10.1 CHEMICAL CHARACTERIZATION OF PARTICULATE MATTER AT THE LA PORTE SITE USING AN AEROSOL MASS SPECTROMETER

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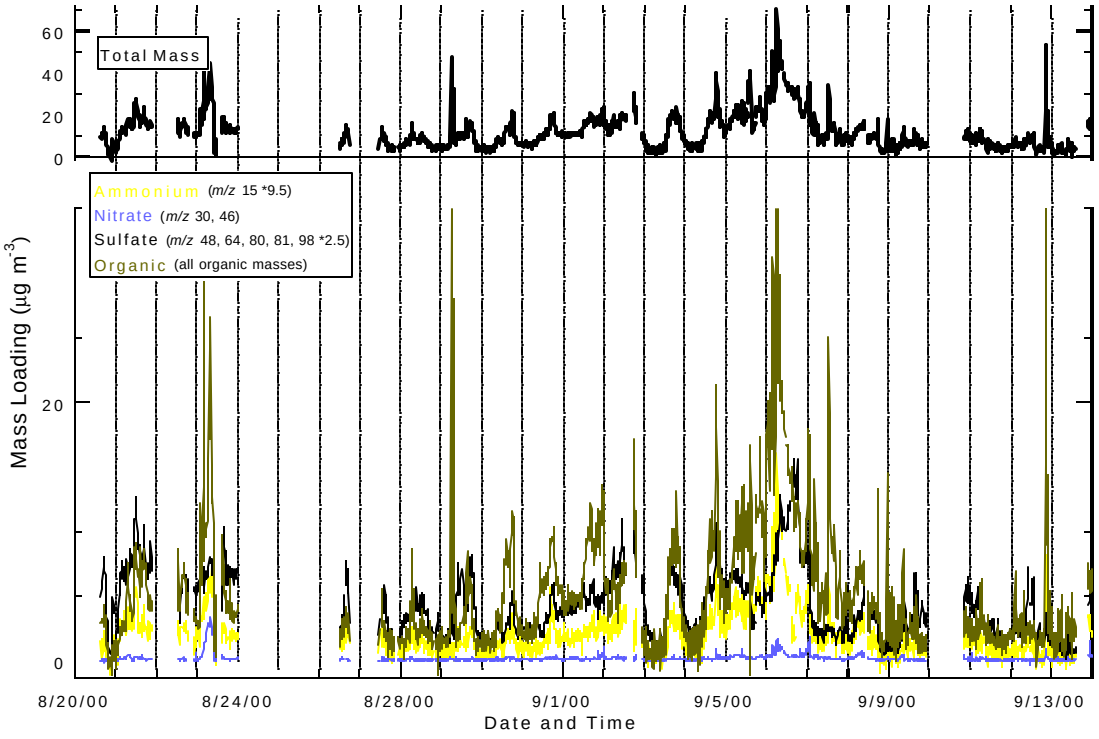
As part of the TEXAQS study, we deployed an aerosol mass spectrometer (AMS) at the La Porte site from 20 August 2000 until 15 September 2000. The AMS obtains real-time chemical composition data on aerosols using a quadrupole mass spectrometer equipped with electron ionization source. Quantitative mass loading data of the ensemble aerosol is obtained, along with individual particle size distributions for selected mass-to-charge ratios. The AMS deployed at La Porte obtained chemical composition data and particle size distributions 10 minute averaging times for the duration of the study. The total measured aerosol mass concentration ranged from approximately 2 μg m^{-3} to a high of ~70 μg m^{-3} on 6 September, known to be a biomass burning plume. Averaged over the study, the organic mass concentration made up ~30% of the total mass loading. The rest of the mass was made up of inorganic species, dominated by sulfate, which averaged ~40% of the total mass concentration.

During the study, changes in the chemical composition of the aerosol were governed to a large degree by meteorology. The study can be separated into several distinct periods with different meteorological conditions. From the period of 28 September to 4 October, the meteorology was characterized by a pattern where winds switched from an ocean breeze in the morning, to a land breeze in the afternoon. A different meteorology occurred on 5-7 September. During this time, winds came from the northeast.

Figure 1 shows a summary plot of the total mass concentration observed during the entire study, as well as the mass loading due to ammonium, sulfate, nitrate, and organic carbon. Ammonium and sulfate each contributed up to ~20 μg m^{-3} at their highest concentrations. Organic carbon contributed anywhere from 1-2 μg m^{-3}, to ~40 μg m^{-3} during the biomass burning plume associated with northeasterly winds on 6 September. The mass concentration of particulate nitrate was typically less than a few μg m^{-3} for the entire study, with the largest nitrate event occurring on 23 August. Small amounts of chloride were detected in the particles, typically less than one μg m^{-3}, with the largest value also detected on 23 August.

The total organic mass detected can be separated into several different organic aerosol types identified based on simple evaluation of mass spectral and size distribution data. Three organic particle types appear to be from discrete primary sources of organic aerosol.

Figure 1



One organic particle type displays mass spectra similar to those observed from diesel exhaust emissions. The temporal variation of this type shows sharp spikes, consistent with primary combustion sources and sharp plumes that drift pass. A second organic particle type is responsible for the largest particle mass concentration observed during the entire study, occurring during a fire episode on 5-6 September. These mass spectra exhibit characteristic peaks representative of markers for compounds from biomass burning, including levoglucosan and dehydroabietic acid. A third organic particle type observed during the study exhibits peaks in the mass spectra that are characteristic of fluorinated hydrocarbons. These spectra are similar to mass spectra of pump oil. This particle type contributes up to several μg m^{-3} to the ambient particle mass concentrations during certain days of the study. It is likely that this particle type is the result of a local source at the La Porte site. This particle type illustrates the importance of real-time mass spectrometric measurements, as a bulk filter measurement using gravimetric determination would not determine the presence of this local source contaminant.

During the period from 28 August through 4 September, a consistent meteorological pattern was observed where winds cycled from a sea breeze to a land breeze during the day. Each afternoon, the wind was blowing such that transport from the heavily industrialized ship channel to the La Porte site took place. During this time, another organic particle type was observed to exhibit a strong diurnal variation, with a mass contribution of anywhere from 1-8 μg m^{-3}, with the peak occurring during each afternoon. This particle type appears to be due to secondary aerosol chemistry occurring in the atmosphere, and resulting in organic vapor deposition into the particulate phase. The mass spectra of this particle type exhibits peaks characteristic of oxygenated organic compounds. In particular, dicarboxylic acids appear to be present. In addition to the organic composition, ammonium and sulfate are observed to correlate with the cycle.

Figure 2 shows an enlarged view of the total mass loading and the contribution from ammonium, sulfate, nitrate, and organic carbon during this time. During each day from 28 August to 4 September, the mass concentration of ammonium, sulfate, and organic carbon increased during the day and reached a maximum during the late afternoon/early evening. The mass loading then decreased into the evening. For the period from 30 August to 2 September, a gradually increasing background mass concentration of aerosol is observed. Although sulfate and organic carbon both exhibit the diurnal variation, the relative ratio between them changes, indicating different sources and perhaps different. On the evening of 2 September, rain was observed at the La Porte site. The elevated background disappeared subsequent to the rain showers. However, the diurnal cycle continued on 3-4 September, with substantially reduced background levels similar to that observed on 29-30 August.

Figure 2