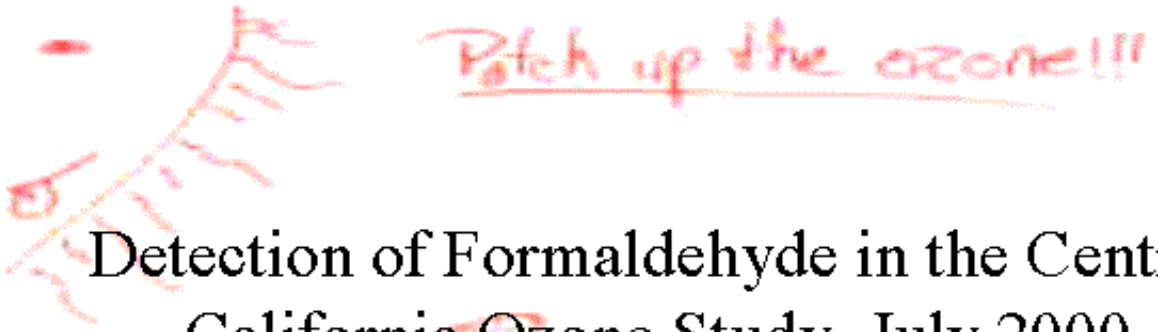

Detection of Formaldehyde in the Central California Ozone Study, July 2000

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Summer 2000

BROOKHAVEN
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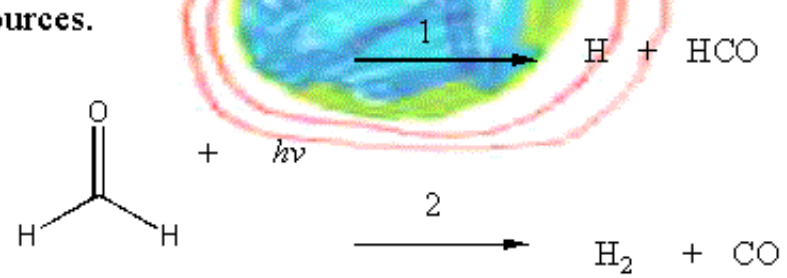
Formaldehyde Importance

- Formaldehyde is common to virtually all tropsopheric chemistry because it is an oxidation product of hydrocarbons and, upon photolysis, serves as a free radical source.

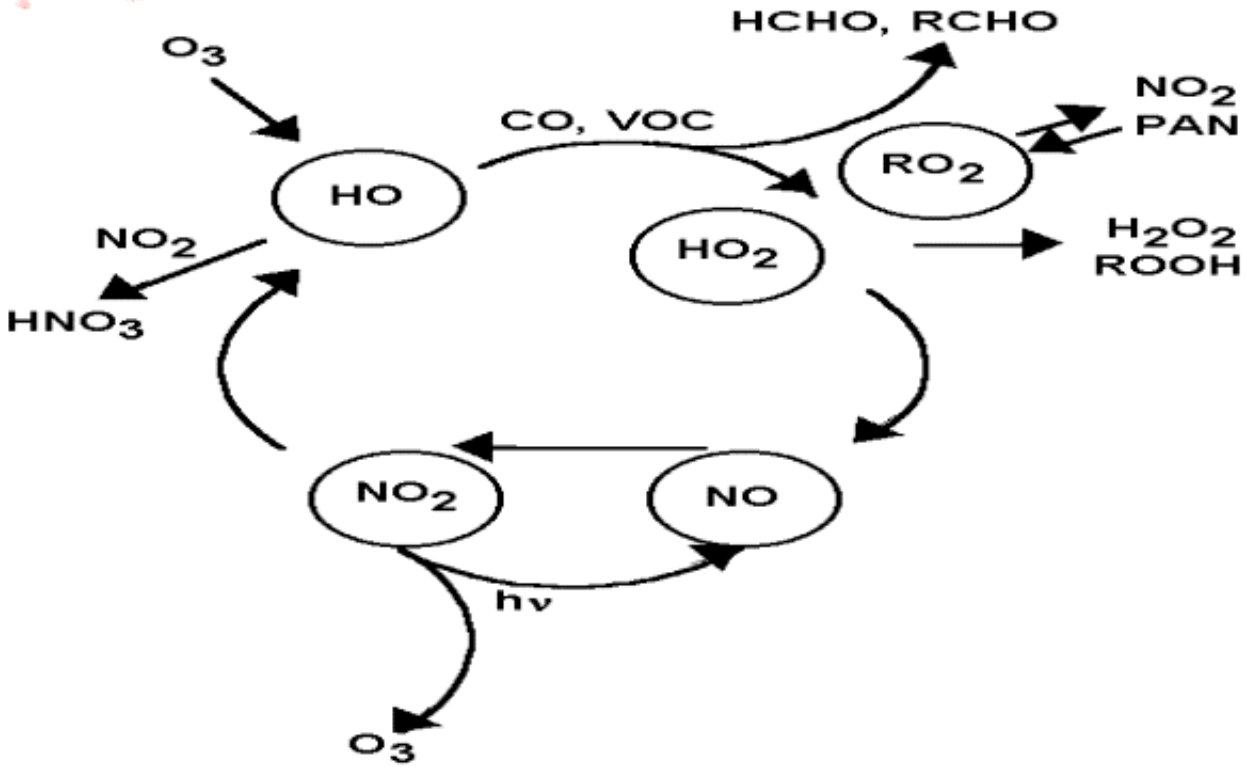
- It is also a major product of the OH-isoprene reaction and is emitted from various sources.



Pathway 1 predominates at shorter wavelengths and pathway 2 prevails at longer wavelengths. The wavelength range for photolysis is 301 to 356 nm

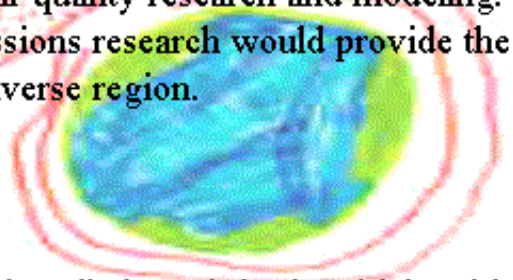
Patch up the ozone!!!

Ozone and Formaldehyde Relationship



Central California Ozone Study, July 2000

The Central California Ozone Study was commissioned in order to attain aerometric and emissions data for air quality research and modeling. An integrated effort of meteorological and emissions research would provide the needed data to represent the complexity of this diverse region.



The San Joaquin Valley is a distinct air basin which cultivates and hoards ozone. Peak O_3 concentrations have been observed in the Central Valley. And thus a study that focuses on the meteorological effects and air pollution of the valley would help to facilitate emission reduction and target the data and relationships needed to develop an accurate model.

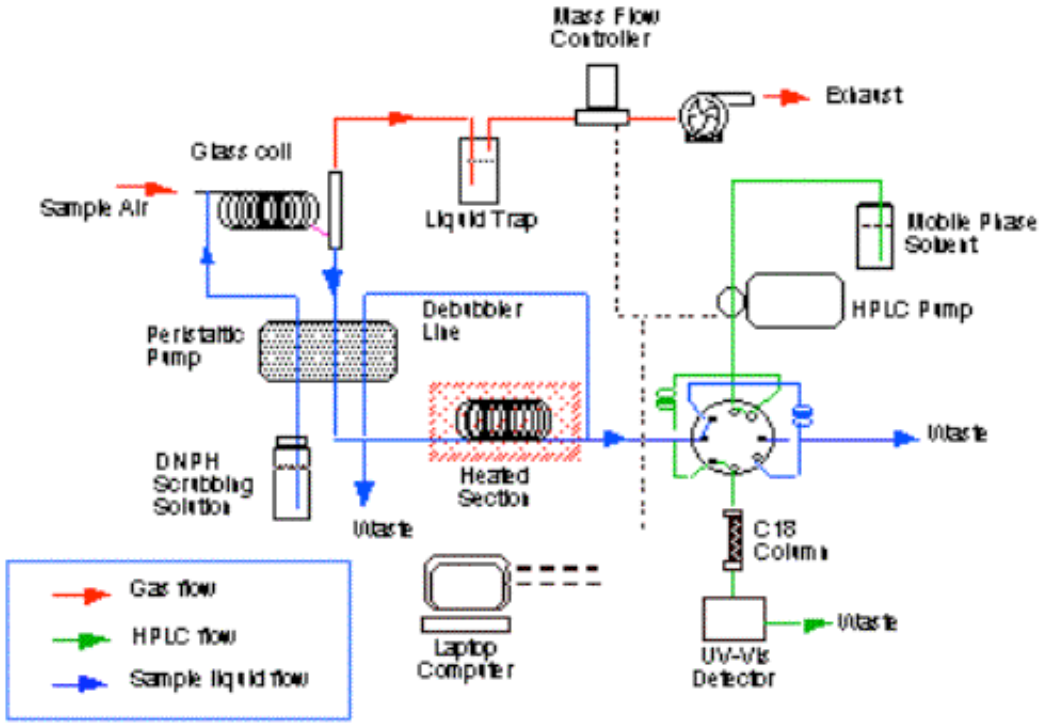
The Gulfstream Research Aircraft

The G-1 aircraft is considered a 'heavy aircraft' whose sole purpose is dedicated to research. It operates at low altitudes, below 10,000 ft, in order to sample within the boundary layer (surface to ~1 km) and the mixed layer. It is tailored with various instruments including those capable of making PAN, NOx, NOy, O_3, and, of course, HCHO measurements.

For the CCOS, a morning and afternoon flight schedule was executed for the intended days of the study, thus allowing for the collection of a complete data set and the vertical air distribution of air pollutants within the valley. Flight patterns included 3 days of the south central San Joaquin valley, which focused on Fresno and the immediate areas, and 1 day of western in-flow sampling of the Pacific Ocean air.

Instrumentation: HPLC

Schematic Diagram of the Aircraft Formaldehyde System



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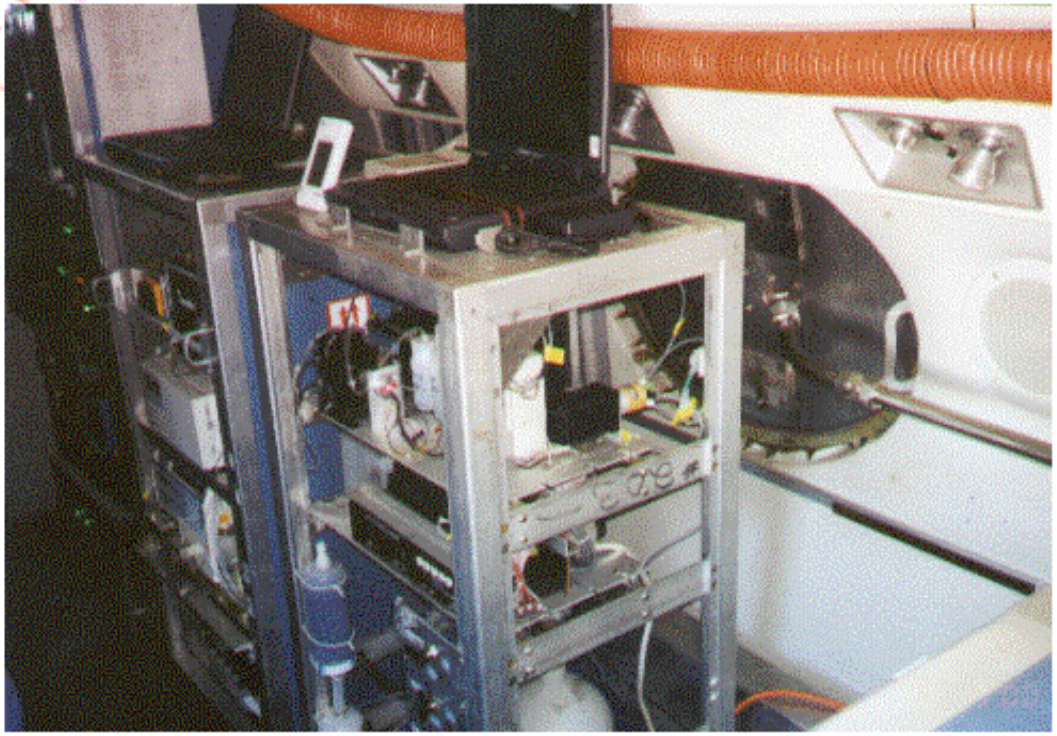
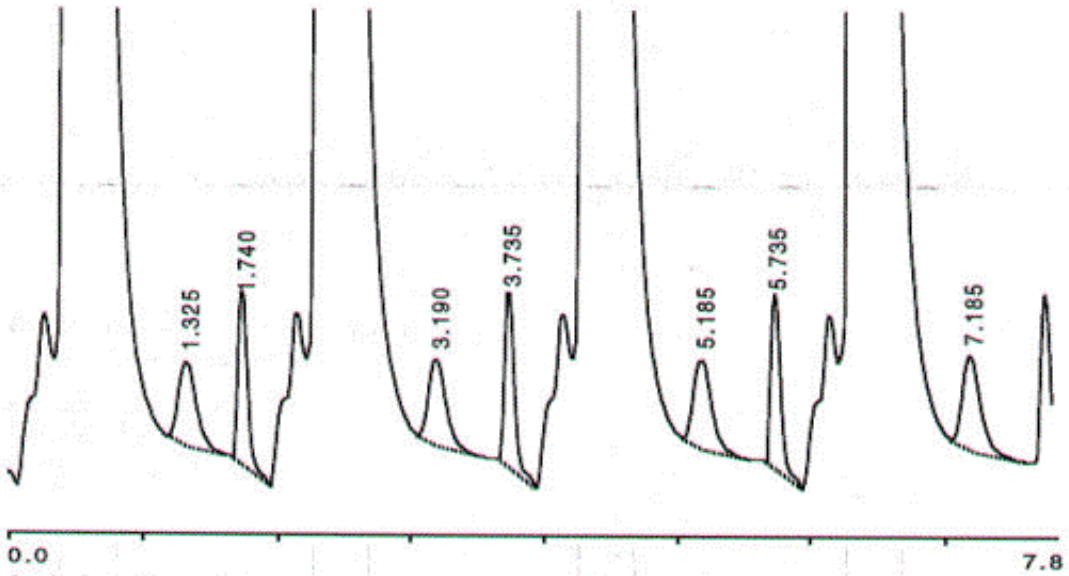
Formaldehyde Analyzer in G-1

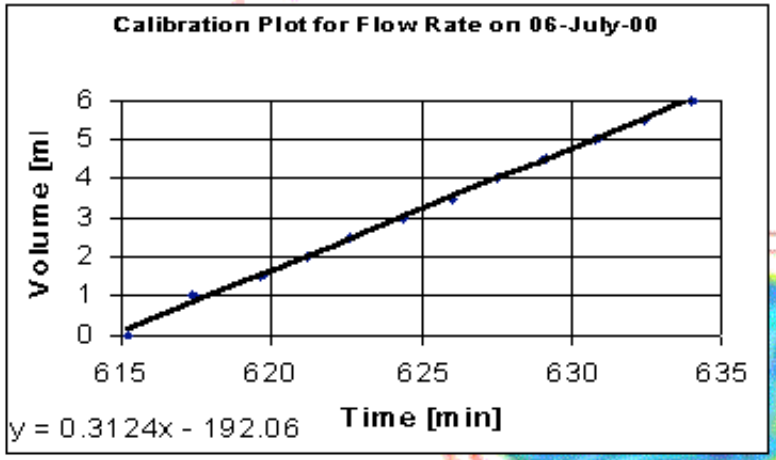


Sampling Technique



The sampling method and analysis procedure consists of scrubbing gaseous formaldehyde using a glass coil, then succeeding analysis utilized high performance liquid chromatography following derivatization with 2,4-dinitrophenylhydrazine. The HPLC injection occurred every 2 minutes and the resulting chromatogram were collected by Ranin Mac Integrator Software and subsequently integrated. A typical chromatogram (8 minutes elapsed, 4 injections) is shown above where formaldehyde is the first peak and the following peak is void volume.

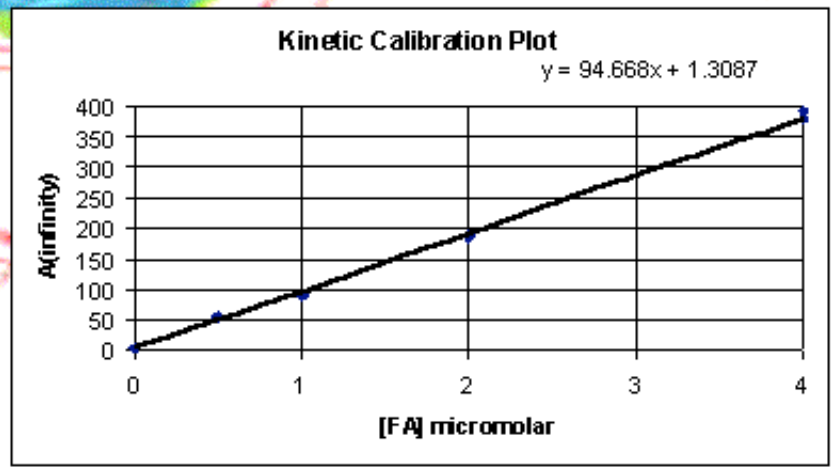
Calibration and Kinetics



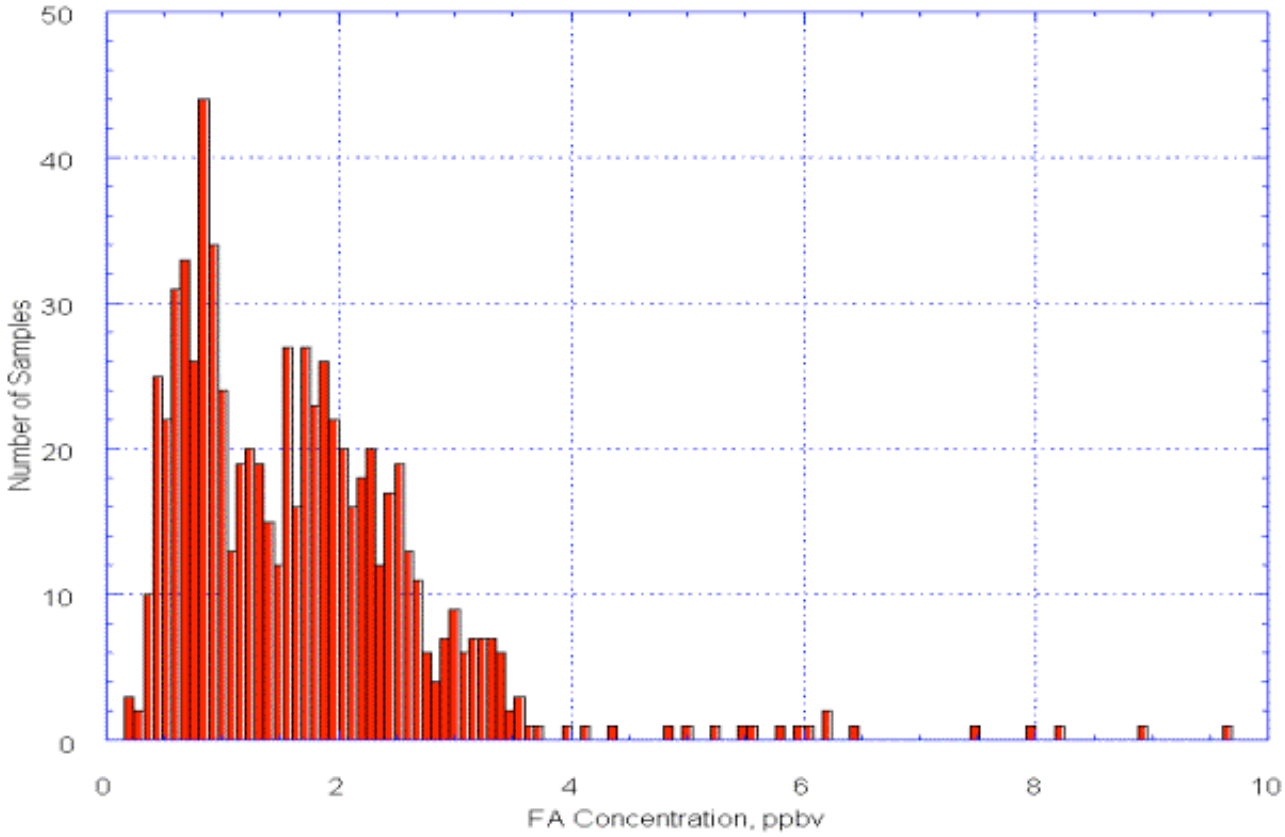
On July 6, the formaldehyde system was tested to determine the actual flow rate. This, in turn, was used to calculate the delay time which was found to be about 8 minutes. The calibration plot illustrates that the actual flow rate was 0.3124 ml/min.

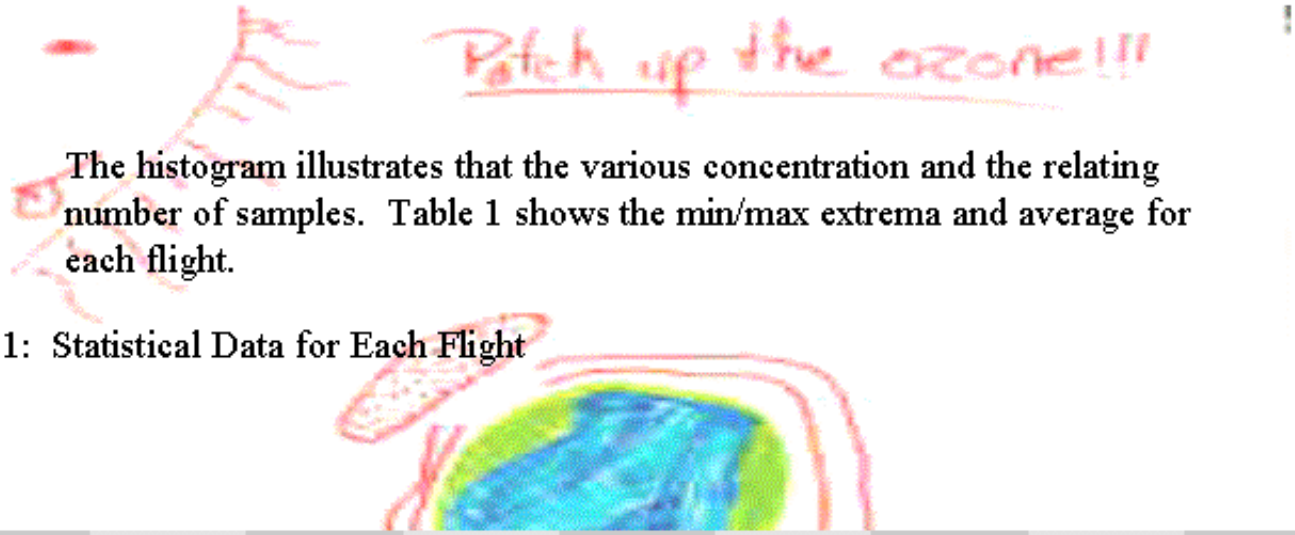
Experiments were carried out in the lab to ascertain the kinetic behavior of the derivatization of formaldehyde and DNPH.

The kinetic plot satisfies the equation, $\ln(\lambda_\infty-\lambda_0) = \ln(\lambda_\infty-\lambda)-kt$, thus the rate constant, k, is 0.001036 sec^{-1}.



Results


Distribution of [FA] for all CCOS Flights
Number of Samples
FA Concentration, ppbv
0
10
20
30
40
50
0
2
4
6
8
10

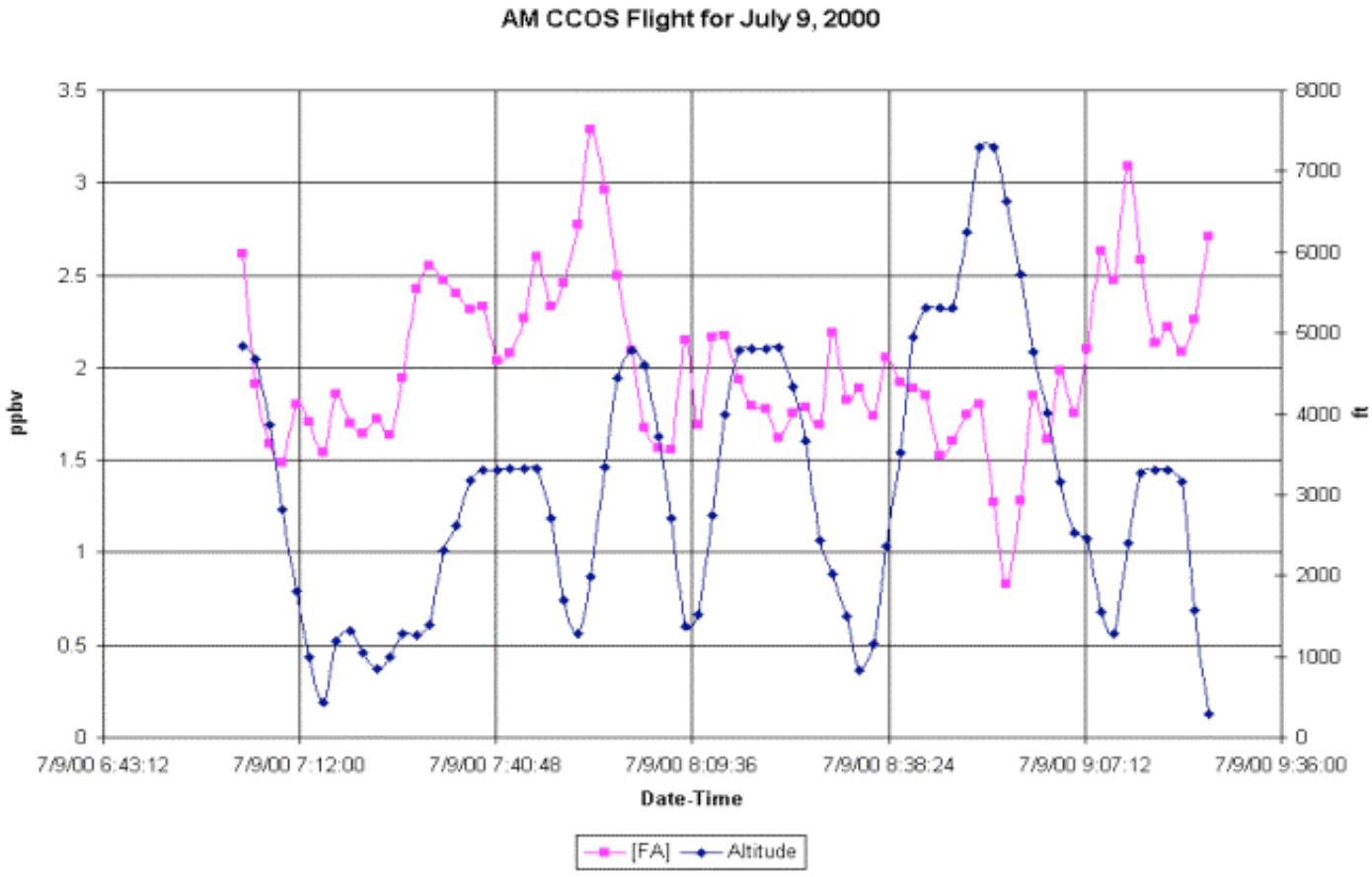


The histogram illustrates that the various concentration and the relating number of samples. Table 1 shows the min/max extrema and average for each flight.

Table 1: Statistical Data for Each Flight

(ppbv)	Jul 8 AM	Jul 8 PM	Jul 9 AM	Jul 9 PM	Jul 10 AM	Jul 10 PM	Jul 11 AM	Jul 11 PM
Min:	0.222	0.221	0.832	0.882	0.418	0.652	0.467	0.229
Max:	3.594	7.450	3.289	5.489	8.888	9.678	8.223	5.947
Median:	0.710	0.925	1.921	2.342	1.827	2.291	2.062	1.000
Average:	0.824	1.183	2.017	2.346	1.908	2.475	2.277	1.242
Std Dev:	0.493	0.859	0.443	0.832	1.218	1.364	1.397	0.961

Aircraft Data Relationship with Formaldehyde Concentration



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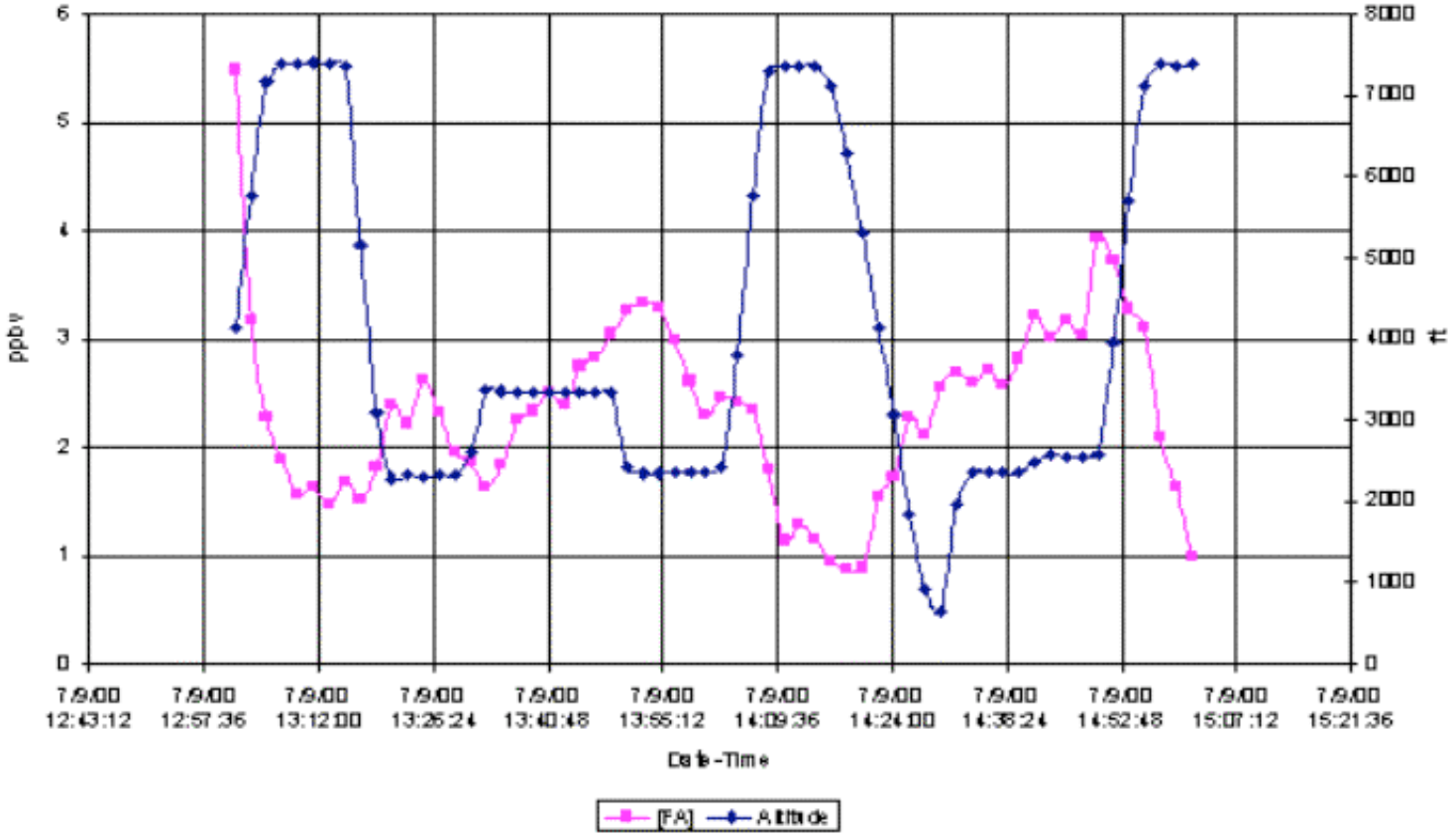
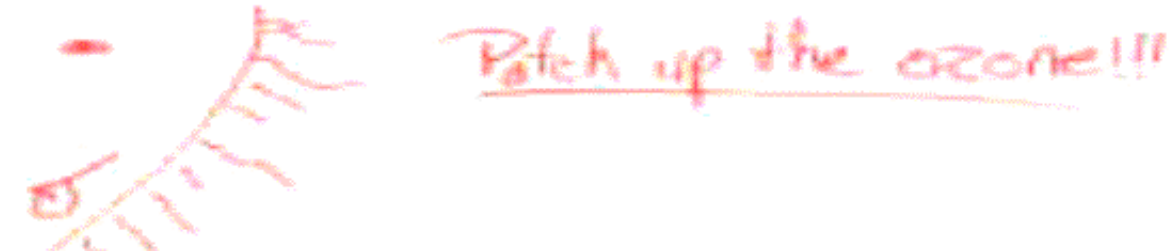
PM CCOS Flight for July 9, 2000

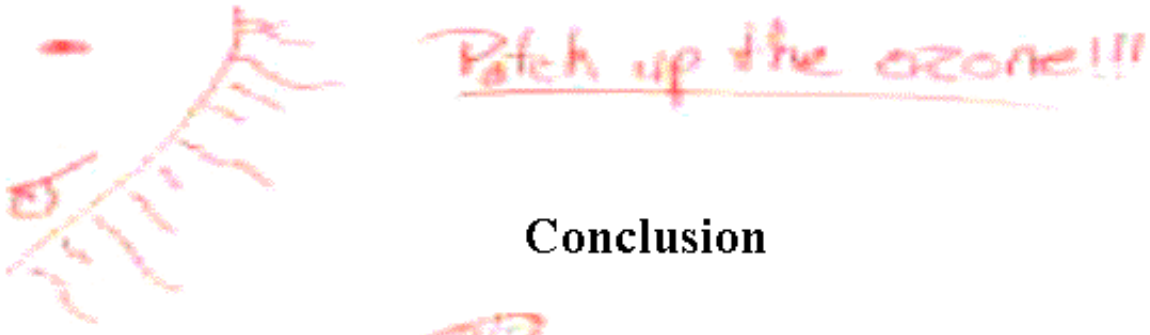




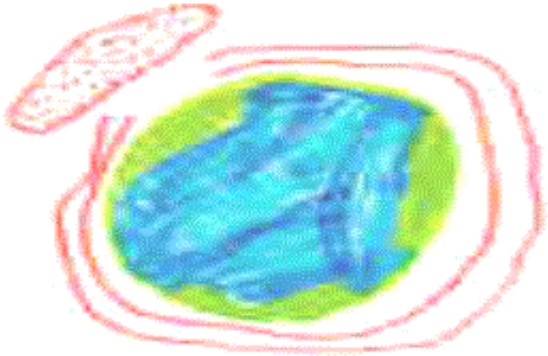
Plots of altitude, time, and concentration for the AM and PM flights of each day were constructed. An example of these plots, shown on the previous two slides, are given for July 9, 2000.

It can be generalized that for high altitudes, the formaldehyde concentration is low and for low altitudes, the formaldehyde concentration is high. This is manifested in the altitude/concentration/time plots of each flight.

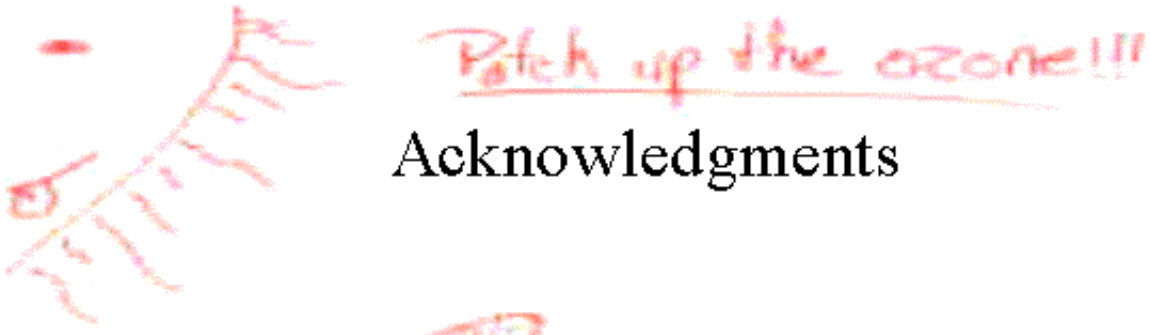
Assessing other data such as NOx, NOy, and ozone during the flights (note that the data in unavailable at this time) and correlating it with formaldehyde concentration will provide an improved understanding of emissions, transport, and their effects.



Conclusion

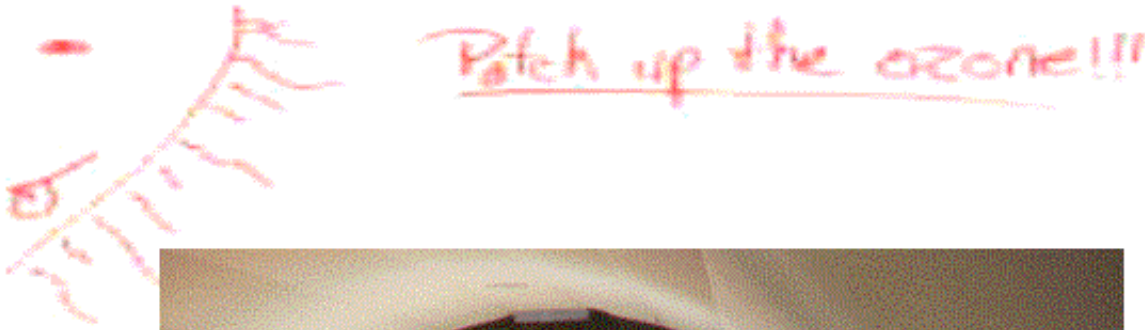


At this time, data is still being analyzed and therefore no conclusions can be drawn about the ozone and other greenhouse gases, their levels and effects in the San Joaquin Valley.

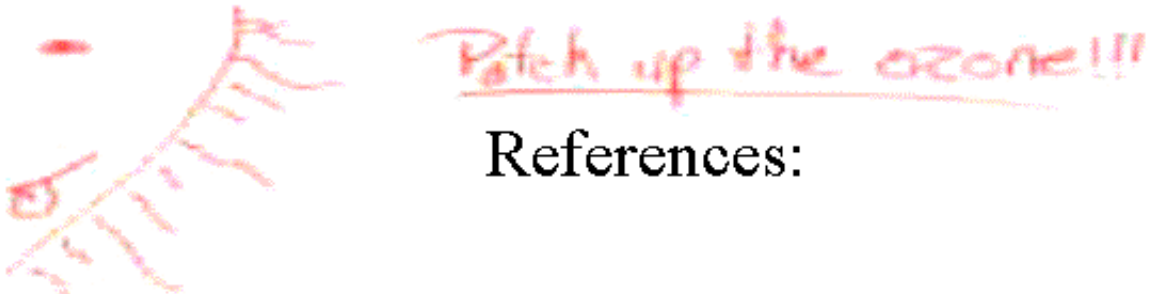


Acknowledgments

- Thanks is due to the Department of Energy and the Global Change Education Program.
- Sincere thanks my mentor, Yin-Nan Lee and Jeff Gaffney. Also to everyone on the Central California Ozone Study.
- Thanks to Song . . . . for everything!
- And of course, the Environmental Chemistry Division and Brookhaven National Laboratory.



The End



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