

# The Ozone of Houston in September 2013

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## Introduction

In the month of September 2013 the Hildebrandt Ruiz research group participated in the DISCOVER-AQ (Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality) field campaign in Houston, TX. This was organized by NASA and included several universities and research groups taking ground measurements as well as satellite and plane measurements. A schematic of the key measurement stations and flight paths is shown below in Figure 1. NASA organized this campaign to meet their goal of better understanding of satellite and plane measurements (easier to take over a large area) verses those taken on the ground (where the air quality matters the most). Funding for the ground work, however, came in part from the Texas Commission on Environmental Quality (TCEQ). Taking the role as the “Texas EPA,” the TCEQ is especially interested in the policies needed to keep large Texas cities in compliance with EPA’s national ambient air quality standards (NAAQS). Houston struggled for many years to meet these standards due to a large amount of oil refining and chemical production. While other cities still struggle, Houston now stays just below the standards thanks to policies which are made in smart ways based on air quality models and field measurements such as those from DISCOVER-AQ.



Figure 1 – Map and schematic of key measurement sites and flight paths for DISCOVER-AQ

In air quality it is important to know the emission sources for pollutants as well as the destination of important emissions. This is where GIS can be a big help in this field. There is a lot of work yet to do on understanding data taken during DISCOVER-AQ. A good place to start is in trying to understand the difference between a high and a low pollution day. There is a lot of variation in the levels of pollution in a city even with anthropogenic factors held constant. Anthropogenic factors do not vary by large amounts on a day to day or even month to month basis. They change slowly over the course of years. Meteorological conditions, on the other hand, can cause pollution to vary by large amounts in timeframes as short as hours.

There are many airborne pollutants which could be analyzed as part of this study but Ozone ( $O_3$ ) was chosen as the first and will be the only pollutant discussed in this project. Ozone is an important airborne pollutant because it is one of the six that are regulated by the Clean Air Act, the others being  $SO_2$ , Lead,  $NO_x$ , CO, and Particulate Matter (PM). Of these six, ozone and PM receive the most attention because their source includes formation from other compounds which are emitted. This makes these two pollutants harder to control. Ozone is formed from complex interactions between volatile organic compounds (VOCs) and oxides of nitrogen ( $NO_x$ ) and is not emitted directly. Both VOCs and  $NO_x$  have many emission sources but one that is harder to control is vehicle emissions. For this reason ozone is harder to control. However, for this reason ozone makes a good compound of choice for an air quality study because it is formed through the interaction of other pollutants and makes good surrogate for overall air quality.

## Data Sources

The bulk of this study uses data from the TCEQ. The TCEQ has monitoring stations (like the one pictured in Figure 2a) set up throughout Texas. In a big city like Houston there are many monitoring stations which are tracking multiple pollutants as well as other parameters such as those meteorological. The map of these stations for Houston is shown in Figure 2b where light blue represents a site which measures ozone.

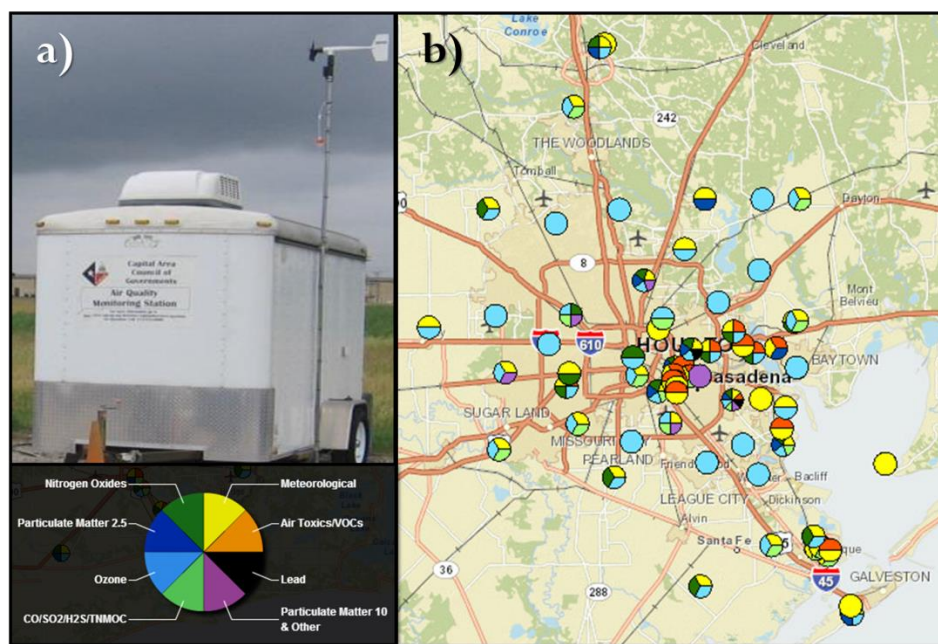


Figure 2 – a) a typical monitoring site. b) map of Houston from TCEQ's GeoTAM mapping service showing their monitoring sites and what each site monitors.

Thousands of data points were obtained from the TCEQ via their Texas Air Monitoring Information Service (TAMIS) web interface. Each of the 42 sites records an average ozone measurement hourly, which means that for the entire month each site contains  $24 \times 30 = 720$  measurements. There are 42 different sites which each contain 720 data points, meaning there is a lot of data to manage.

The other data source is a model called the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT). This model has an online interface and uses archived meteorological data to compute estimated back trajectories for a parcel of air that is found at a specific location and height. The requested time period can then be shown on a map to give a picture of the path a particle or parcel of air would have taken over that time period. Because there is a lot of room for error based on the accuracy of the archived meteorological data the model computes multiple back trajectories based on small changes made to conditions. The online service can output a picture of a GIS generated map or it can directly output a shape file. For this project the shape files were used since they allowed more flexibility in the maps produced.

## Methods

### Ozone data from TCEQ

Because of the sheer amount of data from the TCEQ there was a lot of room for decision on how to best represent the data. There is changing spatial data as well as data changes with time. Each of the 42 sites is going to have a diurnal cycle of ozone build up starting in the morning and continuing during the time when the sun is the most intense. A sample of this is shown in Figure 3 below. Data represented in this way could be interesting, especially if we focus on high pollution days and watch for trends at the sites that reach the highest concentrations. There are many ways to look at these data but this project will focus on looking at “high” and “low” pollution days and comparisons between them.

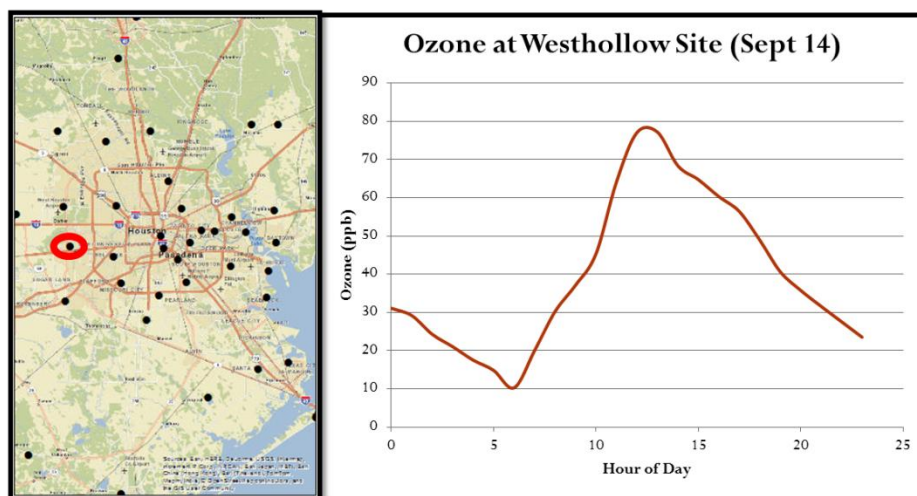


Figure 3 – A sample of a time series shown for one site during an entire day for the ozone concentrations at the Westhollow site on September 14<sup>th</sup>.

In this project the most meaningful analysis was found by going back and forth between time and spatial data. Initially, looking for trends in 30,000+ points of data could be daunting. Spatial data can be shown for specific time periods but finding meaningful time periods is the first step – so data were first analyzed with respect to time. To do this an excel-based function was created to find the highest concentration reached on each day at each site. Then, in a similar way an excel function charted which

days had the highest and lowest peaks for each site. In this way the “high” and “low” pollution days were found.

Once the high and low pollution days were found it was back to looking at spatial data and how to represent it. The most unappealing way (which is still frequently used) is to just overlay a map with textboxes that show concentrations. This method was not considered, but instead we looked at ways to interpolate spatial data from discrete measurements. The various attempts to represent the data are shown in Figure 4. Thiessen Polygons are shown first in Figure 4a. These do not do a poor job at estimating concentrations outside of those that are actually measured. For instance, the northernmost data point has a concentration of 20-25 and is shown connecting to a dark green polygon, representing a concentration of 0-5, as if there is a finite line where concentrations suddenly switch from high to low. Since this is not the case in real situations the Thiessen Polygons do not make a good spatial representation.

The Kriging method is shown next in Figure 4b. This method is a huge improvement on Kriging because transitions from high to low concentrations are made gradually over space. The representation does have some strange areas, however. In the area near the bottom there are some jagged edges which do not seem to be explained by the data we started with. It is not that these COULD not be real but it would be a big assumption to say that they are there. The best method of spatial interpolation seems to be the Spline method in Figure 4c. It seems to be the best guess of what the concentration profiles would actually look like. There are smooth transitions from higher to lower concentration like we would expect for well mixed air masses. This type of figure was chosen to conduct the analysis of ozone on different days.

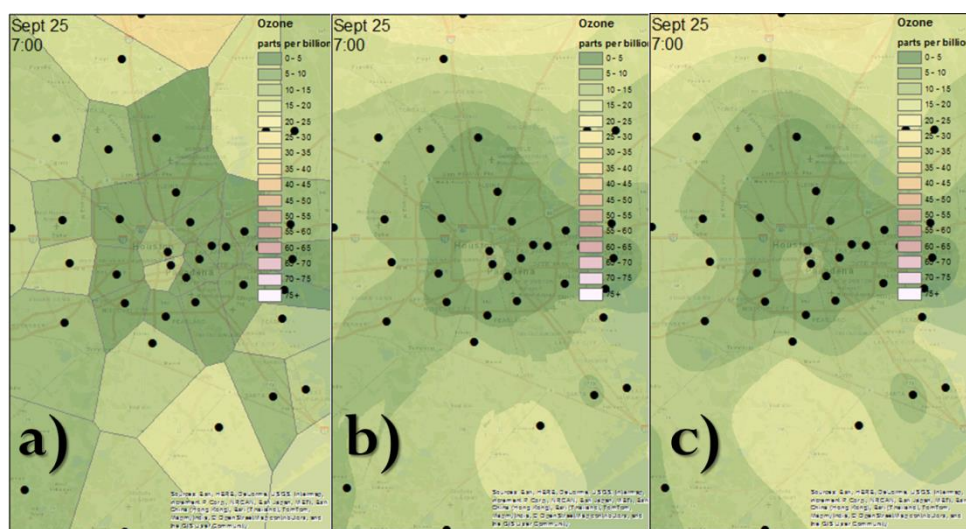


Figure 4 – the a) Thiessen Polygon, b) Kriging, and c) Spline methods of interpolating spatial data.

## HYSPLIT Model

To run the HYSPLIT model we first select the location of the trajectory endpoint, in this case downtown Houston. There are different meteorological data sets (GDAS, EDAS, NAM, etc) and GDAS was chosen for



this work. The user chooses between a single trajectory and an ensemble in which small variations are made to inputs to give multiple possibilities for trajectories. We chose to make ensembles to get a better picture of the possible trajectories. The user then chooses the trajectory ending height (can go up and down throughout the trajectory) as well as the back trajectory time frame. After selecting these options the online service runs and gives a shape file which can then be loaded to ArcGIS where it can be compared and analyzed along with the back trajectories of other days.

## Results

High and low pollution days are not compared using techniques discussed in Methods. Figure 5 (right) shows a closer view of the legend which is used throughout the remaining figures. The colors change in increments of 5 parts per billion from 0 up to 75 parts per billion. Everything above 75 parts per billion (ppb) is colored with the bottom color of the legend (very light pink). This 75 threshold is important because this is the National Ambient Air Quality Standard (NAAQS) for ozone for the EPA. The 75 ppb standard means that a monitor should not exceed 75 ppb on an 8 hour average more than 3 days a year. The 4<sup>th</sup> highest day is the one counted and this should not exceed 75 ppb. This is important because it means in the following figures that an exceedance of 75 ppb does not necessarily mean that Houston has become a non-compliance city – however it does mean that it may be close if the concentration is well above 75 ppb.

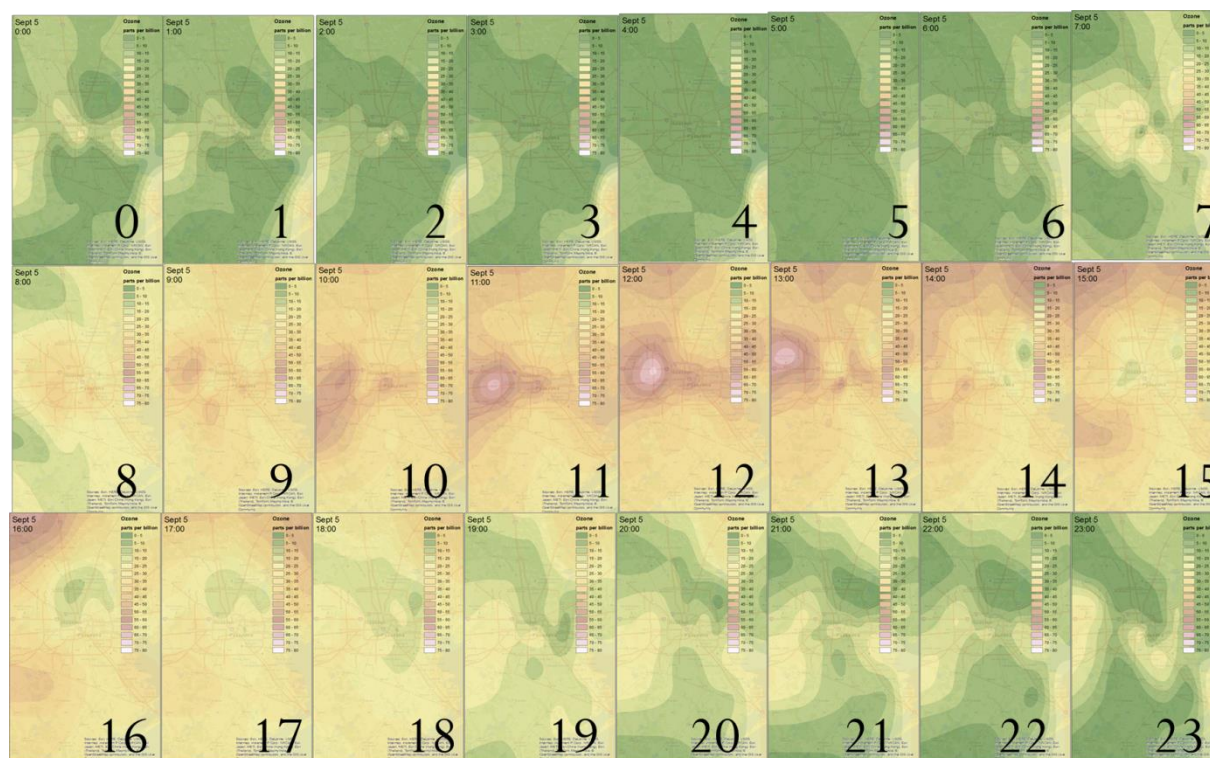
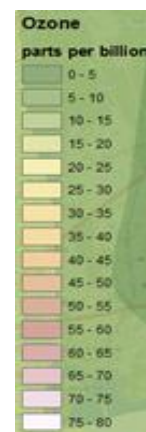


Figure 6 – the 24 hour progression of ozone concentrations on September 5<sup>th</sup>, 2013 (a cleaner day).

Figure 6 shows the progression of ozone concentrations over 24 hours on what was found to be a relatively clean day (September 5<sup>th</sup>, 2013). We note that the background concentrations during the night on this day are very low, most below 5 ppb by 5 am. Traffic emissions in combination with sunlight lead to ozone formation by around 7 am. Ozone production causes concentrations to continue to build almost homogeneously until a local “hotspot” begins to form around 10 or 11 am. This hotspot develops on West Houston, suggesting that there is either more ozone forming potential in that area or that there are westward winds causing downtown and East Houston’s pollution to accumulate in the west. In any case, the important part about this particular day is that this hotspot is blown away or dissipates after only a few hours. By 3 in the afternoon this hotspot has been blown out of Houston and can now disperse in a more rural area. There is a saying in the air quality field: “dilution is the solution to pollution.” On this cleaner day no build up has happened and Houston’s air remains relatively clean.

September 14<sup>th</sup> was chosen as an intermediate day. It had more widespread ozone levels above 75 ppb. Figure 7 shows the progression of ozone concentrations on this day. It is quickly noted that the background levels of ozone on this day start much higher than those on the clean day. Ozone levels are 5-10 ppb higher than those seen on the clean day before ozone production actually begins. This not only points to higher ozone on the previous day than was likely seen on the day previous to the clean day but also means there are likely more ozone precursors in the ambient air even before people hit the roads and start producing more. Another observation is that a hotspot begins to form in the same area and around the same time as in the clean day (around 11-12). Contrary to the clean day, however this hotspot is not quickly blown off the map. It seems to linger a little longer. At 2 pm part of this high concentration area seems to be blown north.

In general for Figure 7 it is seen that hotspots which form are not blown away but seem to linger. This is very apparent when comparing the hotspot which forms with that similar hotspot formed in the clean day. A more subtle effect is that this lack of meteorological ventilation leads to widespread increases of ozone across all of Houston. There are not significantly more places which exceed the 75 ppb EPA standard during the day but there are definitely more places which come close. To put it simply, there is a lot more red on the map. This comparison is good for understanding the difference between a clean day and one that is not quite so clean. However, neither day would cause any harm towards Houston meeting the EPA standard. Only at a few times and places does ozone exceed 75 ppb and it would definitely not do so during an 8 hour average. Houston is known to have struggled to meet these standards in the past so a look at a “bad” pollution day more interesting in that it gives insight into how close Houston may be currently to meeting the EPA standard. Figure 8 shows a bad pollution day (September 25<sup>th</sup>).

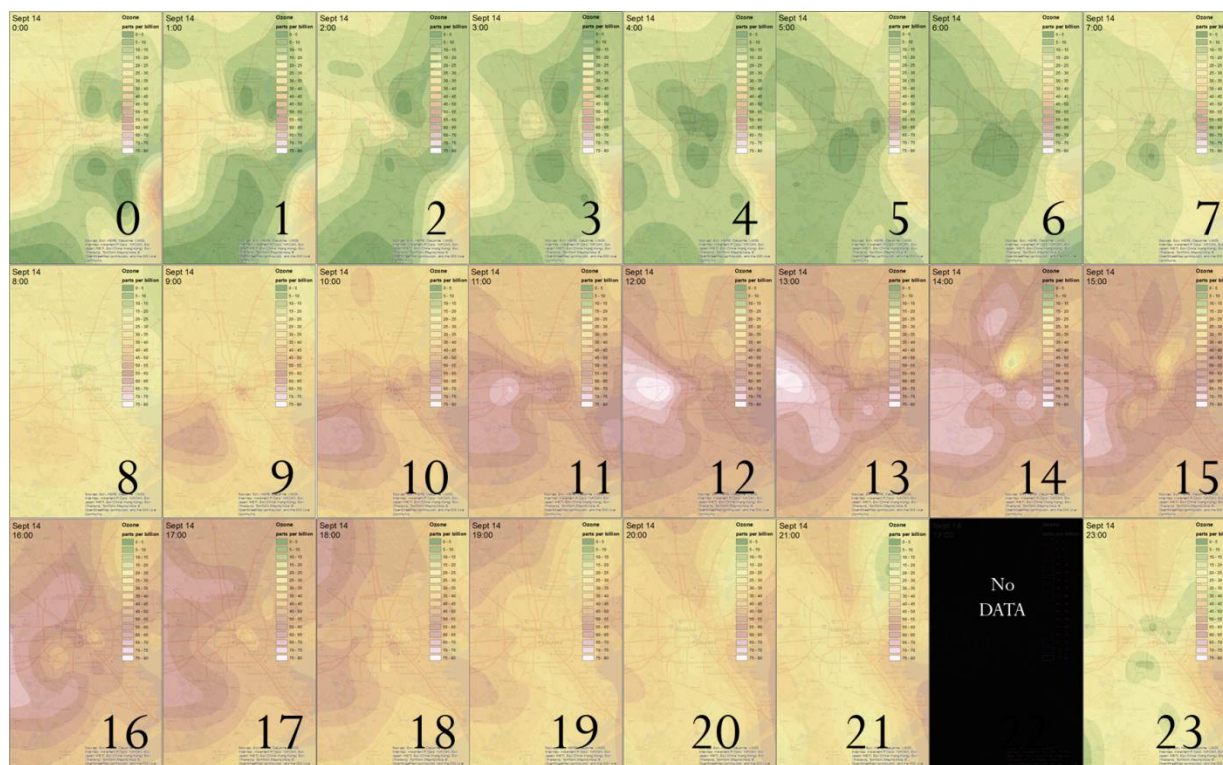


Figure 7 - the 24 hour progression of ozone concentrations on September 14<sup>th</sup>, 2013 (a less clean day).

Figure 8 shows what can happen when ozone gets out of control in Houston. It is interesting to note that for the most part this day starts with very *low* concentrations of ozone, similar to the clean day (Sept 5). One unusual part of this days beginning is that there appears to be a premature hotspot in the northwest part of Houston which is already there at midnight and continues throughout the night. This monitor was reading ozone at 52 ppb at midnight – very unusual. These points were almost thrown out as bad data until it was noticed that at a nearby location at the very north of Houston there is also a higher than normal reading of 22 ppb. It is not quite as high as 52 ppb but given the distance between the two it seems reasonable that there actually might somehow be a local hotspot of much higher than normal ozone in one location. As strange as this is at the beginning of this day it does not seem to be affecting ozone levels in the rest of Houston and at 7 am when ozone begins to form throughout the rest of Houston the effect of this hotspot vanishes.

Aside from that hotspot the rest of Houston is off to a clean start all the way until 6 am. From 7 to 9 am ozone production takes place throughout Houston. It is interesting to note that from these three time periods ozone production seems slower right in central Houston where we would expect some of the highest pollutant levels. This actually shows an important part of ozone production. As mentioned, ozone is formed from complex reactions between volatile organic compounds and oxides of nitrogen. However, an interesting thing happens at high concentrations of nitrogen oxides. A competing reaction, the formation of compounds called organic nitrates, begins to happen, causing ozone production to go down. This interesting phenomenon is seen very clearly during these three hours on this day.



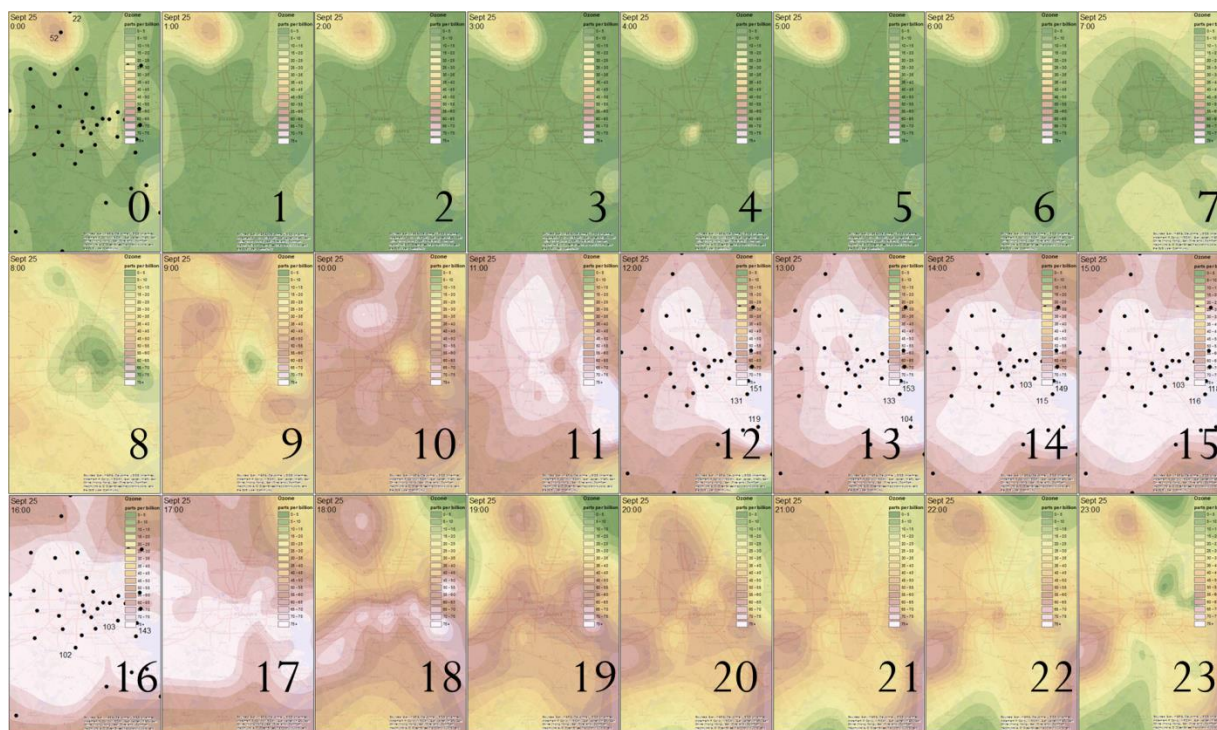


Figure 8 – the 24 hour progression of ozone concentrations on September 25<sup>th</sup>, 2013 (a polluted day).

On September 25<sup>th</sup> 2013 ozone first begins to exceed 75 ppb around 11 am and after this there is widespread exceedance all the way until 5 pm. Noteworthy concentrations have been labeled on the maps from noon to 4 pm. At 12 pm the three highest measurements were all by the bay and ship channel – an area known generally for high emissions as it contains refining and chemical manufacturing. These concentrations are 151, 131, and 119 ppb. An hour later these concentrations have not changed much are respectively 153, 133, and 104 ppb. An hour after that the sites that were previously measuring 153 and 133 ppb are still among the top three but one closer to downtown is now the third highest at 103 ppb. This, along with the following hours shows slow, westward movement of the more polluted air towards downtown and more populated areas. It is clear, however, from the maps that there is very little movement of air overall. This adds to the problem as lingering pollution has more time to react before being diluted away from the city.

In the 8 hour period between 10:30 am to 6:30 pm it looks like several sites in Houston exceeded the NAAQS for ozone on September 25<sup>th</sup>. It seems apparent that part of this was due to slow moving air which allowed pollutants to build rather than disperse into more rural air outside the city. However the change between these three days does not seem to be the only effect. September 14<sup>th</sup> clearly had higher ozone levels to begin with. The fact that on September 25<sup>th</sup> ozone levels jumped so rapidly when the sun came out suggests that there were already high levels of volatile organic compounds and oxides of nitrogen in the air before traffic really took off. These observations point to another cause of a high ozone day and to look at this we need to broaden the area we are looking at. To do this we use the HYSPLIT model.

Figure 9 shows the results from the HYSPLIT model for the three different days. The differences are pretty apparent. The dots show the progression of a hypothetical parcel of air over the three days before 3 pm on day indicated. The different paths show other potential paths based on small changes to the model. It is clear on September 5<sup>th</sup>, the cleanest day, that most of the air which made it to Houston had been floating out in the Gulf of Mexico for the past few days. It would be difficult to say whether it came from the south or east based on the result but it may have been a mix of the two. Marine air is cleaner than continental.

The polluted day, September 25<sup>th</sup>, is a much different picture. It seems that the air that made it to Houston on this day came through Louisiana, and it did so slowly. Slow moving continental air has plenty of time to pick up both biogenic and anthropogenic emissions. Anthropogenic emissions would include both volatile organic compounds and oxides of nitrogen – both the ingredients for ozone production. Biogenic emissions would not contain oxides of nitrogen, but can have plenty of volatile organic compounds, especially from an area so densely vegetated.

The in-between day, September 14<sup>th</sup>, seems to be a mix in air source as well as pollution levels. It seems that the air could have come either just offshore or just onshore. Likely it is a combination of these which means a combination of cleaner marine air and more polluted continental air. The two lines going northward all the way to Missouri and Minnesota indicate that there is potential that some of the air that made it to Houston came from the northern United States – though it is likely a small portion. The air covers more distance which means that it is moving quickly than on the other two days.

The general message from HYSPLIT is that we have more to explain differences in ozone levels than just local airflow patterns. Stagnation of air over Houston does seem to increase pollution levels but the rapid formation of ozone on the polluted day points to their being more ozone forming potential on this day. HYSPLIT shows that this air was purely continental and based on the high ozone observed on September 25<sup>th</sup> it seems likely that somewhere along the path that the air flowed it was able to pick up significant levels of pollution.

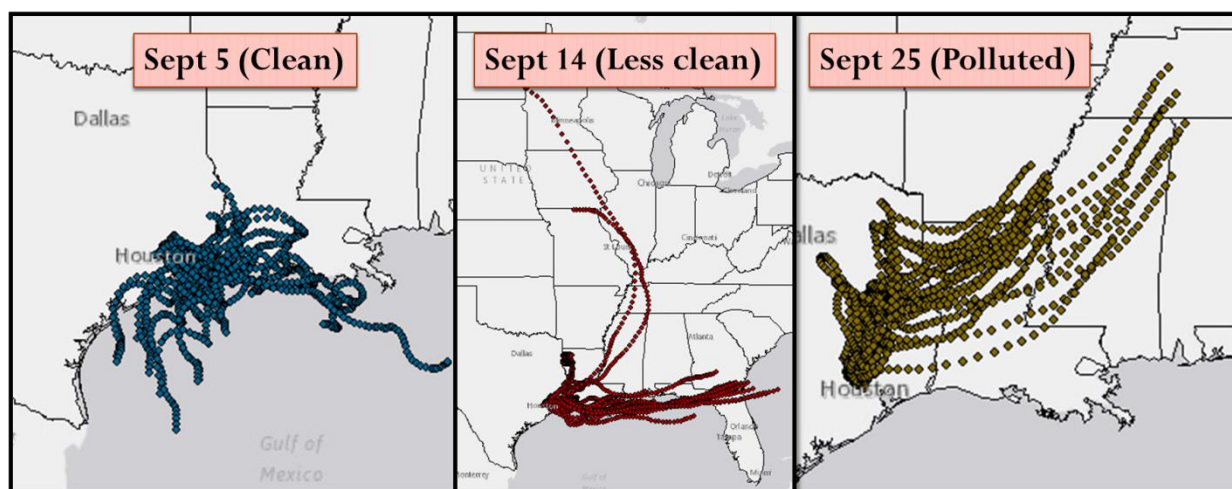


Figure 9 – results of the HYSPLIT model for the three different days.

## Conclusions and Future Work

Using GIS we have been able to get a better picture of pollution and its build up in Houston, TX. We were able to track the flow or lack of flow of plumes and masses of air as they moved through Houston. Both local and regional effects contribute to weather there is a buildup of pollution. Other effects, such as chemical changes to the atmosphere from different emissions and different amounts of sunlight were not looked at. However, the airflow into and within Houston and the surrounding area seems to be able to explain most of the changes that were observed. Part of the cause of a polluted day is limited airflow within Houston and the nearby areas. With no chance for dilution the ozone precursors are allowed to build up. Just as important though is the source of the air which is in Houston on a given day. Clean air from the Gulf of Mexico does not contain as much pollution. Air which travels slowly over land on its way to Houston has plenty of time to build up pollutants. Quick moving air over land also seems to have increased pollutants but also probably has more dilution taking place as there is more mixing happening. Understanding the flow of pollution in a busy and historically polluted city like Houston is critical to staying within air quality standards as they continue to tighten.

Looking at three different days was only a first look at understanding Houston's pollution. There are many more polluted days both in September 2013 and at other times that could be analyzed to get a better picture of how a polluted day happens and what can be done to mitigate these effects. The time series of individual sites may provide more insight as well. In addition, there are more pollutants than ozone that could be looked at for future work. Particulate matter would be the obvious next choice. It is one of the most harmful to human health and is also fairly well monitored. A similar approach to this study could be taken to track and analyze PM and get a better understanding of it. It would also be interesting to see if it has the same "bad" days as ozone did and whether the high concentrations are found in the same areas.

Another dataset that could be added to enhance what is already known would be census data. On both of the lower pollution days there was a hotspot which formed on the west side of Houston. It would be interesting to look at more days and find out how often this high ozone area appears. After this it would be interesting to see what type of area that part of Houston is. If it is residential then this could be harmful for those living there. If it is industrial then that may indicate that some of the industry activity may need to be cleaned up if future regulations come into place.

Any of these directions for future work would be very valuable but the work that went into this project so far has been very valuable too. Houston will probably always struggle to keep up with air quality standards but that is only because there is so much opportunity in Houston created by a high amount of chemical manufacturing and refining – both very important to our modern lifestyle. Because these things are so important to our lives we want to make sure that we understand the effects very well so that any regulations that must be put in place will be done in a very smart way that will keep the prices low on the things we rely on yet keep those who live in the city from suffering the consequences of production.

**Data Sources:**

Texas Commission on Environmental Quality:

<http://www5.tceq.state.tx.us/tamis/index.cfm?fuseaction=home.welcome>

HYSPLIT (maintained by the Air Research Lab of NOAA):

<http://ready.arl.noaa.gov/HYSPLIT.php>

ArcGIS for basemaps