common source for these high concentrations might be expected.

August 8, 2000 also has an interesting wind pattern. Aldine samples were not collected for that day but HRM3 and LaPorte had an identical average wind direction ( $157^\circ$ ). Therefore, the air parcel sampled at LaPorte would have originated over Galveston Bay, passing over LaPorte (with a total organonitrate group loading of  $0.7 \text{ } \mu\text{g}/\text{m}^3$ ) then passing over HRM3 (with a total organonitrate group loading of  $2.6 \text{ } \mu\text{g}/\text{m}^3$ ). Features to be noted in the spectra with intense organonitrate peaks are strong doublets in the  $1100 \text{ cm}^{-1}$  sulfate peak, strong absorbances due to aliphatic C-H stretches and water, and the lack of strong carbonyl absorbances. The doublets in the sulfate peak suggest large amounts of bisulfate in the sample and therefore relatively high acidity. The presence of intense C-H stretch absorbances suggest unoxidized organics are present in the sample and the presence of water absorbances suggest that the aerosol is hydrophilic. Somewhat surprising was the lack of carbonyl peaks. Strong carbonyl absorbances were anticipated because typical urban secondary organic aerosol would contain both organonitrates and carbonyls. Since there is no correlation, three hypotheses can be entertained. The first is that there is a primary emission source of organonitrates. The second hypothesis is that there is an unusual plume chemistry occurring that does not produce carbonyl functional groups but does produce organonitrate functional groups. A final possibility is that the peak at  $1260 \text{ cm}^{-1}$  has been incorrectly assigned to the organonitrate functionality. Given the consistent presence of the bands at  $860 \text{ cm}^{-1}$ , and the band at  $1630 \text{ cm}^{-1}$  (when not obscured by water), misassignment seems unlikely. The organonitrate concentrations and size distributions were compared to data collected in the South Coast Air Basin during the Southern California Air Quality Study (SCAQS) (Mylonas et al. 1991). The SCAQS samples were collected in Duarte, CA during the summer and early fall of 1987 for 58 days. Duarte is a foothill receptor site located about 35 miles northeast of downtown Los Angeles. Mylonas found maxima in the size ranges  $0.05\text{-}0.26 \text{ } \mu\text{m}$  and  $0.5\text{-}1.0 \text{ } \mu\text{m}$ . This corresponds to the maxima found in the Houston profiles, but the Houston sample set contained some samples with very intense organonitrate absorbances, unlike any observed during SCAQS. Specifically, the concentrations of organonitrate molecules (assuming a molecular weight of  $150 \text{ g}/\text{mole}$  and using the same spectrometer and calibration data) ranged from  $0.8$  to  $4.0 \text{ } \mu\text{g m}^{-3}$  and averaged  $2.1 \text{ } \mu\text{g m}^{-3}$  in Los Angeles. The concentrations in Houston ranged from  $0$  to  $20 \text{ } \mu\text{g m}^{-3}$  and averaged  $1 \text{ } \mu\text{g m}^{-3}$ . In addition, high concentrations of organonitrates in Los Angeles were correlated with high concentrations of ozone and large carbonyl absorbances, indicating that the organonitrate absorbances were likely due to components of secondary organic aerosol. In contrast, many of the Houston samples with strong organonitrate absorbances had relatively weak carbonyl absorbances, and no correlation was found between the concentration of R-ONO<sub>2</sub> in the Houston atmosphere and the concentrations of NO<sub>x</sub> and O<sub>3</sub> ([www.tnrc.state.tx.us/air/monops](http://www.tnrc.state.tx.us/air/monops)), as shown in Figure 11.

**Organonitrate Concentration Versus Peak Concentration of NO<sub>x</sub> and O<sub>3</sub> on the Same Day at the Same Site**

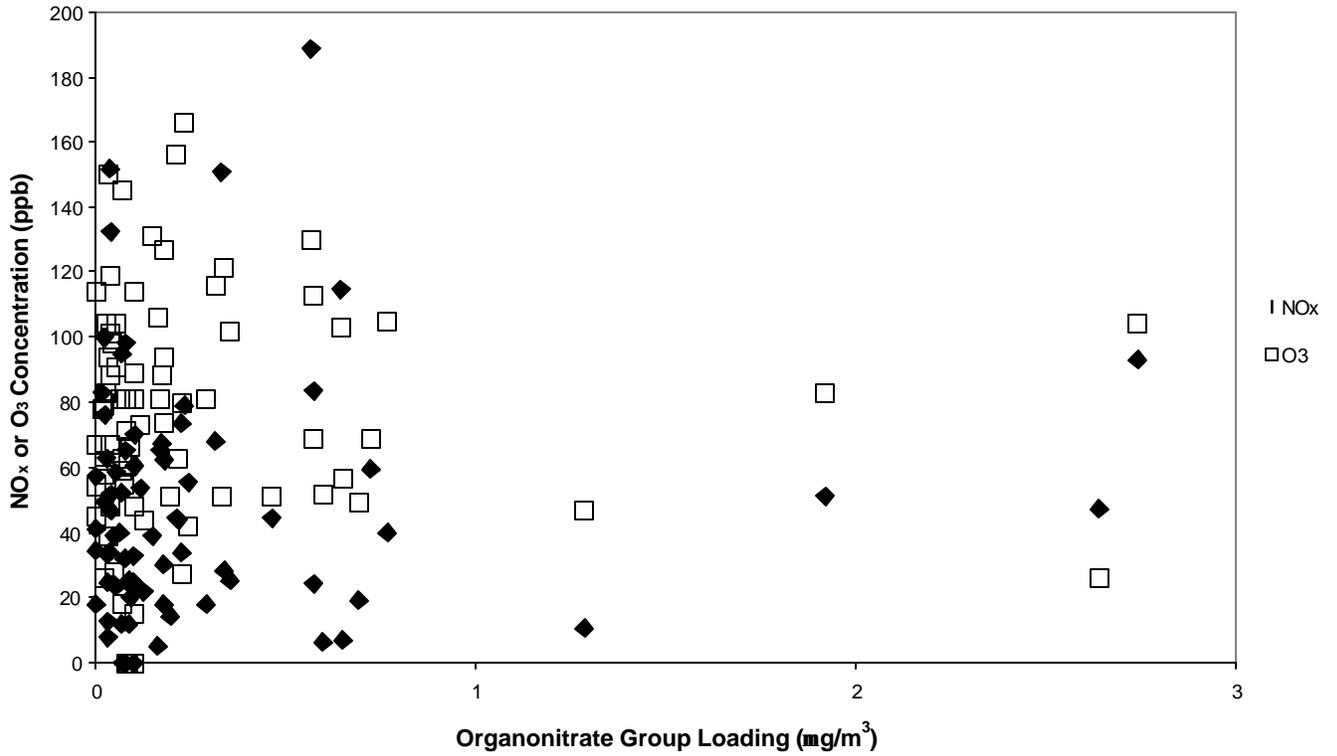


Figure 11. Organonitrate concentrations versus maximum daily concentration of NO<sub>x</sub> and O<sub>3</sub>, measured at the same or a nearby site.

## Conclusions

Measurements of the size distributions of organonitrates in fine atmospheric aerosol in Houston and estimates of organonitrate concentrations reveal that on most days, concentrations of organonitrates are relatively low, and are similar to concentrations observed in Los Angeles. Size distributions for most days peak in size fractions near 0.1  $\mu$ m, near 0.5  $\mu$ m, and/or near 1  $\mu$ m, consistent with observations in Los Angeles. However, on a number of days, very high concentrations of organonitrates were observed at the HRM3 and LaPorte sites, which can be source dominated. The spectra from these events suggest that the aerosol containing high organonitrate concentrations was acidic, hydrophilic, and contained high concentrations of organics. Because the spectra do not contain strong carbonyl absorbances, it is unlikely that the high organonitrate concentrations are due to the chemistry that is typical of urban secondary organic aerosol formation. Instead, the data suggest that the events are due either to primary emissions or unusual plume chemistry.

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