P1.14 MEASUREMENTS OF PHOTOCHEMICAL SPECIES AT LA PORTE AIRPORT DURING TEXAQS-2000

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1. INTRODUCTION

The TEXAQS-2000 study was an effort to characterize the regional air chemistry of the Houston metropolitan area. This is a region with a large variety of intense emission sources. There are 1) the typical urban, mostly mobile, sources of NO_X and VOC, 2) coal-fired and gas-fired power plants which are point sources of NO_X and SO_2, and 3) areas with high concentrations of industrial activity. These industrial zones contain oil refineries, specialty chemical operations, fertilizer production operations, and other facilities that emit a wide spectrum of compounds. In addition, the location of the area - within a few tens of kilometers of Galveston Bay and the Gulf of Mexico - also provides for high temperatures, high humidities, high solar insolation, and a significant marine component with respect to the atmosphere. These conditions combine to make the region susceptible to intense air pollution episodes. In order to understand better the air chemistry of these episodes, a large number of surface sites and aircraft were deployed. One of the most intensively instrumented sites was located at the La Porte Municipal Airport from mid-August to mid-September, 2000. This airport is located 35 kilometers east of the Houston downtown area, about 10 kilometers west of Galveston Bay, and about 15 kilometers south-southeast of the heavily industrialized Houston Ship Channel area. In addition to extensive measurements from aerosol and remote sensing instrumentation, measurements of the gas-phase species NO, NO_2, NO_y, O_3, CO, SO_2, and surface meteorological variables were made from the top of a 10 meter tower.

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2. METEOROLOGICAL INFLUENCES

Temperatures during the study period ranged from 20 C to over 40 C, with the high temperature setting an all-time record for the area. Relative humidities ranged from about 24% to saturated, with an average of 75%. At the La Porte site, the average surface wind data were consistent with a regular offshore-onshore flow pattern. At sunrise, winds were light and variable, but toward mid-morning a south-easterly flow had set up with wind speed increasing to about 6 mps by mid-afternoon. At this time the wind direction started to move from south-easterly through south to a nearly westerly direction after midnight along with decreasing wind speeds. Northwesterly wind was regularly observed, but wind from the north through the northeast sector was not a common occurrence. Boundary layer heights were measured nearby with a 915 MHz profiler. On average, the data show an increase of the mixed layer from about 400 m after sunrise to a maximum of about 1600 m by mid-afternoon. Boundary layer heights to 2 km and higher were observed on occasion.

3. EMISSIONS CHARACTERISTICS

The influence of the urban area and associated mobile source emissions was clearly seen in the data. Levels of CO and NO_y peaked in the morning (0500 to 0900 CST), corresponding to a morning rush hour traffic pattern. Mixing ratios of these compounds were highly correlated with a measured ratio of CO to NO_y of approximately 8 that was consistent with the ratio estimated from mobile source emission inventory data. There was no evidence of an afternoon rush hour peak, probably because winds were from the southeast (i.e., Galveston Bay area) and because the mixed layer was still more than 1 kilometer deep. Maximum NO_y levels were seen in plumes of short duration (~1 hour) from nearby point sources. Levels of NO_y in excess of 90 ppbv were routinely

observed. Occasionally, these NO_y plumes were correlated with high levels of SO_2 or CO. These correlations provide an indication of the source of the plumes. For example, coal-fired power plant emissions usually have strong NO_y:SO_2 correlations while gas-fired power plants typically only emit NO_y. Power plants generally do not emit high levels of CO; the principal source of CO is vehicular traffic.

4. O_3 SYSTEMATICS

The diel O_3 pattern showed that, on average, O_3 levels rose from a low of 5-10 ppbv just before sunrise to a maximum of 80 ppbv at about 1400 CST. During the night O_3 generally did not go to 0 ppbv except for the plumes containing high levels of NO_y, which was a common occurrence. However, in the early morning on weekdays O_3 at La Porte almost always vanished because of reaction with fresh NO_x from rush hour traffic. The mid-afternoon peak that is typical of photochemically produced oxidants was also present in the O_3 data from La Porte. However, these afternoon O_3 levels varied widely. The typical southeasterly through southerly winds brought air from the Galveston Bay/Gulf of Mexico sector. Under these conditions peak O_3 levels were as low as 50 ppbv with the levels of the other trace gases correspondingly low. On occasion, however, episodes of highly elevated O_3 (>200 ppbv) were observed. These episodes appeared to be related to air that had originally passed over the industrialized Ship Channel area to the north and northwest and then either transported directly to the site or transported first over the northern part of Galveston Bay followed by a changing regional airflow that then brought the photochemically processed air over the La Porte measurements site. For this latter case on August 30, westerly flow apparently took the air parcel over the polluted Ship Channel in the early to mid morning period, but by early afternoon the wind had become light and variable. During this time the air parcel was over the northern part of Galveston Bay which allowed vigorous photochemistry to proceed with little depositional losses. Around 1530 CST the wind then shifted to an easterly-northeasterly direction which transported the plume over the La Porte site where the peak O_3 level observed was almost 220 ppbv. The high (>200 ppbv) O_3 values lasted from 1530 to almost 1730 CST which is well after the normal peak O_3 levels would be expected.

Differences in photochemical processing could also be discerned by combining the O_3 data with the ratio NO_x:NO_y. For the above example of August 30 at least two distinct peaks in O_3 were observed in the afternoon with slightly different NO_x:NO_y ratios. At 1330 CST O_3 peaked at 140 ppbv and the ratio NO_x:NO_y = 0.30. This is likely the O_3 that resulted from photochemical processing of the urban emissions in the region on this very hot and sunny day. The maximum O_3 of 215 ppbv was seen at about 1630 CST and was associated with a lower ratio NO_x:NO_y = 0.25. This lower ratio suggests a somewhat more photochemically processed air mass than the earlier plume, but the higher O_3 indicates a much greater initial reactivity. This reactivity likely was a result of the air mass acquiring reactive VOCs (e.g., ethylene and propylene) during transit over the Ship Channel earlier in the day.

5. SUMMARY

Based on the data collected from the four weeks of this study, it is clear that there are many factors that influence the air quality at the La Porte site. Certainly a wide range of air pollution episodes was observed at the site which was seen not only in the O_3 data, but also in the NO_x:NO_y data. These data suggest at least 3 distinct types of contributions to O_3 air quality at this site. The case seen most often - southeasterly to southerly air flow - shows relatively clean levels of most pollutants and relatively low levels of peak O_3. There is also a clear urban influence that is likely responsible for producing moderate to high levels of O_3, depending mostly on meteorological conditions. At the extreme are those rare episodes when the winds move highly polluted parcels from over the Ship Channel area at the right time of day to allow intense photochemical activity to occur prior to transport to La Porte. For these cases, timing is everything. If the parcels were transported at night, then not only would there not be photochemistry to produce O_3, but the O_3 that is already there would be removed by reaction with other pollutants in the air mass.