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DETECTION AND ANALYSIS OF CARBONYL COMPOUNDS IN RURAL CLOUDWATER

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Steven Bart Bertman

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ABSTRACT

technique for aqueous determination of А new aldehydes and ketones was field tested along with a new technique for ambient air analysis. The work was done during the summer of 1984 on Whiteface Mountain in Wilmington, NY. Both techniques utilized carbonyl derivitization as their 2,4-dinitrophenyl hydrazones and subsequent analysis by reversed phase HPLC. Analysis of the blank levels for the ambient air method shows the levels found to be non-detectable. The aqueous method worked well. Formaldehyde, acetaldehyde, and acetone were the only species found in cloud water. They were generally present in concentrations between 0.5 uM and 4 uM. Little fluctuation was observed throughout the sampling period. These data were then incorporated with routine data collected on cloud water and a kinetic analysis was performed.

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I would like to dedicate this work to my parents. Their constant love and support have been a source of strength without which my education could not have been possible. During the course of my work I have become indebted to many people for their support and assistance. Their help is greatly appreciated.

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Teven B. Restman

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INTRODUCTION

Aldehydes are known to be ubiquitous in our atmosphere. They exist primarily in urban areas. The primary source is the incomplete combustion of organic compounds mainly in automobiles, factories, and power They can be produced by photochemical reaction plants. of hydrocarbons with ambient molecules and/or radicals. They are reactants in many oxidation reactions involving ozone and radicals and can also be photochemically dissociated to form other radicals and products. This is an important occurrence for the formation of photochemical smog. (1) Aldehydes are thought to be health hazards as well as precursors and products in atmospheric reactions.

In order to set standards, to identify what levels of these compounds are significant, it is necessary to determine concentrations. Many techniques have been tried and tested. Most of these methods, though, only test for formaldehyde or perhaps for total aldehydes. The most useful and widely used technique for selective and quantitative analysis of aldehydes in ambient air is the derivitization reaction with 2,4-dinitrophenyl hydrazine (DNPH) followed by analysis of the resultant hydrazones by high performance liquid chromatography (HPLC). This is routinely used for ambient air analysis.(2-9)

DNP-NHNH2 + RCH=O ----> H2O + RCH=NNH-DNP

Originally, this reaction was carried out in a two-phase reaction mixture consisting of an aqueous phase and some organic phase. Kuwata, et al used an aqueous reaction mixture and extraction with chloroform. (3) This extraction was necessary because of the equilibrium nature of the reaction, as is shown above. Since water also a product of the reaction, a high concentration is of water gives incomplete conversion to the hydrazone product, as predicted by LeChatlier's principle. By extraction, the product is eliminated from the reaction solution. Hydrazones are more soluble in organic solvents than in water thus they move from the water solution to the chloroform. In this way, the reaction can be driven essentially to completion. (2)

Kuntz, et al developed a method whereby the DNPH is dissolved in acetonitrile and air is drawn through the solution. (4) The hydrazones form in this solution and since there is little water present the reaction proceeds to completion without the need for extraction. An

aliquot of this solution can then be <u>directly</u> injected into the HPLC. When extraction with chloroform is used, not only is separation of the two phases needed but the chloroform has to be evaporated and the resulting crystals dissolved in acetonitrile before injection into the HPLC. Obviously, this new method is much more efficient for air analysis because of the elimination of several steps and elimination of extraneous handling of the derivatives.

Recently, work has begun on a new method for trapping the hydrazones. This entails the coating of a solid phase with the acidified acetonitrile solution of DNPH and then sampling the air by drawing through the solid sorbent. Presumably, the organic carbonyls will selectively adhere to the DNPH impregnated on the solid surface. One method developed was the coating of silica gel with the solution. (10) There seems to be some problems with this in terms of loss of sample, and the collection efficiencies tend to be a bit lower than those the impinger method such as that used by Kuntz, et for Kuwata and coworkers used cartridges with al. (4)nonpolar Cl8 packing instead of the polar silica gel. (8) Percent recovery is much better than that for the silica and chromatograms obtained from the C18 cartridges gel are cleaner with less interference than the chromatograms obtained from the impinger method. (11,22) These

cartridges are already used for concentrating components from solutions, usually from biological systems. (8,12) These cartridges were field tested during the summer of 1984 on Whiteface Mountain and the results are reported here.

With all the work being done to develop and compare methods for gaseous determination of aldehydes, it is unusual that much less work is directed toward the determination of these levels in aqueous samples such as in cloud and rain water. Many of the reactions which occur in the atmosphere probably occur in the aqueous phase and there is a complex relationship between gaseous pollutants and aqueous pollutants. For example, Kok has shown that the levels of aqueous hydrogen peroxide tend to increase after periods of photochemical smog. (13) For the carbonyl compounds, current techniques test for formaldehyde levels only, in cloud and rain water. (33)

In order to measure aldehyde levels other than formaldehyde, several new techniques for determining aqueous concentrations were investigated during Spring,1984 and they are reported here. One is essentially a variation on the method for gaseous determination using the C18 cartridges. All take advantage of the efficiency and selectivity of the DNPH method.

In order to develop models and mechanisms for the numerous processes which occur in the atmosphere, simulateous data need to be obtained for as many concentrations and conditions as possible. In this way trends can be seen and equilibrium and kinetic models can If all the components of a certain be tested. equilibrium are measured, they can be checked against what might be predicted by theory. This information can then show whether or not there is some interference occurring. Data on other conditions may be able to suggest some reason for this interference. Data were collected in this manner on Whiteface Mountain during July-August 1984. SUNYA's Atmospheric Sciences Research Center Field Station in Wilmington, NY has the facilities to monitor many conditions. Cloud water concentrations of S(IV), SO2, NOx, H2O2, pH, inorganic ions, ozone, and HCHO, are collected along with weather information. The methods for aqueous analysis were also field tested.

Ultimately, a complete model of atmospheric reactions is desired. For the aldehyde system, as with other specific systems, certain reactions are more meaningful than others. Aldehydes are known to form addition products with S(IV) in acidic, aqueous solution.

RCHO + HSO3- ----> RCHOHSO3-

There is some speculation that this phenomenon may interfere with the oxidation of S(IV) in cloud and rain droplets, a major source of acidic precipitation. (14-18) Data from analyses performed for the ASRC were collected for the purpose of modeling the cloudwater system. Simultaneous data of the following concentrations were collected: H2O2, S(IV), pH, aldehydes. This kinetic study is an example of one of the ways in which the data could be analyzed.

EXPERIMENTAL

CHEMICALS

<u>Acetonitrile (ACN)</u>: Burdick and Jackson HPLC grade ACN was used for reagent preparation and as a solvent for analysis.

<u>2,4-dinitrophenylhydrazine (DNPH)</u>: Eastman Organic Chemicals; recrystalized twice before use.

Sep-Pak C18 cartridges: Waters Associates; Milford, MA

INSTRUMENTATION AND APPARATUS

High Performance Liquid Chromatography:

Analysis was done on a Varian 5000 HPLC equipped with a 254nm uv detector and connected to a Tracor 970A variable wavelength detector for monitoring at 360nm. Samples were run isocratically at 65%/35% ACN/water at a flow rate of 1.5 ml/min on a 25cm x 4.6cm 10 micron Alltech C18 column.

Cartridge Preparation:

The air cartridges were prepared using the method described by Kuwata, et al.(8) A reagent solution consisting of 0.2% DNPH and 1% H3PO4 in Acetonitrile was made. 2.0 ml of this was then injected through the cartridges at a flow rate of 2 ml/min. The cartridges were dried under vacuum and hooked directly to a stream of nitrogen. The dried cartridges were capped with glass rods and refrigerated until they were used.

Pump:

An SKC model 224-02 universal sampler was used for air sampling.

SAMPLING PROCEDURES

Gaseous:

We found that only one cartridge needed to be used for air sampling. The cartridge was hooked up to the hand held pump and air was sampled at a flow rate of 0.5 liters/min for 1.5 hours. An auxilary line was run out of a high volume line which the ASRC used for determining SO2 and NOx. The pump automatically corrected the flow and kept it steady at 0.5 l/min. It was calibrated using a bubble flow meter at least once before each sampling period. After sampling, the cartridge was capped off with glass rods and refrigerated until analysis, within five days. For analysis, the cartridge was leached out with 2 ml ACN and this solution was run through the HPLC.

Aqueous (cloud and rain water):

For the first aqueous method a cartridge was used for

extraction. The reagent solution used by Kuwata et al also used at first, 0.5g recrystallized DNPH was was dissolved in 500 ml of 2N HCl. (3) This solution was then extracted twice with CCl4 (rather than chloroform) to eliminate any hydrazones formed from impurities in the Two milliliters of the solution to be analyzed water. was combined with 1.0 ml of this reagent solution. The resulting 3 ml was then injected through a Cl8 cartridge extract the water. The cartridge was washed with 2.0 to of acetonitrile to leach out the hydrazones. m1 The hydrazones, then in an acetonitrile solution, could be directly analyzed by HPLC. The second reagent solution used H3PO4 in place of HCl. The third and final method did not used cartridge extraction. The same solution made for air cartridge preparation was used as a reagent. solution. In this case, 1.5 ml of the solution to be analyzed was added to 0.5 ml of this reagent solution. The resultant mixture was then analyzed directly by HPLC.

Field Work:

Samples of cloud water were taken from the cloud water collectors atop the field station observatory at the summit of Whiteface Mountain. They were taken every one to two hours during cloud cover events when collection was possible. After the samples were stabilized by derivitization with the DNPH solution, they were stored and refrigerated. Since there was no HPLC at

the ASRC field station, the samples had to be stored until they were able to be transported from Wilmington, NY to Schenectady, NY. Transportation and analysis was generally accomplished within five days of sampling.

General Cloud Water Sampling:

Several analyses were performed for the ASRC during the summer. Determination of S(IV) and HCHO concentrations for routine cloud water samples were run regularly. Periodically, H2O2, pH, and particulate concentration determinations were also performed.

Cloud water impacted on the cloud water collectors which were basically a system of thin, teflon strings stretched between two plates. The droplets, once heavy enough, would run down the strings into a funnel at the bottom of the plates. The funnel was connected to a long tube which ran down into the lab from the roof of the observatory. The tubes emptied directly into glass pH electrodes corrected for temperature. Thus the pH of the cloud water was continually being monitored. The electrodes had to be calibrated every 6-12 hours. During the summer of 1984, two types of cloud water collectors were being used. The passive system was designed by the ASRC. (19) These collectors could not differentiate between rain and cloud water when it started to rain. The other collectors were being tested by the ASRC. They

used a motorized fan to draw clouds in and past a similar teflon mesh of strings. This system was supposed to eliminate rain from the water which is analyzed. Both collectors were run simultaneously to see if there would be any difference in the chemistry of the water collected.

Other analytical techniques:

Aqueous hydrogen peroxide was determined using a relatively new technique. (20) Parahydroxyphenyl acetic acid (POPHA), in the presence of the enzyme peroxidase, reacts with hydrogen peroxide to form a fluorescent dimer which can then be monitored. The determination of H2O2 was done on the summit of the mountain immediately after the water came into the lab. This is done to minimize the degree of natural degradation of this reactive compound.

The other tests waited until the samples were taken down to the main lab further down the mountain. The chemiluminescent technique for formaldehyde involves the reaction with gallic acid. This reaction forms several products and is not very well characterized. (34)

The technique for S(IV) utilized a standard technique. (21) Sulfur (IV) was stabilized with a formaldehyde solution as soon as the sample came into the lab. The stabilized sample was then transported with the others down the mountain. During analysis, the addition product is cleaved by 2N NaOH into free formaldehyde and free bisulfite ion. Pararosaniline hydrochloride then reacts with the bisulfite ion to form a dark violet product which is monitored. Formaldehyde is needed for the color development of this product. The problem with this method is that it does not discriminate between the S(IV) which comes into the lab free and that which is already tied up as the addition product. The analysis is for <u>total</u> S(IV) which includes HSO3-, H2SO3, SO3(2-), as well as the aldehyde addition products present.

RESULTS AND DISCUSSION

Aqueous cartridge results:

As was shown, the derivitization of aldehydes by DNPH is catalyzed by acid. Scoggins tested three acids, HCl, H2SO4, and H3PO4, to determine which acid gives the best results in water and at what concentration. He determined that 0.5M to 1.5M HCl gives the best recovery of the hydrazones. (24) For the first aqueous method, the HCl solution used by Kuwata, et al was made up. (13)

When this was used, though, the HCl was found to alter the cartridges in such a way as to cause some of the Cl8 packing to come through when the hydrazones were dissolved out with ACN. This has severe implications with regard to the use of the HPLC. When the cartridges are prepared for air sampling according to Kuwata et al, phosphoric acid is used in place of HCl. (8) Originally it was believed that this switch was made because H3PO4 is a much less volatile acid than HCl. Thus, the acid will tend to stay on the cartridge better when sampling is done, facilitating the catalysis. It may also be true that H3PO4 is not as detrimental to the cartridges as the HCl was found to be.

To test this, parallel tests were run by injecting, in sequence, 2ml ACN, 5ml water, 3ml of acid (either HCl or H3PO4), and then 2ml more ACN. When the HCl was injected, packing came out. When the H3PO4 was injected, no packing came out. It would seem, then that the H3PO4 should be used. However, there are also problems with this. First, DNPH is less soluble in H3PO4 than in the HCl. Second, H3PO4 is a weaker acid than HCl and this may affect the reaction efficiency.

When the aqueous phosphoric acid solution of DNPH was used for derivitization, the hydrazones were retained well on the cartridge and the water was passed through efficiently. There were no derivatives detectable in the water which came through. However, the reagent solution itself was unstable and the DNPH constantly precipitated from solution making it a cumbersome working solution. It had to be filtered often. More importantly, the hydrazones were found to be unstable when formed in an aqueous reagent solution.

Aqueous reagent solutions were tested for efficiency and stability. (Table 1) The derivitized solutions showed considerable decay over a period of only a week. The solutions obtained after extraction of the derivatives from the water by cartridge are about 60%

better (more stable) than the solutions which had no extraction. This makes sense considering the interference water plays in the reaction, but even the extracted solutions showed significant decay.

As a result of these findings, a different approach was tried. Stability of the hydrazone solutions was especially important in this work because they had to be stored and transported. Since Kuntz, et al found that an ACN solution could be used in an impinger for ambient air sampling, we thought that the same idea could be used for the water sampling. Once again, the ACN solution used for cartridge preparation was used for derivitization. It was found that when no extraction was used, the ACN/H20 solutions were efficient at derivative formation and the derivatives were stable over time. The stability was also checked using some field samples collected in July. (Table 2) Therefore, the method used for a majority of the summer consisted of direct addition of the cloud water to an aliquot of the ACN solution of DNPH. (see experimental section)

Air Cartridge Sampling Results:

As was mentioned, the Cl8 cartridge technique for ambient air analysis was field tested this summer. They were used not only on Whiteface Mountain but also daily in Schenectady. Frequent blank cartridges were

sacrificed and leached for analysis. Standard deviations for 28 blanks are given in Table 3. According to Long and Winefordner, a sample is quantifiable if it is greater than ten standard deviations from blank levels, detectable if it is between three and ten standard deviations, and if it is less than three standard deviations, it is undetectable, (23) Unfortunately, almost all of the ambient air levels found on Whiteface this summer were non-quantifiable by this criterion and a great many of them were also undetectable. The data are listed in Appendix D. These concentrations are for the ACN solutions from the leaching of the cartridges. Forty-five liters of air were sampled for each cartridge the ACN solution volume totaled 2 ml. The and atmospheric pressure at the summit of Whiteface is around 850 millibarrs. The values are reported in micromolar and not parts per billion (ppb) because this is the limiting factor in determining detection limits.

This was enough to render the air data useless for the purpose of modeling. It did show up a serious flaw in the technique. At first, it was thought that the method of preparation was faulty. When these blank levles were compared to those reported by Kuwata, however, it turns out that they are very similar. (8) This indicates that his original method for preparation is flawed. It should be pointed out that there is a

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problem only for the levels found on Whiteface. For the Schenectady work the values were acceptable. This is probably the case for work in other urban areas. In order to use the cartridge technique in rural areas (and it is quite desirable to do so) the method must be changed.

Theoretically, the interferences are coming from impurities in the solvent, drying media, or recrystallized DNPH. The cartridge will concentrate these impurities naturally to the point where they are detectable. It is possible that during preparation a 'pre' cartridge connected to the good one will selectively extract out the impurities and purify the reagent for the second cartridge. Another solution might be to sample for a longer period of time thus a larger volume of air. The blank levels Kuwata reported are for 100 L volumes of air whereas only 45 L volumes were used this summer. It is desirable to sample for as short a period of time as possible. The concentration values are actually averages over the time of sampling. The more time spent sampling, the less value obtained is useful for time dependent phenomenon.

Summer Data Analysis:

Reagent blanks for the aqueous data were sent back to Schenectady with each set of samples. A similar analysis

as was used for the air cartridge blanks was performed on these blanks. Contrary to the air results, only acetone appeared consistently in the blanks. All acetone levels found in actual field samples, when the ACN/DNPH solution was used for derivitization, were in the quantifiable range.

Individual data for cloud water aldehydes and ketones are given in Appendix C. A summary for the summer is given in Table 4. As can be seen, only three carbonyl compounds were consistently present, the three simplest compounds. The table shows the concentrations of the compounds for each event sampled. Average concentration is given along with the range for each compound during each event. In scme of the samples, one or more of the compounds was not detected and these were not counted for the average of that particular compound.

In general, there was little fluctuation in the concentrations found. Not only was there little change during a single event, but there was also surprisingly little variation in the values obtained throughout the entire summer. Of the three compounds, formaldehyde was the most prevalent and consistent. It is also the smallest and simplest. Grosjean and Wright h reported findings of a study on cloud water carbonyls done in urban areas on the west coast of this country. (25) They used an <u>aqueous</u> DNPH reagent solution for derivitization and so their quantitative results are questionable. However, their qualitative results are useful.

They report the presence of many higher aldehyde and ketones other than the three that were found on Whiteface this summer. Presumably, these were produced via fossil fuel combustion, or some other anthroprogenic source, since it is unlikely that these large molecules were natural products. If these large molecules were produced from natural sources, then they probably would have also been detected on Whiteface. If, as Grosjean suggests, the clouds act as scavengers of these polar molecules, then would also act to transport them over they geographical distances. The fact that larger molecules are not found in a rural area indicates some other fate for them. There are several possibilities. They could simply be washed out of the clouds during periods of They could naturally degrade to smaller carbon rain. chain compounds. Being very reactive compounds, they could also react with one of the numerous other molecules which exist in the atmosphere.

The data also shows that there is little change in the concentrations of the compounds found. If any or all of the three fates for these compounds acted alone, then there would be possibly large fluctuations in

concentration. There must be some form of replenishment of the carbonyls that are lost. The data almost suggests steady state situation. Aldehydes are produced а photochemically from hydrocarbons in the air. These then replace the aldehydes that are lost from the atmosphere by degradation, reaction, or washout. Previous work on Whiteface showed that low levels of only the simple aldehydes also exist in the gas phase in rural areas. (5,22) It would seem, then, that the aldehydes present in the atmosphere do not last long in one area or in one Were they to be transported long distances, air mass. vestiges of them at least would have been found on Whiteface. There are several urban areas not far from Wilmington, NY which are in the path of prevailing winds. (Appendix G) Oswego, Buffalo, Rochester, Syracuse, Toronto, and Montreal are some of the major industrial areas within 200-300 miles of the mountain. It would be interesting to trace air masses originating in one of these areas with respect to aldehyde content to see if this steady state is accurate. It would also be interesting to see if any other reactive organic molecules act in the same manner. It is possible that part of the replenishment of the aldehydes is the degradation of other organic pollutants which have not, as yet, been elucidated.

Kinetic Study:

One possible sink for the aldehydes is reaction with Most aldehydes react with S(IV) to form aqueous S(IV). addition products. The formaldehyde addition product, hydroxymethanesulfonic acid (HMSA), has been studied a bit lately to determine its role in the quite atmosphere. (16-18) No other work to date has been done specifically on the addition products of the other aldehydes in the atmosphere. They would more than likely behave similarly to HMSA. The oxidation of S(IV) in clouds by hydrogen peroxide has been suggested as a major if not the major pathway for this reaction. (26-31) HMSA is thought to be stable to this oxidation in slightly acidic solution such as typical cloud water. In order to make use of some of the data collected this summer and to test this hypothesis, a kinetic analysis was done.

The kinetic equations are in Appendix E. Field data from the event on 7/24/84 at 0500 (EST) were used. The constants at pH=4 were used since this was the closest to the field value. The mechanism of the reaction consists of equations (1) and (2). Assuming steady state for the change in concentration of HSO3-, rate equation (3) is derived. The HSO3- concentration can be described as equation (4). From eq. (2), a rate expression for the production of SO4(2-) is derived (eq. (5)). Substituting eq. (4) into eq. (5) gives eq. (6). This is the total rate expression for the system. If the first term in the

denominator is much smaller than the second, it can be eliminated from the expression. In the present case, this is true. There are three orders of magnitude difference between the two rate constants. Therefore, eq. (6) becomes eq. (7) which can be simplified to eq. (8).

This pseudo first-order rate equation is an interesting expression. What this says is that the rate sulfate production from HMSA is dependent solely on of the amount of HMSA present and its rate of decomposition. The amount of hydrogen peroxide is irrelevant. This would indicate that the addition product is, indeed, stable to oxidation by the peroxide. The rate expression can be used to determine a half life for HMSA decomposition of 1.4 x 10*6 sec. This works out to 16.7 Clouds will generally not last in a static state days. for even close to this amount of time. It is reasonable to conclude, then, that any S(IV) (or formaldehyde) which is tied up as an addition product is stable to oxidation by H2O2.

Hydrogen peroxide is found in much greater concentrations in cloud water than either S(IV) or formaldehyde. Since the oxidation of S(IV) by H2O2 is much faster than the rate of production of HMSA, a problem arises. Namely, how and where do the addition

products form? Several possibilities present themselves: 1) They can form in the gas phase and then dissolve in the cloud droplets. 2) They could form on the aerosol which then act as condensation nuclei. This is unlikely since very little of the carbonyls are found in the aerosol. (32) 3) The H2O2 could be produced after the cloud droplet forms while the other two are essentially present upon condensation. In this case, the addition product is formed before the H2O2, but once the H2O2 is produced the oxidation reaction predominates. 4) It is also possible that at some point in the life of the cloud, the H2O2 is 'used up' and there is an excess of both S(IV) and formaldehyde (or any other aldehyde) present. In any case, the levels of aldehydes and S(IV) are both low while the levels of H2O2 and SO4(2-) are both fairly large and variant. Chances are that the S(IV) detected is due entirely to that which is tied up in the cloud as some addition product. Since the analytical technique is not specific for different addition products, it is impossible to tell if there is another addition product other than HMSA which contributes significantly.

Another problem concerns the DNPH method for aqueous samples. If S(IV) is tied up as as addition product with an aldehyde, does the new method determine how much aldehyde is tied up? Grosjean suggests that the DNPH is a good enough nucleophile to cleave the addition product to give complete analysis. (25) If this is so, the aldehyde values report only the free aldehydes present in It is expected that there should be free the clouds. aldehydes if the steady state model described earlier is After droplet formation, there is some influx accurate. the S(IV) which is present is of aldehydes but immediately oxidized by the H2O2.

Complete Data Analysis:

Appendix F contains some graphs which illustrate the usefulness of collecting simultaneous data. By tracing different concentrations over a period of time and comparing them to each other, relationships can be seen. Figures 1-5 show plots which indicate negative direct correlation between H2O2 and H+, NH4+, SO4(2-), NO3-, and O3 respectively. Figures 6 and 7 show how a frontal passage and change in air mass can affect ozone concentrations and temperature. These two graphs can be compared to the air mass trajectories in Appendix G. The three trajectories for 7/21, 7/23, and 7/25 show the transition from a warm, moist air mass from the southwest

to a cooler, dry air mass from the north. This change is reflected in the graphs. Figure 8 illustrates cloud water concentrations which do fluctuate during a period of sampling as opposed to the aldehyde concentrations which did not. A drastic drop in the concentrations of both H2O2 and SO4(2-) during the early morning hours of This drop is probably due to a rain period at that 7/12. After the rain, the concentrations start to build time. again. What cannot be determined by these data is whether the concentrations are rising due to continued production of the compounds or simply whether the new air coming in after the rain was not affected and still had the compounds in abundance. It would be nice to know just how these reactions take place and under what circumstances.

Acid rain has become a very popular issue lately both in scientific and non-scientific circles. One fact that is becoming more apparent as new data is revealed is that acid rain is really only a symptom of the complex chemical system that exists in our atmosphere. Typically, there is a lack of analysis of organic pollutants. In order to determine exactly what reactions occur, more work must be done on these molecules.

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APPENDICES

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APPENDIX A

Table 1. PERCENT	CHANGE IN CONCENTRATION WITH TIME: COMPARIS	SON OF W	∤ATER
AND ACETONITRILE	DNPH REAGENTS		

DNPH Reagent	<u>Formaldehyde</u>	Acetaldehyde	<u>Time (Days)</u>
H3P04/H20	-91%	-94%	7
H3PO4/H20 (Cart.)	-34%	-34%	7
H3PO4/ACN	-13%	-78	5
H2SO4/ACN	-5%	-12%	7

Table 2. STABILITY OF FIELD SAMPLES

Sample #	Date	Formaldehyde <u>Conc. (uM)</u>	Acetaldehyde <u>Conc. (uM)</u>	Acetone Conc. (uM)
1	7/13	2.08	0.38	0.76
	7/23	2.48	NM	NM
2	7/13	1.63	0.54	0.99
	7/23	1.56	0.35	0.99
3	7/13	0.89	0.47	0.74
	7/23	1.33	NM	0.86
4	7/13	2.37	0.86	NM
	7/20	2.21	0.52 -	1.44
	7/23	1.91	0.62	1.27

Table 3. STANDARD DEVIATIONS FOR BLANKS (uM)

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<u>Compound</u> Formaldehyde Acetaldehyde Acetone (*) 28 blanks	<u>Std.</u> <u>Dev.</u> 0.42 0.51 0.27	<u>AIR CARTRIDGES(*)</u> <u>3(Std. Dev.)</u> 1.26 1.53 0.81	<u>10(Std.Dev.)</u> 4.20 5.10 2.70
Acetone (\$) 6 blanks	0.031	AQUEOUS METHOD(\$) 0.093	0.31

Date (Event #)	Compound	Ave Conc (uM)	Range	<pre># of samples(*)</pre>
6/24-6/25 (1)	Form. Acetald. Acetone	3.29 1.15 13.53	1.78-5.52 0.85-1.64 1.10-133.38(\$)	15/15 6/15 15/15
6/27-6/28 (2)	Form. Acetald. Acetone	2.27 0.56 1.00	1.78-3.08 0.44-0.70 0.54-1.31	10/10 10/10 10/10
7/ 4- 7/5 (3)	Form. Acetald. Acetone	5.11 1.52 1.76	3.21-14.8 0.64-3.10 1.06-3.60	10/10 5/10 9/10
7/11-7/12 (4)	Form. Acetald. Acetone	1.43 0.51 0.83	0.36-2.37 0.28-0.86 0.74-0.99	16/16 5/16 3/16
7/23 (5)	Form. Acetald. Acetone	2.46 0.68 0.98	1.94-3.72 0.32-1.02 0.52-1.29	5/5 4/5 3/5
7/27-7/28 (6)	Form. Acetald. Acetone	2.36 0.64 4.45	1.08-3.86 2.41-6.28	7/7 1/7 7/7
8/1-8/2 (7)	Form. Acetald. Acetone	1.85 0.66 0.64	1.14-2.46 0.43-0.79 0.61-0.68	8/8 4/8 3/8
8/7 (8)	Form. Acetald. Acetone	2.02 0.43 0.51	0.62-3.77 0.33-0.72 0.43-0.58	7/7 4/7 2/7
8/9-8/10 (9)	Form. Acetald. Acetone	3.30 0.65 0.78	2.32-4.08 0.28-1.64 0.32-1.04	8/8 7/8 3/8

 $\underline{\texttt{Table}}$ 4. Cloudwater concentrations of Carbonyl compounds on whiteface $\underline{\texttt{MOUNTAIN}}, \ \underline{\texttt{July-august}}, \ 1984$

(*) Number of Quantifiable/Total Number of Samples
(\$) Likely contamination

Martin Constant Constant of Martin State

APPENDIX B

Hydrogen Peroxide Concentrations ASRC Whiteface Mountain Field Station Summer 1984

Date	Time	Concentration	Date	Time	Concentration
6/18/84	<u>(EST)</u> 324	<u>(ppb)</u> 111.91	6/18/84	(EST) 2330	(ppb) 839.34
0/10/04	329	130.57	6/19/84	013	1063.17
	351	82.07	0/13/04	021	1193.73
	420	141.76		115	1025.86
	423	190.25		150	1119.12
	452	115.64		157	895.30
	459	78.34		243	1678.69
	531	126.83		251	1305.65
	536	134.30		354	1977.12
	614	596.87		419	2238.25
	619	1081.82		426	1809.25
	644	652.82		458	2462.07
	649	746.08		504	1827.90
	718	503.61		544	1827.90
	723	466.30		620	1566.77
	751	820.69		954	447.65
	802	690.13		1028	932.60
	824	1268.34		1038	671.48
	840	1100.47	6/24/84	1130	1488.48
	908	1342.95		1336	1313.36
	913	1063.17		1510	1488.48
	944	876.65		1538	875.58
	950	708.78		1613	700.46
	1015	335.74		1643 1712	525.35 404.95
	1021	317.09		1744	350.23
	1321	839.34		1817	218.89
	1327	858.00		1817	175.12
	1413	1268.34 1231.04		1919	131.34
	1422 1527	2200.95		1947	153.23
	1841	1231.04		2017	87.56
	1849	1268.34		2048	240.78
	1928	484.95		2125	306.45
	1935	447.65		2148	186.06
	2010	130.57		2216	394.01
	2017	167.87		2249	448.73
	2046	298.43		2319	437.79
	2052	261.13		2345	525.35
	2136	298.43	6/25/84	015	295.51
	2144	317.09		050	350.23
	2215	205.17		119	569.12
	2223	242.48		149	831.80
	2317	466.30		410	1335.25

Date	Time	Concentration	Date	Time	Concentration
6 (07 (0.	<u>(EST)</u>	(ppb)		(EST)	(ppb)
6/27/84	2240	85.71	7/12/84	002	41.02
	2322 2350	246.43		020	54.69
6/28/84	036	364.29 407.14		047	13.67
0/20/04	040	450.00		121	41.02
	108	471.43		147 215	41.02
	116	428.57		252	54.69 246.09
	150	257.14		340	355.47
	155	278.57		410	403.32
	222	214.29		438	560.55
	230	150.00		507	341.80
	304	85.71		538	170.90
	308 337	42.86		607	177.73
	344	192.86 192.86	7/24/84	320	427.23
	405	171.43		350	310.09
	413	128.57		415	192.94
	434	171.43		444 500	303.20 413.45
	439	128.57		516	385.89
	504	107.14		530	737.32
	516	150.00		545	840.68
	534	128.57		615	723.54
	545	107.14		654	840.68
	606	107.14		710	757.99
	616 827	42.86 1200.00	7/27/84	1240	905.97
	832	1200.00		1300	774.46
7/11/84	1329	187.78		1321 1344	526.05 496.82
	1341	125.18		1410	650.25
	1413	137.70		1440	1008.26
	1419	100.15		1512	1169.00
	1451	425.63		1545	803.69
	1459	425.63		1943	>1056.48
	1514 1523	425.63 801.18		2015	578.65
	1552	>876.29	7/28/84	708	62.89
	1601	701.03		715 745	56.60
	1847	75.11		745 815	6.29 238.99
	1901	200.30		840	540.88
	1923	118.93		906	477.99
	1932	187.78		945	691,82
	1955	325.48		1012	503.15
	2002	>876.29	8/1/84	1607	982.87
	2022 2033	>876.29		1832	291.22
	2054	701.03 388.07		1853	600.64
	2101	300.44		1910	364.03
	2124	250.37		1935 1950	218.42
	2132	200.30		2030	81.91 54.60
	2220	491.97		2043	101.93
	2233	342.00		2100	276.66
	2314	68.35		2135	131.05
	2332	27.29		2158	65.52

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Date	Time	Concentration	
Date	(EST)	(ppb)	
8/2/84	210	>572.44	
	342	1399.29	
	413	>2862.19	
	427	4293.29	
	450	4452.30	
	528	5756.18	
0/7/04	611 103	1717.31 2115.08	
8/7/84	128	1650.79	
	155	1044.64	
	227	257.94	
	315	670.64	
	340	851.19	
	410	322.42	
	440	128.97	
	510	361.11	
	540	386.91	
	607	232.14	
	838	1289.68	
	1943 2015	2302.86 2458.39	
	2015	1960.58	
	2115	1306.96	
	2144	2146.81	
	2213	1742.62	
	2238	1400.34	
8/9/84	2018	520.51	
	2050	660.16	
	2156	228.52	
	2220	114.26	
	2250	76.17	
	2325	50.78 12.70	
8/10/84	2352 250	<12.70	
0/10/04	320	1002.93	
	420	38.09	
	505	<12.70	
	520	<12.70	
	546	<12.70	

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APPENDIX C

Aqueous aldehyde concentrations(uM) for each event Union College DNPH method Summer 1984

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<u>Time</u> (EST)	Formaldehyde	Acetaldehyde	Acetone
1030 1130 1250 1335 1425 1519 1626 1717 1819 2011 2126 2227 2328	5.52 2.42 1.78 2.92 2.45 3.71 3.93 4.52 4.71 3.44 2.13 2.66 2.45	6/24/84 1.64 0.85 1.36 1.28 0.87 0.92 - - -	1.70 1.10 133.38 (*) 25.04 (*) 23.72 (*) 2.38 2.35 2.48 1.73 1.28 1.33 1.64
128 403	3.47 3.22	- 6/25/84 - -	1.66 1.84 1.32
2100 2200 2300 2330	2.49 2.81 2.39 1.98	6/27/84 0.44 0.65 0.46 0.63	0.96 1.02 0.99 0.97
0115 0215 0315 0415	1.78 1.83 3.08 1.94 2.10 2.34	6/28/84 0.70 0.64 0.57 0.39 0.70 0.45	1.19 1.07 1.31 0.93 0.97 0.54
1930 2030 2200	14.80 3.21 3.52 5.48 3.54	7/4/84 3.10 0.64 1.82	3.16 1.32 1.36 1.12

<u>Time</u> (EST)	Formaldehyde	Acetaldehyde	Acetone
0100 0227 0411 0530 0702	3.42 5.72 3.92 3.56 3.91	7/5/84 - 0.98 - 1.08 7/11/84	1.06 1.33 1.23 3.60 1.68
0805 0900 1000 1045 1255 1357 1506	2.08 1.63 2.26 2.22 1.05 0.62 1.03	0.38 0.54 - - -	0.76 0.99 - - - -
1606 1829 1928 2100 2247	0.89 1.27 0.36 1.50 2.50	0.47 - - - 7/12/84	0.74 _ _ _ _
0013 0111 0341 0515	1.11 0.91 1.52 2.37	- - 0.86 7/24/84	
0300 0400 0500 0600 0700	2.08 1.94 2.25 2.32 3.72	0.51 0.32 	1.12 0.52 - 1.29
1340 1440 1550	1.08 1.75 2.10 3.44 2.52	7/27/84	4.76 5.64 4.63 2.41 6.28
	1.79 3.86	7/28/84 - -	4.46 2.96

<u>Time(EST)</u>	Formaldehdye	Acetaldehyde	Acetone
		8/1/84	
1345	2.25	0.79	0.61
1515	2.46	0.71	0.63
1600	1.14	-	-
1820	1.93	-	-
2000	1.30	-	-
2200	2.17	-	-
		8/2/84	
0346	1.21		-
0555	2.37	0.43	0.68
		8/7/84	0.00
0118	1.32	0.33	-
0319	0.62	-	_
0513	1.53	_	_
0848	1.88	0.38	0.43
1100	1.80	-	0.45
1930	3.77	0.72	0.58
2130	3.24	0.29	0.58
2150	5.24	0.29	-
		8/9/84	
1900	3.57	1.64	1.04
2100	4.08	0.88	0.98
2300	3.76	0.46	0.32
		8/10/84	
0100	3.31	0.28	_
0300	3.05	-	_
0500	3.02	0.29	-
0920	3.26	0.31	_
1050	2.32	0.70	_
		0.,0	—

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APPENDIX D

<u>Time</u> (EST)	Formaldehyde	<u>Acetaldehyde</u>	Acetone
1335 1939		6/27/84 5.69 1.86	3.56 4.4.5
0130 0825	2.66 2.28	6/28/84 1.46 4.32	4.00 3.18
1832 2330	3.09 2.10	7/4/84 2.39 1.58	5.36 5.40
0530 1300 1935	1.38 2.32 1.24	7/5/84 1.10 1.04	3.43 4.13 3.99
0105 0805		7/6/84 1.81 1.02	5.06
1146	1.40	7/10/84	3.50
0745 1220 1304 2215	1.20 1.55 1.89 1.02	7/11/84 0.82 2.02 1.48 1.05	3.98 4.44 3.62 3.41
	1.44 0.89 1.48 1.06	7/12/84 1.22 0.47 0.91 0.70	3.64 3.30 4.50 3.44

sromolar concentration values for air cartridges Summer 1984

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Time(EST)	<u>Formaldehyde</u>	<u>Acetaldehyde</u>	Acetone	Propanal
0845 1200 1501 1850 2200	- - 1.16	7/18/84 0.64 0.81 1.00 1.93 0.95	2.56 2.54 2.51 4.41 3.02	2.04
1200 1740 2310	1.28 1.77 2.90	7/23/84 0.78 0.89 0.30	3.15 3.72 2.00	3.43 1.51
0405 0710 1835	1.48	7/24/84 0.88 0.33	4.94 1.72 1.24	3.21
1830	1.72	7/26/84 0.57	1.73	
0000 0600 1230 1840	2.80 2.58 1.52 2.08	7/27/84 1.39 5.08 1.26 3.28	3.67 1.13 1.04 1.66	
0950	0.60	7/28/84 0.83	1.44	
1500 1800	3.42 0.95 0.35	8/1/84 1.42 6.79 1.87	2.92 2.46 3.39 0.92	
0200 0600 1325		8/2/84 0.80 1.89 1.44	2.21 3.20 1.39	
2305	1.26	8/6/84 0.92	1.81	
	0.83	8/7/84 1.65 3.06	4.40 2.03	

Time(EST)	Formaldehyde	Acetaldehyde	Acetone
1908	0.64	8/9/84 1.25	2.42
0310 0900 12 4 5	0.63 1.00 0.78	8/10/84 1.23 1.92 1.88	2.71 2.38

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Appendix E

(1) HMSA
$$\frac{k_1}{k_1}$$
 HSO₃ + HCHO

(2)
$$HSO_3^- + H_2O_2 \xrightarrow{k_2} H_3O^+ + SO_4^2$$

(3)
$$\frac{d[HSO_3]}{dt} = 0 = k_1[HMSA] - k_1[HSO_3][HCHO] - k_2[HSO_3][H_2O_2]$$

(4)
$$[HSO_3] = \frac{k_1[HMSA]}{k_1[HCHO] + k_2[H_2O_2]}$$

(5)
$$\frac{dLSO_4^{-1}}{dt} = k_2[HSO_3^{-1}][H_2O_2]$$

(6)
$$\frac{d[so_4^2]}{dt} = \frac{k_1 k_2 [HMSA][H_2O_2]}{k_1 [HCHO] + k_2 [H_2O_2]}$$

(7)
$$\frac{d[so_4^2]}{dt} = \frac{k_1 k_2 [HMSA][H_2O_2]}{k_2 [H_2O_2]}$$

$$(8) \quad \frac{d[SO_4^2]}{dt} = k_1 [HMSA]$$

Constants:

$$\begin{bmatrix} HCHO \\ HCHO \\ HCHO \\ HCO \\$$

Appendix E (cont.)

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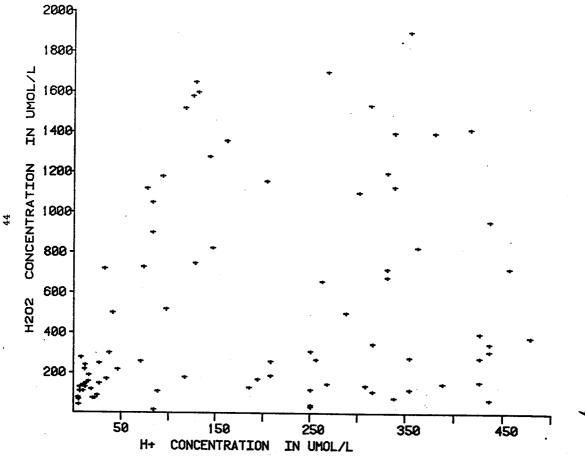
$$kt_{1/2} = ln2$$

 $t_{1/2} = 0.6931/ 4.8 \times 10^{-7}$
= 1.4 x 10⁶ sec

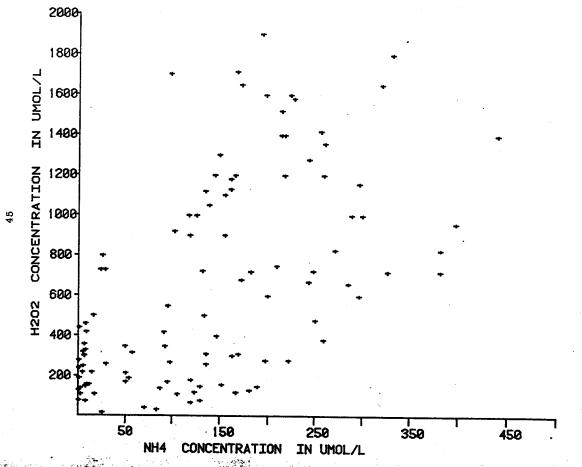
APPENDIX F

Complete data analysis

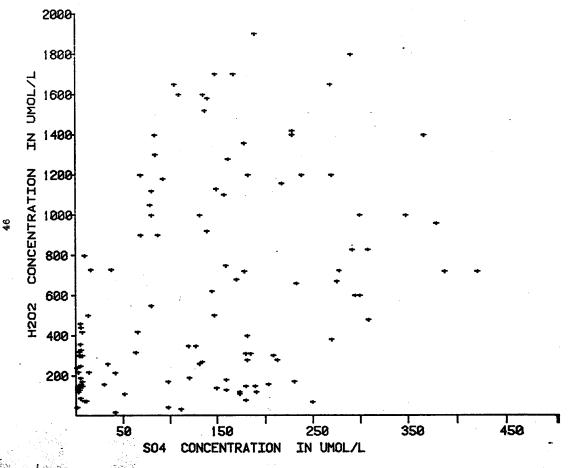
WHITEFACE SUMMER 1982



WHITEFACE SUMMER 1982

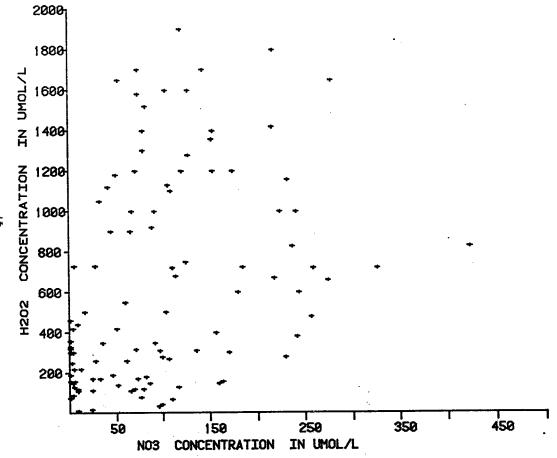


WHITEFACE SUMMER 1982



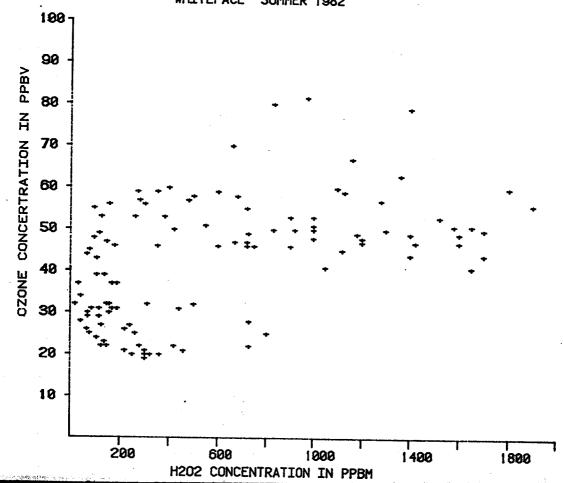
Mgure 3

WHITEFACE SUMMER 1982

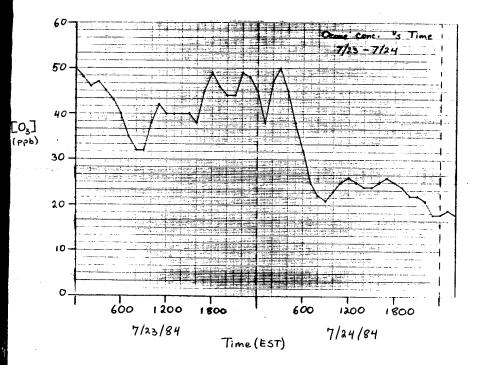


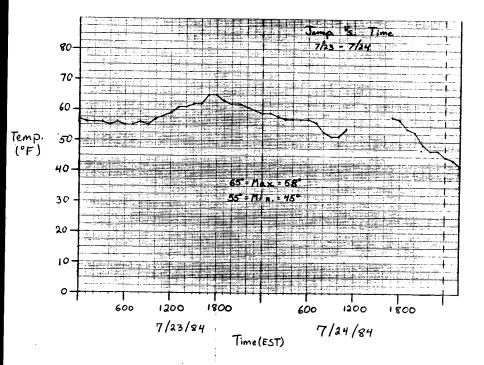
47

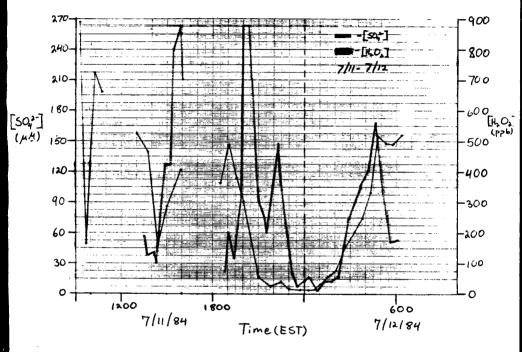
WHITEFACE SUMMER 1982



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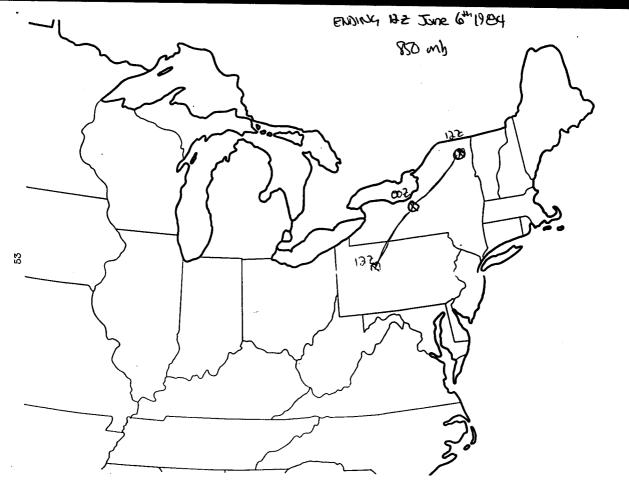




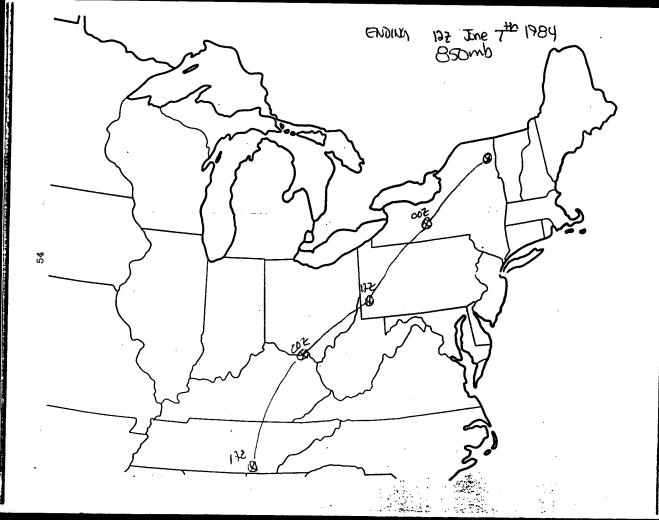
APPENDIX G

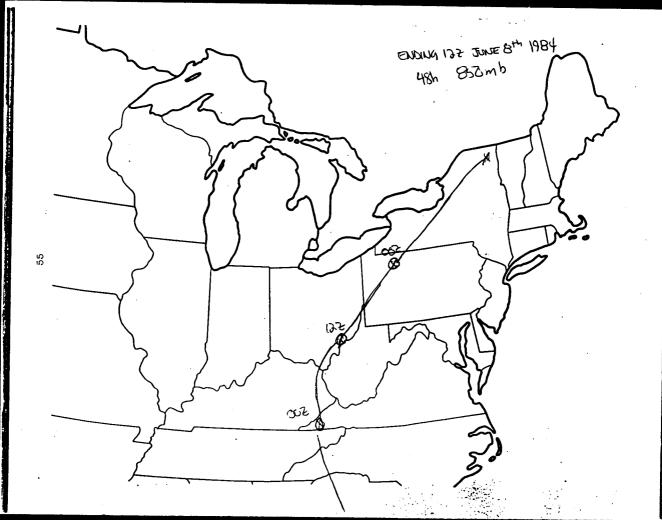
Approximate air mass trajectories for the summer of 1984. The target point is the summit of Whiteface Mountain. The lines show the general history of the air mass which was present at the mountain on the date shown. 850 millibarrs is the atmospheric pressure at the summit and is also the reference pressure used on the weather maps from which this information was taken.

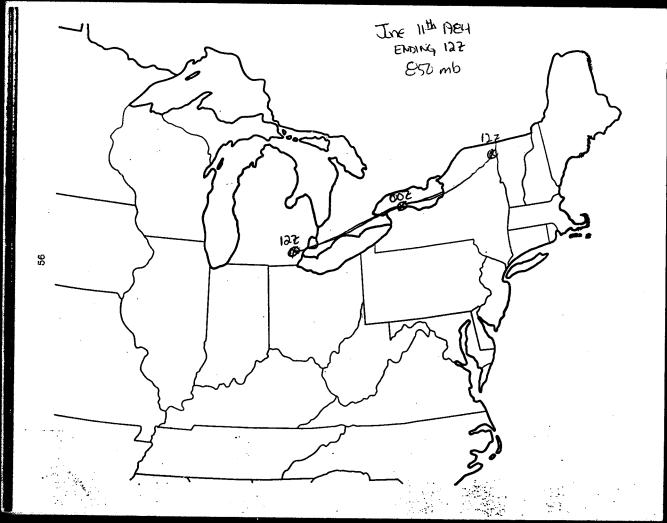
3 A A

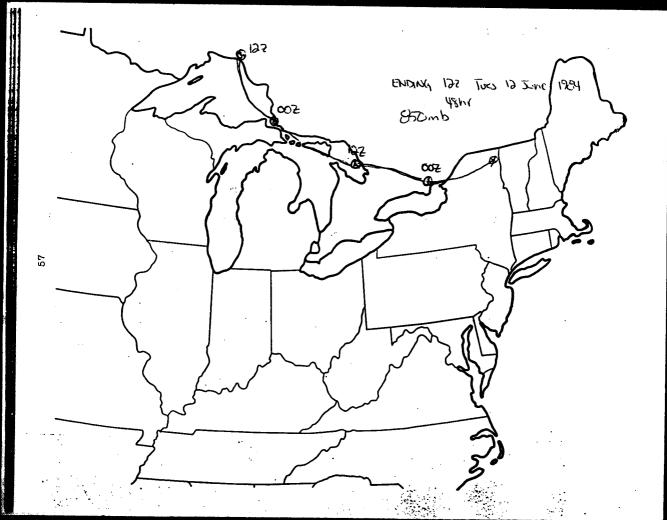


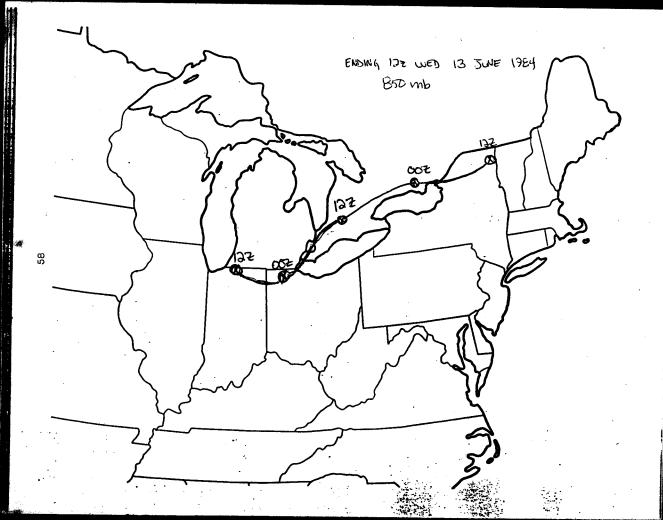
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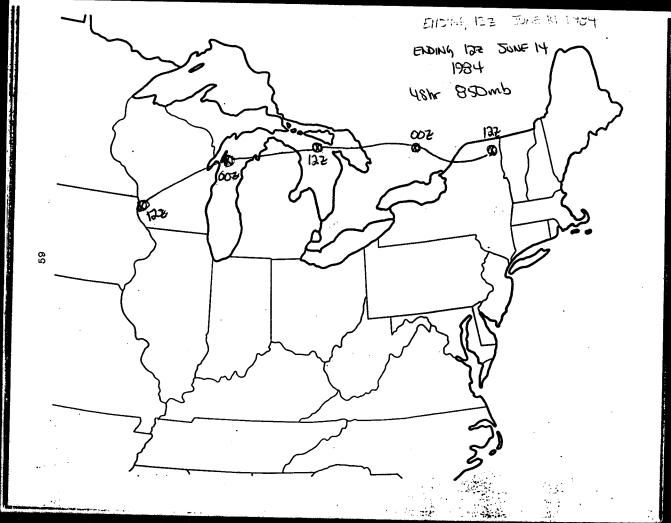


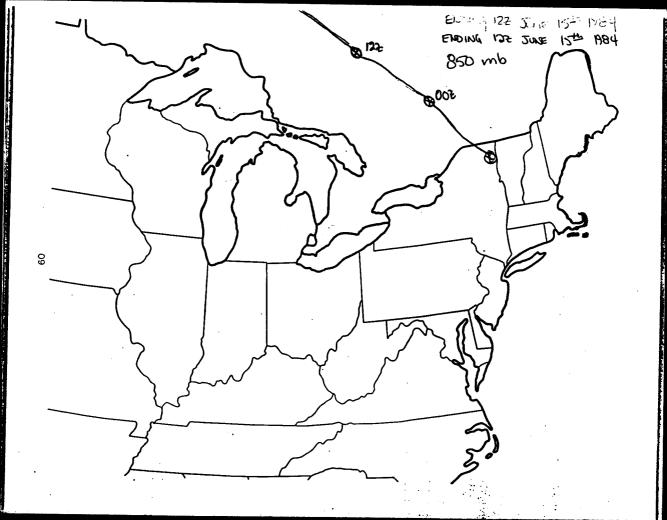


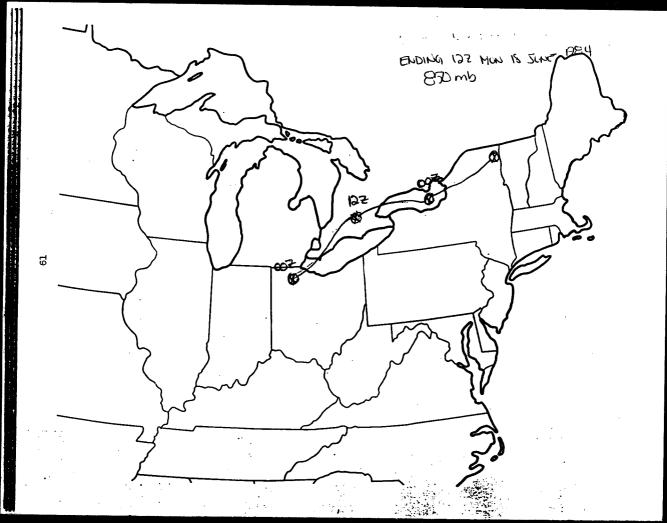


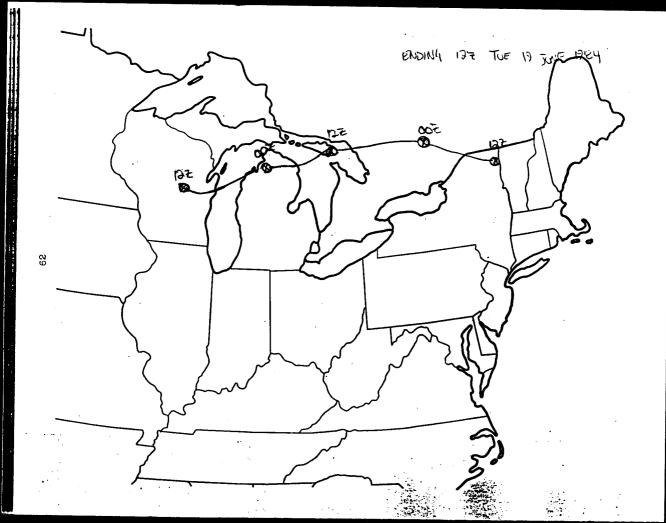


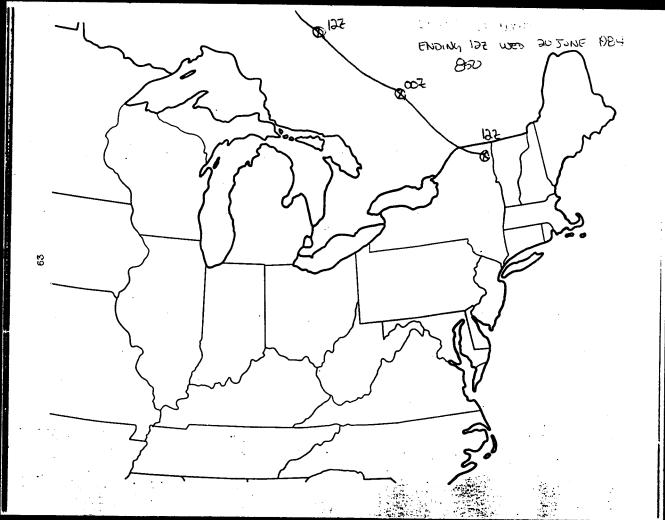


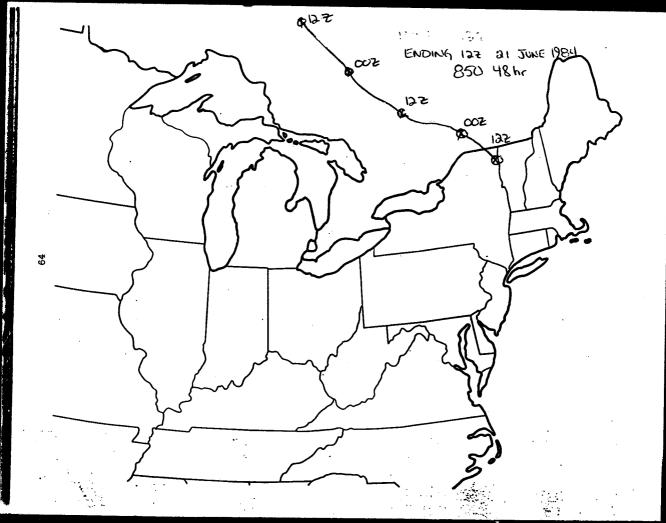


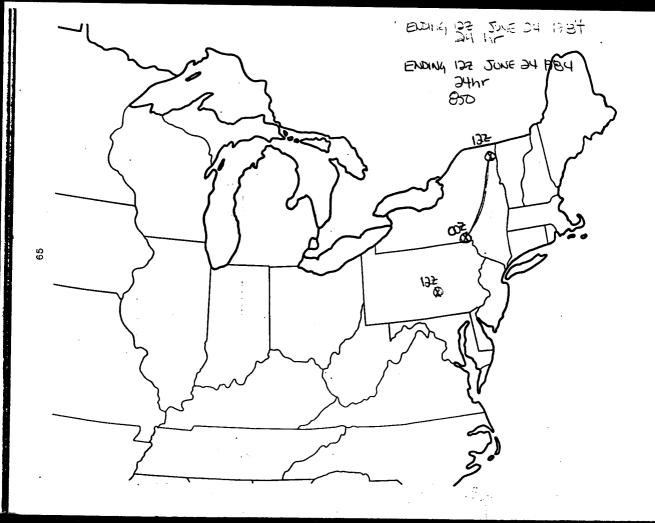


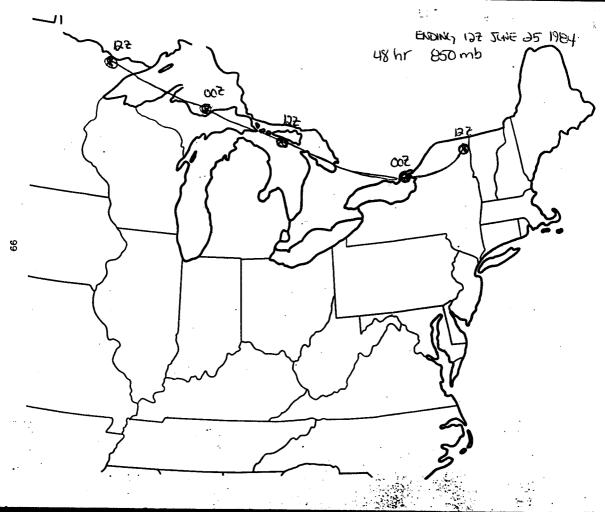




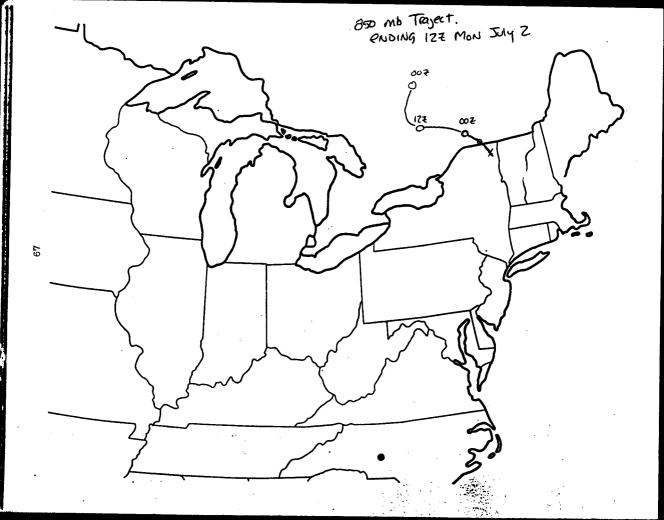


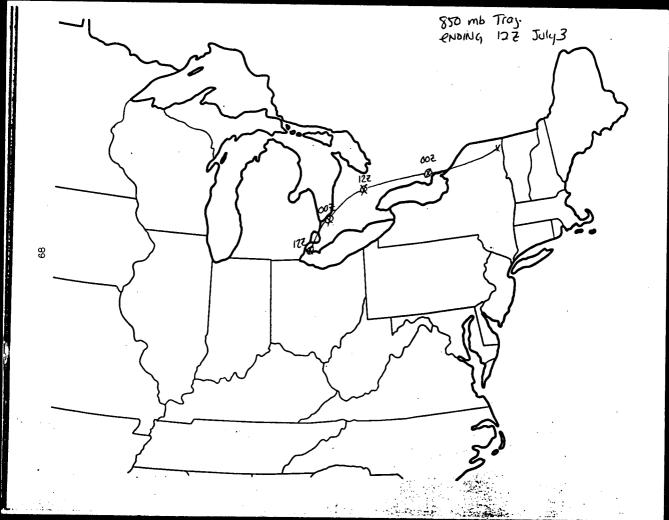


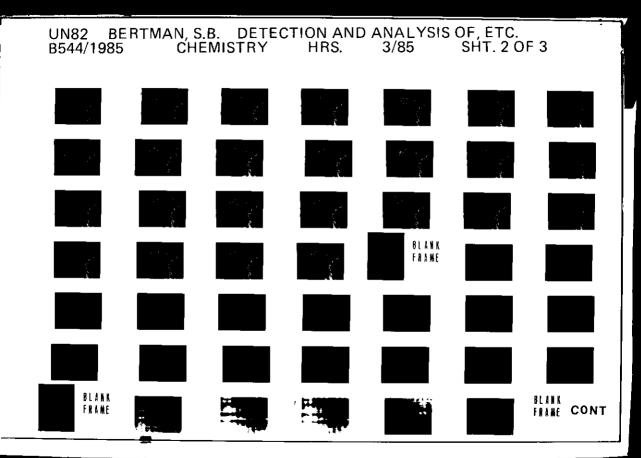


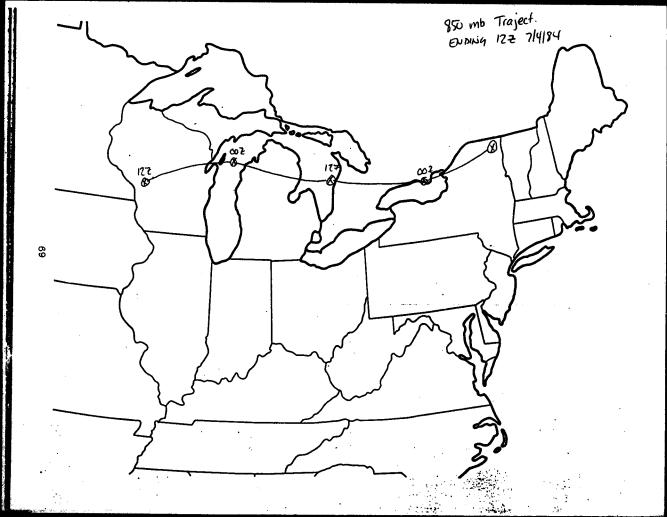


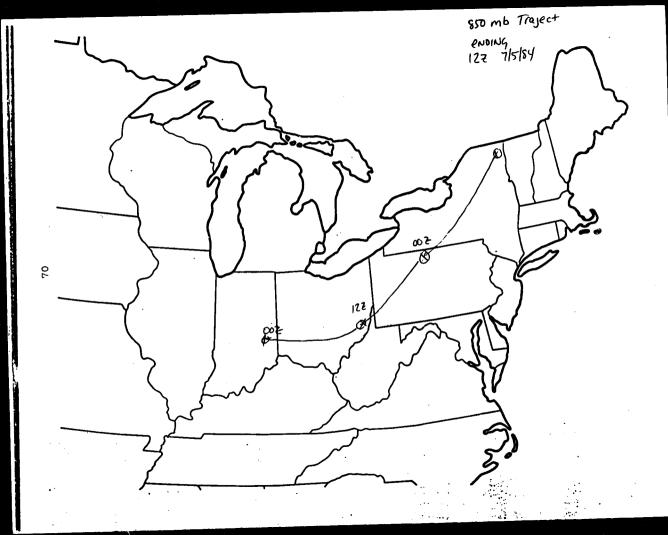
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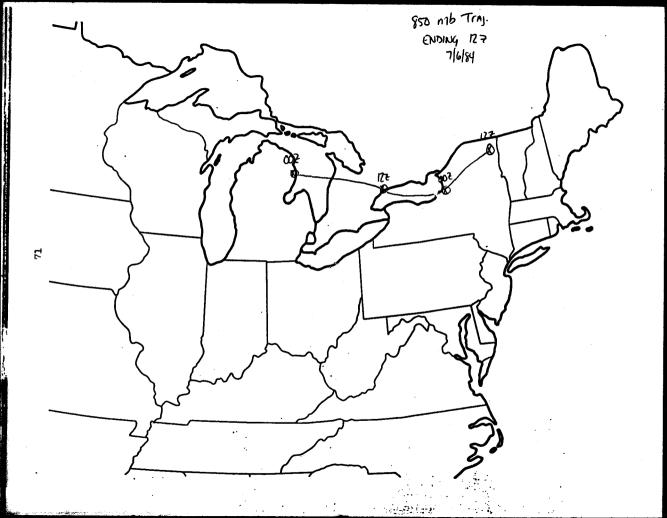


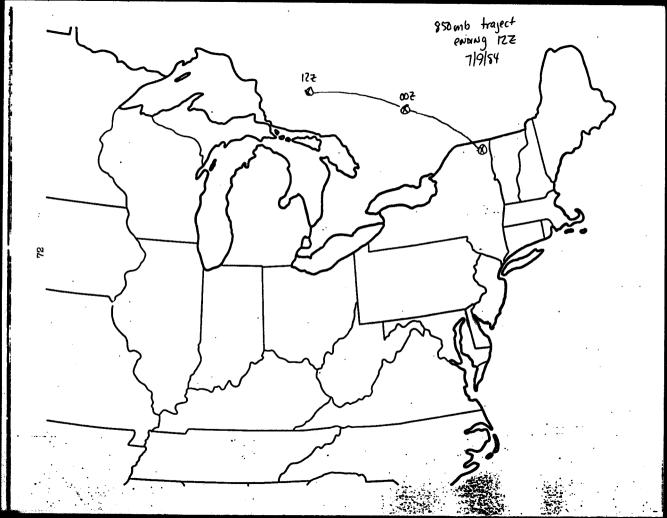






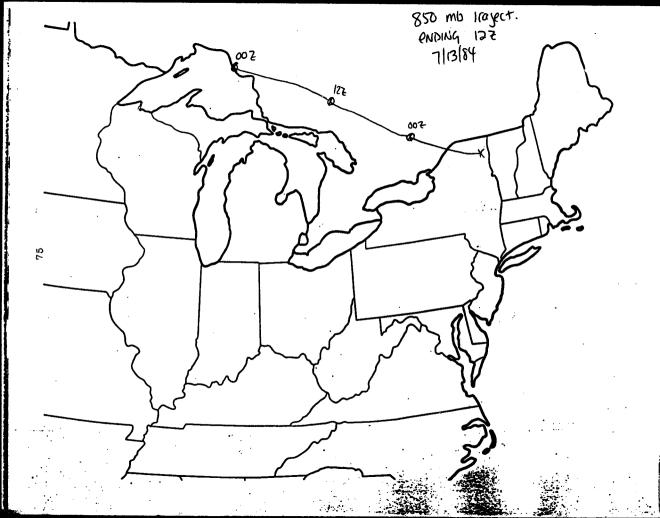


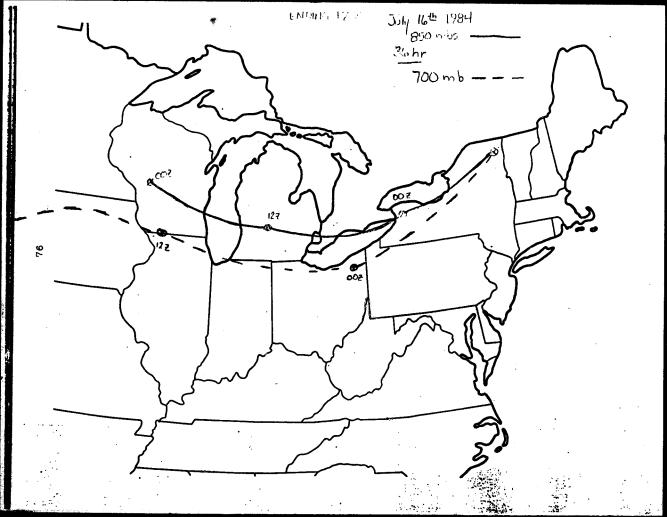


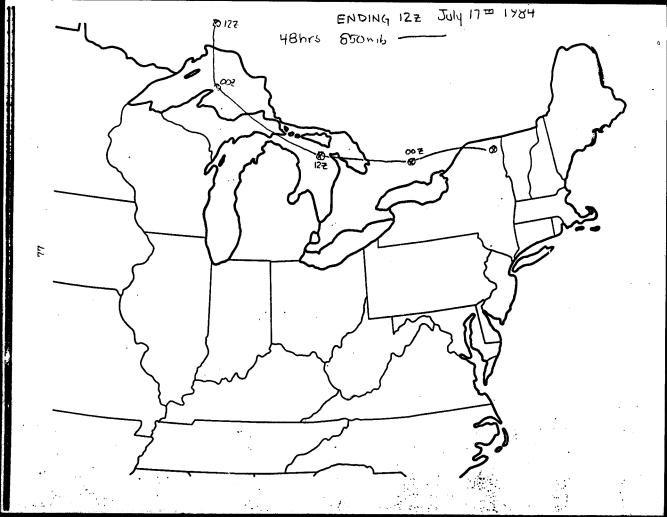


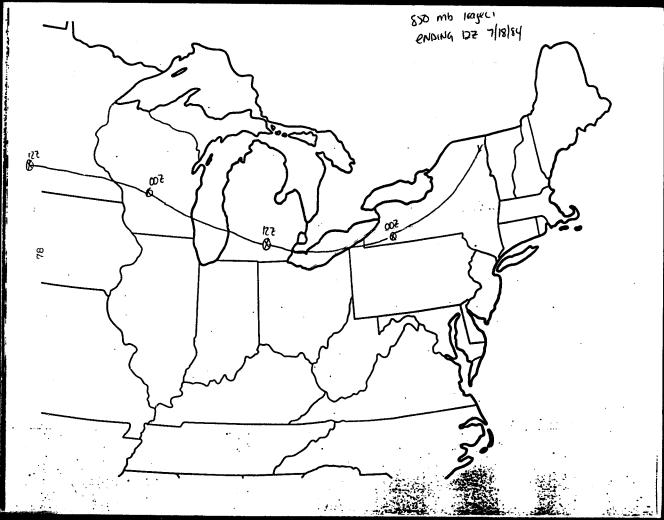


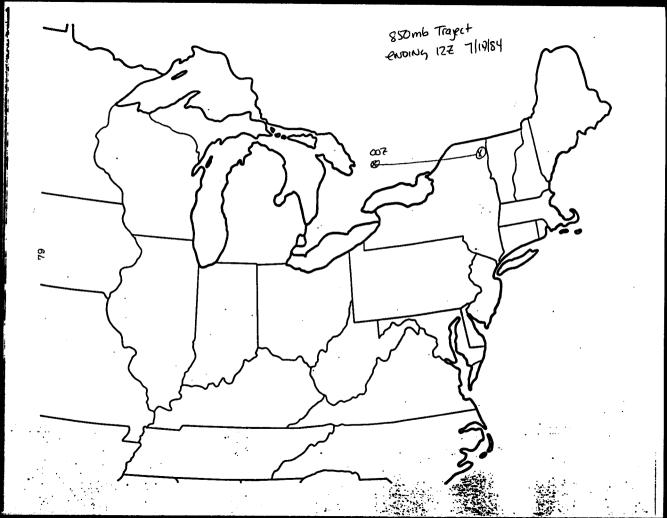


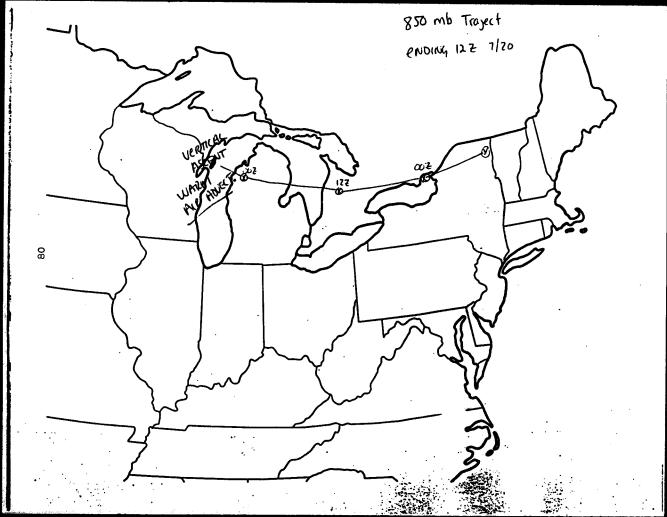


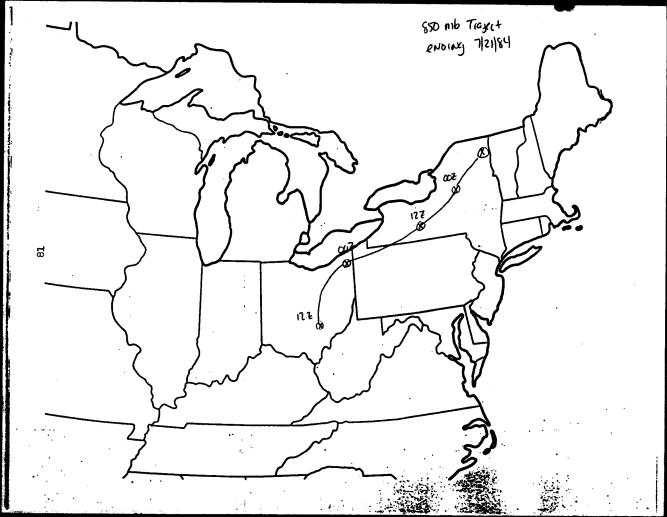


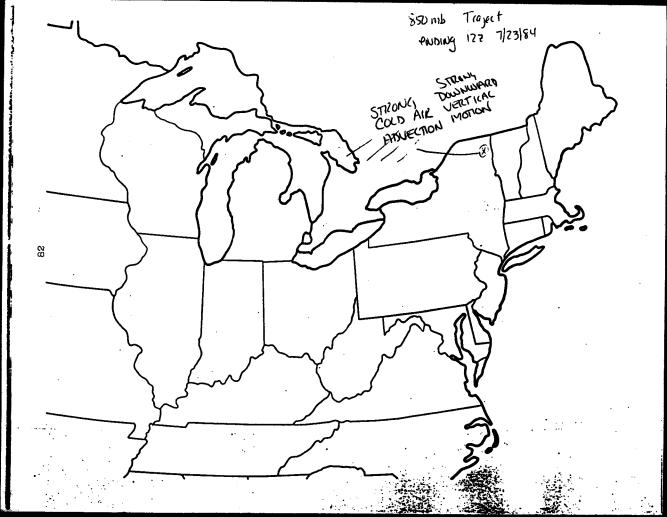


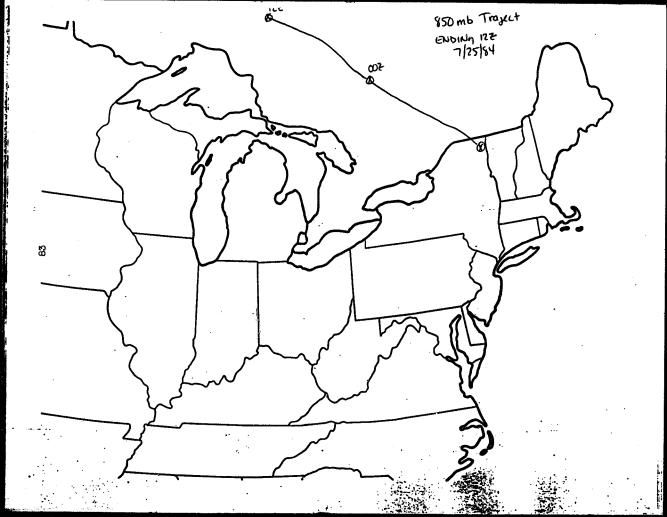


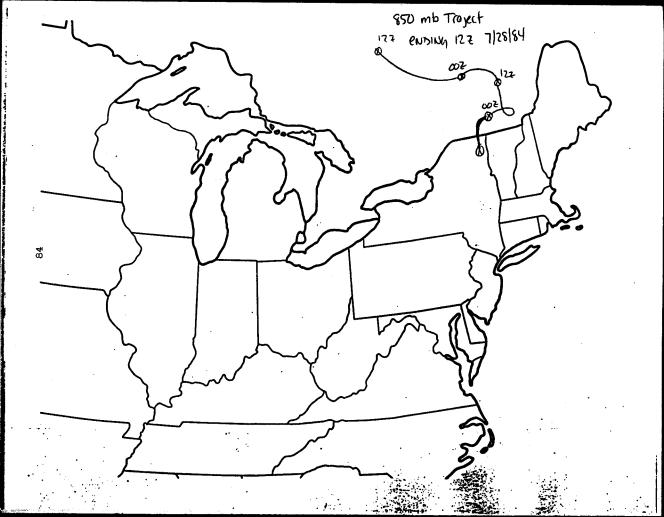




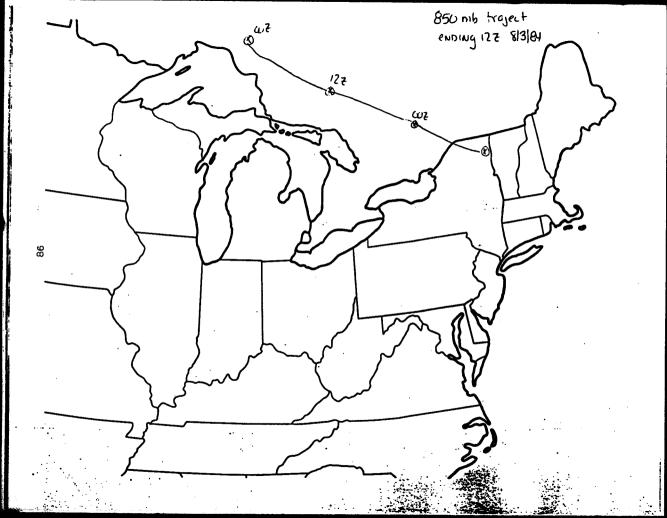


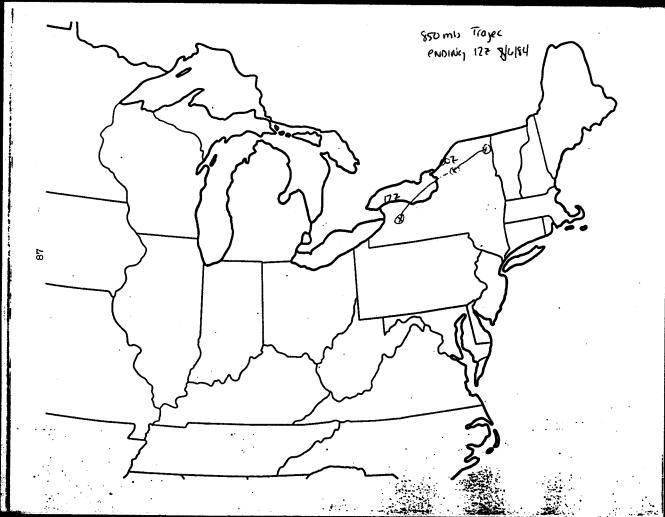


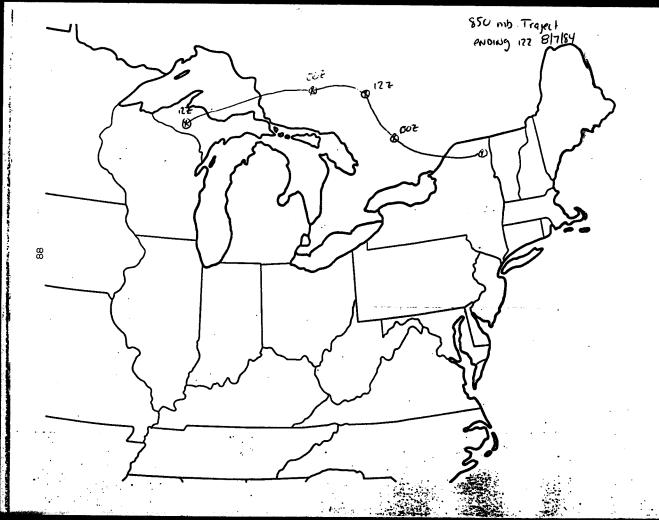


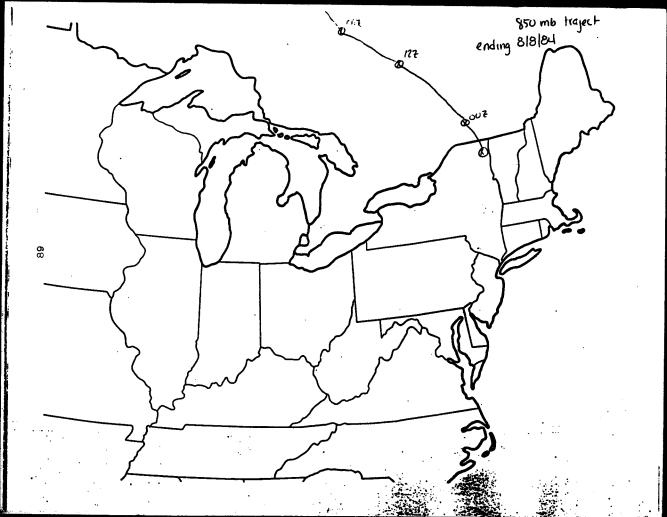


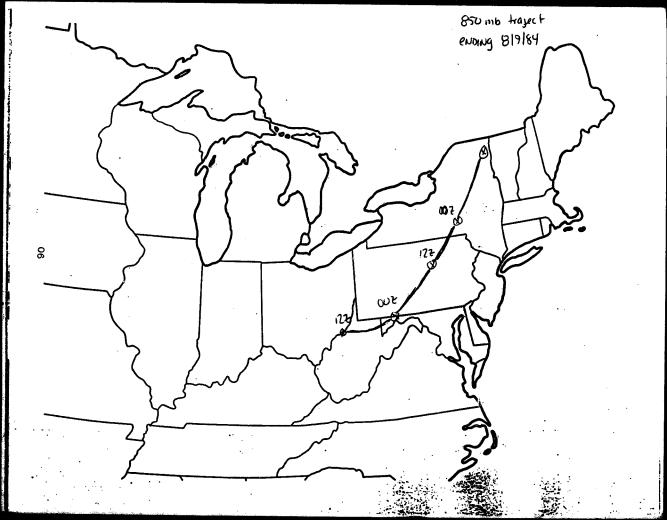


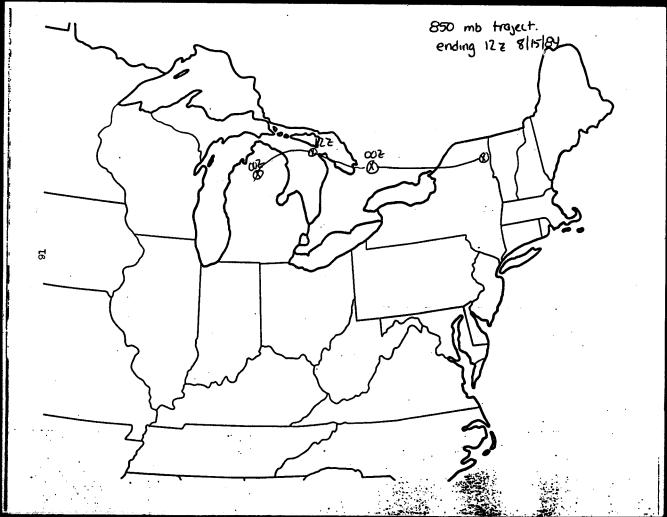


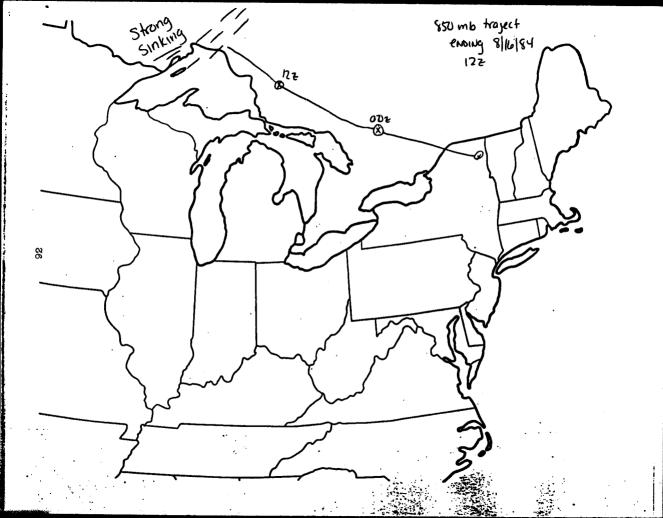














APPENDIX H

Complete data for all cloud water samples taken by the ASRC on Whiteface Mountain during the summer of 1984. Samples were taken and labelled consecutively throughout the summer. The dates for each sample is given as well as the time for each in Eastern Standard Time. Four different collectors were used for samples. They are identified by a letter in front of the sample number. Collector 'A' was the ASRC colector.

1	SMP #	START	END	DATE	pH-F	pH-L	C1	NO3	S04	Na	NH4	к	HSO3	нсно	H202
1	A1	0355	0409	061984	3.47	3.54	5.61	103.	123.		41.5			10/10	11202
	A2	0444	0449	061884	3.81	3.87	2.68	47.6	66.5		28.9				
	A3	0522	0529	061884	3.90	3.92	2.57	38.4	56.8		26.7				
	44	0551	0610	061884	3.78	3.79	2.12	57.6	78.8		38.7				
1	45	0635	0647	061884	3.71	3.84	2.85	50.2	72.9		41.2				
- 1	46	0707	0715	061884	3.84	3.92	2.45	34.7	58.0		32.9				
- 1	47	0736	0752	061884	3.77	3.85	2.53	39.7	65.1		40.7				
1	48	0810	0833	061884	3.82	3.91	2.22	36.6	58.3		38.4				
	49	0859	0905	061884	3.90	3.93	3.95	32.8	49.5		31.1				
	410	0932	0942	061884	4.16	4.13	1.35	21.1	33.8		21.3				
	411	1002	1011	061884	4.20	4.24	.802	10.7	25.1		11.7				
	412	1256	1310	061884	4.20	4.24	1.42	21.5	23.9		18.8				
	113	1311	1342	061884	4.20	4.20	.880	19.4	20.9		13.5				
	414	1400	1410	061884	4.14	4.14	1.23	25.2	24.7		17.5				
	115	1430	1440	061884	4.06	4.07	2.17	27.7	33.4		27.6				
	116	1459	1514	061884	4.04	4.04	3.15	28.6	38.9		35.6	1.09			
	17	1536	1550	061884	3.91	3.95	2.70	35.5	55.4		56.2				
	18	1820	1833		3.99	3.94	3.87	40.9	56.6		61.2				
	17	1906	1920	061884	3.99	4.07	1.87	23.1	43.3		46.9	1.22			
	20	1950	1959		4.13	4.14	2.60	15.4	39.0		40.3	1.09			
	21	2109	2123	061884	3.79	3.75	3.65	45.7	112.		98.7	1.79			
	22	2214	2224	061884	3.84	3.81	2.76	39.7	97.8		93.2	1.88			
	23	2250	2258	061884	4.02	3.98	1.15	24.6	66.1		64.8	.919			
	24	2355	0007	061884	3.77	3.74	3.21	54.4	107.		99.9	1.75			
	25	0055	0104	061984	3.79	3.81	3.36	50.7	94.1		93.3	1.51			
	26	0145	0154	061984	3.95	3.94	2.25	36.6	75.7		82.8	1.28			
		0224	0236	061984	4.05	4.00	1.98	30.9	61.3		70.1	1.15			
		0325	0333	061984	4.03	3.99	2.28	31.1	61.8		66.5	1.55			
		0401	0412	061984	4.02	3.97	2.23	32.8	66.0		66.6	1.15			
		0504	0511	061984	3.93	3.91	3.02	36.8	72.5						
		0608	0614		3.95	3.97	2.19	30.5	55.1		53.0	1.02			
		0814	0819	061984	3.75	3.72	1.37	18.4	109.		47.0	.048			
		0856	0903	061984	3.65	3.58	1.94	21.8	149.		55.6	.341			
		1004	1010	061984	3.70	3.69	1.80	18.6	114.		49.3	.876			
		1103	1118	062484	3.11	3.31					171.8	24.8			
		1327	1335	062484	3.60	3.59	109.	133.	216.	105.	160.	19.0			
		1426	1437		3.74	3.61	130.	153.	199.	120.	143.	15.6			
		1530	1535	062484	3.86	3.79	65.1	84.9	117.	65.0	77.2	6.20			
		1633	1637	062484	4.00	3.99	20.4	37.9	61.8	19.3	41.3	2.59			
A	40	1732	1738	062484	4.31	4.25	10.8	20.5	41.7	15.1	23.7	3.03			

	SMP #	START	END	DATE	pH-F	pH-L	C 1	N03	S04	Na	NH4	ĸ	H\$03	нсно	H202
	A41	1826	1830	062484	4.41	4.28	6.39	16.4	33.5	5.52	15.9	1.73			
	A42	1930	1935	062484	4.47	4.59	2.44	10.8	15.4	4.66	7.13	.962			
	A43	2030	2037	062484	5.01	4.70	.805	9.98	7.20			<.5			
	A44	2130	2133	062484	4.06	4.30	1.23	. 20.2	28.3	.892	25.8	. 959			
	A45	2230	2235	062484	4.51	4.32	1.29	21.0	27.2	.793	29.4	.659			
	A46	2330	2335	062484	4.51	4.16	2.24	36.9	51.7	1.05	76.0	.959			
	A47	0030	0035	062584	4.74	4.48	.869	14.8	24.2	.727	39.4	.539			
	A48	0133	0139	062584		4.36	1.47	29.4	38.3	.760	75.5	.719			
	A49	0350	0355	062584	4.47	4.32	5.41	82.4	90.5	2.18	197.	5.69			
	A50	2130	2145	062784		3.53	5.19	68.4	193.	2.38	>195.	2.80			
	A51	2304	2310	062784		3.51	8.93	107.	191.	1.94	211.	1.90			
	A52	2335	2343	062784		3.42	10.3	155.	232.	1.45	248.	2.20			
	A53	0020	0027	062884		3.45	10.3	163.	234.	1.99	283.	2.49			
	A54	0057	0104	062884		3.49	8.37	132.	228.	1.55	285.	2.03			
	A55	0136	0145	062884		3.59	6.30	100.	176.	2.48	238.	1.77			
	A56	0208	0217	062884		3.67	7.24	129.	158.	2.90	243.	2.71			
	A57	0248	0255	062884		3.75	7.96	145	121	1.56	202.	1.67			
	A58	0326	0331	062884		3.84	34.4	138.	113.	29.9	180.	12.5			
	A59	0359	0404	062884		3.94	9.36	123	90	4.83	183	3.48			
	A60	0427	0432	062884		3.96	6.81	131	87.9	1.21	187.	<1.02			
	A61	0457	0503	062884		3.98	8.41	95.8	68.6	5.28	136.	2.67			
	A62	0527	0533	062884		4.04	5.29	84.1	70.0	1.73	128.	1.30			
	A63	0556	0601	062884		4.06	6.29	93.0	64.2	2.01	123.	1.30			
	A64	0759	0814	062884		3.78	7.85	83.4	120.	1.81	166.	1.71			
	A65	0839	0855	062884		3.46	14.1	151.	>>191	2.42	276.	3.42			
	A66	1007	1020	070484	2.96	2.88	38.7	586.	818.	11.7	667.	8.56			
	A68	1915	1922	070484	3.11	3.15	10.6	148.	482.	2.21	350.	2.67			
	A69	2015	2023	070484	3.30	3.33	4.49	76.6	322.	1.18	230.	.705			
	A70	2045	2050	070484	3.45	3.50	5.06	44.1	214.	.791	150.	6.34			
	A71	2120	2126	070484	3.52	3.58	2.53	36.8	183.	1.26	134.	< .70			
	A72	2150	2154	070484	3.64	3.74	1.21	23.3	122.	.475	87.6	< .70			
	A73	2222	2228	070484	3.62	3.59	2.24	40.1	186.	.760	138.	.733			
	A74	2250	2256	070484	3.68	3.78	1.35	27.5	99.0	.348	72.7	< .28			
	A75	2322	2326	070484	3.81	3.79	1.35	23.5	97.0	.316	75.0	< .28			
	A76	2350	2354	070484	3.76	3.83	1.12	21.8	93.4	.506	74.8	< .28			
		0027	0033		4.14	4.16	< .48	5.61	48.1	.356	38.4	< .64			
		0112	0116	070584	4.29	4.23	< .48	4.16	37.2	.320	25.8	< .32			
	A79	0140	0143	070584	3.98	3.93	.679	9.95	78.3	.570	61.2	<.32			
1	A80	0207	0212	070584	3.77	3.92	.873	9.23	93.9	.463	56.8	>0.32			

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SNP #	ST	ART E	ND	DATE	oH-F	pH-L	C1	N03	504	Na	NH4	к	HSO3	нсно	H202
A81	024		244	070584	4.30	4.32	< .24	2.35	28.8	.106	16.9	<.32	11000	nonu	1202
A82	031	1 0	314	070584	4.10	4.20	< .48	3.62	38.0	.285	27.2	<.32			
A83	052	20 0	526	070584	3.37	3.32	4.36	105.	>222.	2.13	>200	3.88			
A84	055	52 0	555	070584	3.60	3.60	2.42	51.4	>222.	.748	>200	.776			
A85	062			070584	3.66	3.62	2.37	53.0	178.	.720	187.	1.24			
A86	064	15 0	655	070584	3.29	3.19	13.2	227.	501	2.37	612.	3.79			
A87	091	1 0	915	071184	3.28	3.31	9.37	149.	267.	3.15	203	.956			
A88	094	0 0		071184		3.98	2.19	29.3	49.4	1.35	34.6	< .79			
A89	101	2 1	015	071184		3.41	6.38	108.	217.	1.59	161.	.796			
A90	104	0 1	043	071184	3.45	3.43	6.17	100.	198.	1.53	141.	< .31			
A91	130	0 1	303	071184	3.53	3.54	4.08	63.4	158.	1.37	96.4	.318			
A92	134	0 1	346	071184	3.57	3.65	3.14	48.4	139.	1.53	90.8	< .31	.76571		
A93	142	1 1	425	071184	4.05	4.07	.523	9.64	48.1	.351	32.8	< .31	.45714		
A94	145	7 1	500	071184	3.80	3.85	1.46	25.4	86.3	.989	78.5	.701	.58285		
A95	152	3 1	526	071184	3.71	3.74	2.04	41.4	106.	1.59	94.0	.637	.70857		
A96	155	i 1 11	555	071184	3.68	3.72	2.88	51.6	123.	1.88	106.	.573	.57142		
A97	183		835	071184	3.67	3.74	5.51	55.8	109.	1.92	87.6		.65142		
A98	190			071184	3.62	3.56	10.0	94.1	146.	2.98	112.	1.52	.59428		
A99	193			071184	3.57	3.59	7.98	76.5	114.	2.89	84.0	< 1.5	.51428		
A100	200			071184	3.75	3.79	4.28	54.2	91.3	.830	77.2	.427	.57142		
A101	210	3 21	108	071184	4.43	4.49	.298	9.85	16.6	.311	17.7	<.35	.38857		
A102	214			071184	4.73	4.64	< .24	5.26	8.70	.505	4.83	< .35	.35428		
A103	223			071184	4.30	4.37	< .24	18.6	12.1	.173	4.64	<.35			
A104	230			071184	4.63	4.70	< .24	11.2	4.78	.311	1.12	<.35	.48		
A105	234			071184	4.78	4.79	< .24	6.45	4.41	< .17	.473	< .35	.75428		
A106	001			071284	4.90	4.94	< .24	4.07	4.29	< .17	< .29	<.35	.50285		
A107	003			071284	4.84	4.85	<.25	4.82	4.92	.180	4.71	<.37	.45714		
A108	010			071284	4.62	4.72	<.25	6.61	9.34	.324	11.5	< .37	.41142		
A109	013			071284	4.50	4.56	<.25	9.11	18.9	.541	27.8	<.37	.51428		
A110	020			071284	4.45	4.52	.305	8.58	23.3	.469	35.0	< .37	.54857		
A111	024			071284	4.13	4.21	.916	12.5	46.7	.685	58.8	< .37	.64		
A112	032			071284	3.98	4.06	.967	16.2	61.6	. 685	64.4	< .37	.59428		
A113	035			071284	3.86	3.96	1.32	20.3	74.8	.721	77.0	.755	.36571		
A114	041				3.80	3.82	2.39	30.2	99.1	1.40	90.1	.529	.70857		
A115	044				3.62	3.64	3.56	48.0	155.	1.73	124.	.755	.8		
A116	051			071284		3.64	3.46	42.1	148.	1.08	112.	.755	.77714		
A117	054				3.67	3.65	2.85	38.7	147.	.865	104.	.529	.70857		
A118_	061				3.62	3.62	3.10	42.1	156.	.938	106.	.755	.69714		
A119	030				3.25					5.76	456	2.84	1.4010		
A120	033	6 03	539	072484	3.36	3.39				5.18	382.	2.84	2.0421		
				1											

SMP #	START	END	DATE	pH-F	pH-L	C1	N03	S04	Na	NH4	ĸ	HSO3	нсно	H202
A121	0405	0407	072484	3.46	3.52				3.40	305.	1.42	1.7473		
A122	0435	0437	072484	3.55	3.61				3.02	288.	1.42	1.7473		
A123	0505	0507	072484	3.65	3.71				2.24	248.	.995	1.5368		
A124	0535	0538	072484		3.78				2.32	277.	1.13	1.0105		
A125	0605	0608	072484	3.78	3.83				2.55	283.	1.42	1.0842		
A126	1214	1258	072784		4.05	3.09	47.9	41.1	1.13	42.0	< .34	1.9579	-	
A127	1259	1333	072784		4.02	2.31	41.9	47.2	.946	45.9	< .34			
A128	1334	1405	072784		4.02	2.55	44.0	47.6	1.23	46.8	< .34			
A129	1407	1435	072784		3.94	2.47	53.8	55.3	1.24	52.3	.568			
A130	1436	1505	072784		3.86	3.20	67.2	63.7	1.49	60.0	.189			
A131	1508	1536	072784		3.80	3.78	77.7	65.2	1.62	61.8	.331			
A132	1537	1805	072784		3.81	3.61	72.1	64.2	1.52	49.7	< .33			
A133	1823	1855	072784		3.66	10.4	83.0	108.	27.9	60.9	.742			
A134	1856	1922	072784		3.77	2.37	62.9	75.0	1.43	37.6	< .33			
A135	1927	2007	072784		3.74	2.25	72.7	75.9	1.05	32.9	< .33			
A136	2305	0611	072784		3.39	8.89	172.	182.	7.61	82.4	1.08			
A137	0612	0655	072884		3.82	2.84	80.2	61.0	5.77	43.6	.234			
A138	0656	0734	072884		3.79	3.74	91.4	58.9	3.87	45.8	.140			
A139	0735	0808	072884		3.90	2.75	82.2	49.2	2.45	42.2	.797			
A1 40	0809	0845	072884		3.69	3.79	143.	.81.4	2.61	75.8	0			
A141	0846	0920	072884		3.73	3.40	123.	78.6	2.31	71.4	.156			
A142	0920	1000	072884		3.73	3.11	114.	82.6	2.20	79.3	.468			
A143	1346	1418	080184		3.22		182.	433.	8.52	388.	4.35			
A144	1419	1517	080184		3.26		173.	448.	5.19	427.	2.21			
A145	1518	1546	080184		3.25		179.	413.	3.08	385.	1.62			
A146	1548	1612	080184		3.28		182.	420.	2.54	377.	1.34			
A147	1613	1757	080184		3.39	9.32	136.	334.	2.02	279.	1.76		3.1832	
A148	1759	1822	080184		3.81	1.66	32.0	124.	.666	119.	.656		4.2370	
A149	1825	1854	080184		3.91	.677	16.2	96.5	.322	86.5	.246		4.3654	
A150	1900	1930	080184		3.92	.604	17.8	96.7	.430	93.1	.492		3.7234	
								•					.57877	
A152	2005	2032	080184		4.03	0	7.65	69.6	.235	50.1	.184		3.1456	
A153	2035	2110	080184		3.76	.686	18.6	117.	.235	56.8	.323		3.4666	
A154	2113	2154	080184		3.76	.634	20.8	115.	.323	64.1	.63		2.8428	
A155	2157	2231	080184		3.46	1.38	32.0	220.	.368	69.0	<.5			
A156	2235	0119	080184		3.59	2.00	35.2	166.	1.01	93.3	1.45		3.2255	
A157	0120	0154	080284		3.80	.992	24.1	117.	.389	68.2	.104			
A158	0156	0234	080284		3.78		26.9	107.	.309	77.1	.675			
A159	0236	0305	080284		3.65	2.86	60.3	139.	.593	111.	.450		3.3075	
A160	0307	0336	080284		3.70	1.91	40.7	121.	.748	89.3	.450		2.5968	

SHP #		END	DATE	pH-F	pH-L	C1	NO3	504	Na	NH4	к	HS03	нсно	H202
A161	0338	0405	080284		3.67	2.44	48.1	132.	.619	85.8	1.39		3.6656	
A162	0407	0436	080284		3.60		75.6	147.	.772	103.	. 379		3,8585	
A163	0437	0504	080284		3.56		83.5	167.	.889	121.	-664		3.4168	
A164	0505	0605	080284		3.49		88.8	212.	1.68	152.	1.18		3.9908	
A165	0607	0633	080284		3.59	2.39	45.9	162.					3.4726	
A166	0634	0820	080284		3.45		83.4	228.	1.64	176.	1.23		4.8231	
A167	2353	0024	080684		3.22		168.	458.	3.38	390.	2.57		3.7620	
A168	0026	0102	080784		3.39	8.88	131.	284.	1.85	235.	1.10		3.1832	
A169	0105	0205	080784		3.38	9.12	145.	279.	1.82	209.	1.26		2.2186	
A170	0206	0304	080784		3.45	7.58	107.	221.	1.19	155.	.817		2.1221	
A171	0306	0332	080784		3.57	2.84	77.0	196.	.744	170.	.980		2.4115	
A172	0333	0402	080784		3.57	3.38	73.8	186.	.857	156.	1.10		2.4115	
A173	0404	0432	080784		3.75	2.39	44.8	120.	.405	91.6	2.06		2.8938	
A174	0434	0502	080784		3.38	7.70	122.	276.	.810	214.	.701		2.5080	
A175	0504	0532	080784		3.36	7.54	126.	290.	1.00	225.	1.12		2.6956	
A176	0534	0602	080784		3.38	6.77	112.	262.	.874	199.	.817		2.7886	
A177	0603	0805	080784		3.39	6.47	112.	276.		223.	.856		2.5562	
A178	0807	0842	080784		3.45	3.78	77.4	250.	.831	196.	4.05		2.4632	
A179	0844	1040	080784		3.37	2.80	49.5	288.	.767	171.	.752		3.0172	
A180	1044	1322	080784		3.37	4.97	63.0	328.	.852	286.	.963		4.3012	
A181	1419	1555	080784		3.34		97.8	407.	4.00	399.	2.40		4.6864	
A182	1605	1741	080784		3.44		67.8	365.	3.49	385.	1.50		5.2642	
A183	1743	1852	080784		3.75	4.97	64.3	222.	1.70	335.	1.50		6.2271	
A184	1854	1953	080784		3.93	4.53	55.1	158.	.865	289.	1.00		7.3827	
A185	1995	2103	080784		3.70	5.49	47.6	232.	.976	301.	1.36		7.1259	
A186	2104	2202	080784		3.68	3.45	28.5	180.	.709	197.	.802		7.7679	
A187	2204	2302	080784		3.73	3.14	38.9	142.	.776	147.	.601		7.6395	
A188	1913	1955	080984		3.01	•	285.	601.	6.04	324.	3.09		5.3968	
A189	1956	2026	080984		3.08		265.	534.	5.25	254.	2.47		5.3968	
A190	2027	2049	080984		3.13		245.	442.	4.02	191.	1.54		5.9523	
A191	2051	2117	080984		3.10		278.	475.	4.37	216.	1.54		5.7936	
A192	2119	2143	080984		3.12		244.	451.	3.66	256.	1.26		5.5555	
A193	2144	2216	080984		3.15		207.	400.	3.36	225.	.833		6.0714	
A194	2218	2247	080984		3.19		206.	365.	3.07	206.	< 1.1		5.9920	
A195	2249	2317	080784		3.16		222.	376.	3.49	213.	< .99		4.9271	
A196	2319	2349	080784		3.18		226.	349.	3.58	199.	.785		4.5695	
A197	2351	0018	080984		3.21		224.	299.	3.56	167.	< .86		5.7218	
A198	0020	0047	081084		3.18		247.	329.	3.82	175.	< 1.0		5.0036	
A199	0049	0118	081084		3.19		246.	316.	3.99	163.	<1.09		6.0397	
A200	0120	0147	081084		3.22		220.	300.	3.79	156.	1.21		6.0397	

SHP #	START	END	DATE	pH-F	pH-L	C 1	N03	\$04	Na	NH4	к	HSD3	нсно	H202
A201	0149	0216	081084		3.23		206.	308.	4.14	157.	1.36		5,6026	
A202	0219	0246	081084		3.24		186.	299.	3.45	147.	1.21		5.1258	
A203	0249	0318	081084		3.21		195.	319.	3.41	155.	<1.32		5.0066	
A204	0320	0347	081084		3.07		259.	419.	4.45	217.	<1.68		5.2450	
A205	0348	0415	081084		3.14		229.	387.	3.93	195.	<1.52		4.5082	
A206	0416	0445	081084	•	3.13		247.	401.	4.24	210.	< 1.3		4.6012	
A207	0446	0516	081084		3.21	9.52	204.	330.	3.39	166.	< .94		5.2054	
A208	0537	0543	081084		3.24		191.	310.	3.84	159.	< .98		4.7406	
A209	0544	0610	081084		3.25	7.68	166.	284.	3.69	147.	< 1.0		5.0659	
A210	0611	0810	081084		3.20		184.	322.	3.75	174.	< .97		4.5082	
A211	0815	0853	081084		3.23	9.55	176.	316.	3.07	177.	.587		4.8335	
A212	0855	0937	081084		3.26		151.	295.	2.68	157.	< .82		5.7631	
A213	0940	1013	081084		3.25		154.	312.	2.66	165.	1.05		4.4047	
A214	1015	1041	081084		3.21	9.49	155.	304.	2.65	163.	1.07		4.8412	
A215	1043	1235	081084		3.03		273.	518.	4.37	276.	1.53		4.9206	
A216	2058	2150	081484		4.10	3.21	24.0	60.1	3.36	53.6	.205	.75428	4.2460	
A217	2154	2227	081484		3.78	4.73	42.8	137.	5.82	109.	.861		2.8968	
A218	2229	2257	081484		3.62	5.95	55.6	191.	7.72	142.	.779		4.3650	
A219	2258	2343	081484		3.72	6.10	56.6	145.	5.88	104.	.287		2.8768	
A220	0052	0118	081584		3.93	1.61	24.9	86.7	2.16	56.1	.328		2.9365	
A221	0119	0145	081584		4.16	.466	11.8	49.9	1.11	32.1	.328		3.4920	
A222	0116	0215	081584		4.43	0	6.07	26.1	.599	15.9	.164		2.3412	
A223	0216	0243	081584		4.60	0	3.20	13.4	.449	5.88	.123		1.9841	
A224	0244	0316	081584		4.12	.480	17.2	49.3	.813	21.0	.287		2.9761	
A225	0316	0342	081584		3.95	.553	27.0	76.2	.749	36.6	.246		2.1825	
A226	0343	0400	081584		4.23	.058	14.4	37.9	.428	19.4	.246		2.2222	
A227	0423	0446	081584		3.87	1.17	37.4	81.6	.941	42.5	.574		2.0634	
A228	0453	0520	081584		3.96	1.00	33.7	69.3	.569	35.5	.343		1.9047	
A229	0526	0549	081584		3.93	1.17	35.4	79.2	.611	42.2	.343		1.8254	
A230	0558	0616	081584		3.85	1.75	50.8	90.1	.569	50.6	.304		2.1825	
A231	0738	0809	081584		3.72	3.13	72.9	109.	.526	56.1	. 457		1.9047	

SMP #	START	END	DATE	pH-F	pH~L	C1	NO3	S04	Na	NH4	ĸ	HS03	нсно	H202
Bt	0355	0409	061894	3.48	3.51	1.62	113.	139.		48.3				
B2	0444	0449	061884	3.69	3.87	.503	48.6	66.3		28.6				
B3	0522	0529	061884	3.83	3.87	1.06	39.8	58.4		28.1				
B4	0552	0601	061884	3.75	3.76	1.73	62.2	83.7		40.7				
B5	0635	0644	061884	3.75	3.81	1.90	50.6	72.5		41.7				
B6	0707	0712	061884	3.84	3.94	1.06	34.1	55.8		30.3				
B7	0736	0745	061884	3.87	3.85	1.29	39.9	63.3		40.2				
B8	0810	0824	061884	3.83	3.89	1.42	34.7	54.3		35.9				
B9	0859	0905	061884	3.91	3.95	1.29	30.7	45.4		28.3				
B10	0932	0942	061884	3.97	3.97	1.11	24.9	43.3		24.3				
B11	1002	1011	061884	4.05	4.17	.370	11.1	27.9		14.4				
B12	1256	1310	061884	4.17	4.17	.998	21.4	24.7		19.5				
B13	1331	1342	061884	4.19	4.21	.587	19.4	19.6		11.1				
B14	1400	1410	061884	4.13	4.15	.645	23.9	24.4		17.3				
B15	1430	1440	061884	4.05	4.12	1.12	28.3	31.0		28.3	.730			
B16	1459	1514	061884	4.03	4.04	2.05	27.0	39.2		36.0				
B17	1536	1550	061884	3.95	3.97	2.05	35.3	54.5		56.5				
B18	1820	1833	061884	3.92	3.93	2.54	42.5	58.4		63.0	.866			
B19	1906	1920	061884	3.94	4.13	1.01	18.5	38.2		41.9	.656			
B20	1950	1959	061884	4.07	4.18	.524	13.1	36.2		35.8	.262			
B21	2109	2123	061884		3.74	3.59	45.7	112.		102.	1.79			
B22	2214	2224		3.76	3.81	2.60	36.1	93.5		88.2	1.44			
B23	2250	2258	061884	3.93	3.99	.902	23.0	64.7		63.1	1.13			
B24	2355	0007	061884	3.72	3.74	3.01	54.2	105.		97.4	1.13			
B25	0055	0104	061984	3.73	3.82	3.03	50.5	93.4		93.7	1.42			
B26	0145	0154	061984	3.88	3.94	2.00	37.5	77.3		86.1	1.11			
B27	0224	0236	061984	3.97	4.01	1.81	29.8	60.1		68.4	2.13			
B28	0325	0333	061984		3.98	1.96	28.6	61.0	•	62.2	.978			
B29	0401	0412	061984		3.93	2.04	30.6	65.8		65.4	1.20			
B30	0504	0511	061984		3.89	2.79	35.6	70.6		69.8	.828			
B31	0608	0614	061984		3.97	1.87	29.3	55.4		51.2	. 438			
B32	0814	0819		3.67	3.73	1.12	17.2	106.		46.8	.876			
B33	0856	0903	061984	3.58	3.57	1.72	20.6	150.		54.7	.682			
B34	1004	1010	061984	3.63	3.69	1.45	17.8	114.		49.9	.292			

					WHI	TEFACE CL	OUD WAT	ER					
SHP # START	END	DATE	pH-F	pH−L	C1	N03	SD4	Na	NH4	к	HS03	HCHO	H202

	B51	2304	2310	062784		3.51	7.85	116.	187.	.958	203.	1.60
	B52	2335	2349	062784		3.39	11.0	166.	>201	1.06	>181	1.73
	B53	0020	0031	062884		3.45	10.3	159.	226.	1.37	286.	2.16
Î	B54	0057	0104	062884		3.50	8.46	129.	226.	1.39	285.	1.99
	B55	0136	0145	062884		3.62	5.64	97.7	170.	1.45	219.	1.27
	B24	0208	0226	062884	3.65	3.68	7.52	134.	147.	2.22	241.	2.83
	B57	0248	0255	062884		3.74	8.51	149.	127.	1.66	>183	2.35
	B58	0326	0331	062884		3.81	6.05	129	96.5	1.18	171	1.54
	B59	0359	0404	062884		3.91	6.38	124	94.7	1.15	192	1.95
	B60	0427	0432	062884		3.96				1.16	179.	2.12
	B61	0457	0503	062884		3.96	6.29	112.	82.8	1.21	>163	1.30
	B62	0527	0533	062884		4.02	4.54	79.8	68.7	1.00	127.	1.02
	B63	0556	0601	062884		4.03	5.95	94.0	64.8	1.10	123.	1.02
	B64	0759	0814	062884		3.77	7.56	84.1	126.	1.51	170.	1.71
	B65	0839	0855	062884		3.45	17.4	159.	>>191	3.12	293.	3.76
	B67	1545	1554	070484	2.92	2.99	15.6	212.	690.	2.65	535.	4.07
	B68	1915	1922	070484	3.14	3.14	11.0	150.	490.	1.58	346.	2.25
	B69	2015	2023	070484	3.32	3.34	4.12	74.4	319.	.791	227.	1.12
•	B70	2045	2050	070484	3.49	3.50	5.24	45.2	219.	.712	153.	6.20
	B71	2120	2126	070484	3.53	3.59	2.06	37.9	183.	.554	135.	< .70
	B72	2150	2154	070484	3.64	3.75	1.26	23.3	126.	.316	92.8	<.28
	B73	2222	2228	070484	3.63	3.57	1.82	40.5	184.	.601	140.	.507
	B74	2250	2256	070484	3.68	3.76	1.49	29.3	112.	.633	87.7	< .56
	B75	2322	2326	070484	3.81	3.72	1.40	25.3	115.	.499	85.4	.582
	B76	2350	2354	070484	3.68	3.70	1.35	26.8	121.	.506	99.6	.338
	B77	0027	0033	070584	3.92	3.97	.468	8.57	70.1	.411	59.7	.507
	B78	0112	0116	070584	4.23	4.20	< .48	5.79	43.1	.285	33.8	× .32
	B79	0140	0143	070584	4.00	3.98	.582	8.87	77.3	.356	61.2	.582
	B80	0207	0212	070584	3.74	3.72	.971	13.5	124.	.356	93.4	< .64

SHP #	START	END	DATE	pX-F	pH-L	C1	NO3	S04	Na	NH4	к	HS03	нсно	H202
B86	0645	0655	070584	3.60	3.34	9.08	168.8	354.	2.08	428.	2.60			
B87	0911	0915	071184	3.25	3.26	10.5	169.	317.	3.35	232.	3.02			
B88	0948	0950	071184		3.80	2.30	37.4	101.	1.14	80.2	< .31			
B89	1012	1015	071184		3.42	6.54	102.	208.	1.78	157.	.637			
B90	1040	1043	071184	3.47	3.44	6.80	96.8	193.	2.36	140.	.872			
B91	1300	1303	071184	3.53	3.59	4.18	59.9	150.	1.27	92.5	.318			
B92	1340	1346	071184	3.56	3.59	3.29	48.9	145.	1.27	95.1	< .31	.70857		
B93	1421	1425	071184	4.07	4.11	.209	8.10	44.1	.287	29.7	1.78	.50285		
B94	1457	1500	071184	3.81	3.87	1.36	25.0	88.1	.861	80.4	< .31	.48		
B95	1523	1526	071184	3.72	3.75	1.99	41.8	105.	1.34	91.1	< .31	.70857		
B96	1551	1555	071184	3.68	3.70	2.67	51.3	123.	1.59	104.	.446	.62857		
B97	1832	1835	071184	3.63	3.77	4.43	53.7	107.	.738	85.1	< .34	.60571		
B98	1902	1906	071184	3.63	3.66	8.52	90.0	143.	1.79	106.	< .34	46857		
B99	1932	1936	071184	3.56	3.60	7.53	79.8	133.	.995	107.	.347	42285		
B100	2003	2007	071184	3.73	3.77	3.83	49.2	86.2	.657	73.6	<.35	.68571		
B101	2103	2114	071184	4.43	4.50	< .24	6.96	15.9	.311	19.4	<.35			
B102	2148	2209	071184	4.68	4.64	.497	5.43	10.4	.726	10.1	<.35	1.44		
B103	2234	2319	071184	4.63										

						WHIT	EFACE CL	OUD WATE	R					
SHP #	START	END	DATE	pH-F	pH-L	C1	NO3	S04	Na	NH4	К	HSO3	нсно	H202
B126	1214	1256	072784		4.09	7.66	105.	55.2	2.93	65.0	< .34			
												.46511		
												.41860		
												.45348		
												.44186		
												.65116		
												.52325		
												.48837		
												.37209		
												.43023		
												.31395		
												.30232		
												.37209		
												.33720		
												.38372		
												.38372		
												1.2879		
												1.2322		
												1.2755		
												.81142		
												.68571		
												-56		
												.45714		
												.66285		
												.32198		
												.28483		
												.39628		
												.33436		
and the second														

SHP I	START	END	DATE	pH-F	pH-L	C1	NO3	S04	Na	NH4	ĸ	.50774 .38390 .63157	240	H202
										7		.58823 .44582		
												.50774		
B167	2353	0024	080684		3.25		167.	456.	4.80	394.	2.61	2.	8938	
B168	0026	0102	080784		3.39	8.38	128.	298.	1.80	248.	1.26	3.	3762	
B169	0105	0205	080784		3.45	8.74	136.	262.	1.87	209.	1.10		1221	
B170	0206	0304	080784		3.44	6.92	101.	216.	1.48	153.	.980	2.	1221	
B171	0306	0332	080784		3.54	2.73	74.5	192.	1.17	167.	.940	2.	0257	
B172	0333	0402	080784		3.56	3.23	73.6	187.	.586	158.	1.14		5080	
B173	0404	0432	080784		3.74	2.23	44.7	121.	.447	89.4	.506		7009	
B174	0434	0502	080784		3.36	7.82	123.	280.	.875	213.	1.16		2773	
B175	0504	0532	080784		3.37	7.61	129.	293.	.831	223.	1.75		4632	
B176	0534	0602	080784		3.40	7.16	114.	259.	.853	197.	.662		6491	
B177	0603	0805	080784		3.39	6.75	111.	278.	.938	221.	.506		8350	
B178 B179	0807	0842	080784		3.46	4.28	75.0	245.	1.04	196.	.662		6956	
	0844	1040	080784		3.37	2.67	50.8	288.	.852	169.	.752		8246	
B180 B181	1044	1322	080784		3.39	5.23	61.3	318.	.767	276.	1.50		6222	
B181 B182	1419	1555	080784		3.26		108.	469.	3.58	439.	2.55		9432	
	1605	1741	080784		3.39		72.1	392.	3.06	402.	1.80		3925	
B183 B184	1743 1854	1852	080784		3.70	4.59	59.1	235.	1.53	330.	1.35		8691	
B185	1955	1953	080784		3.92	4.53	55.8	156.	.599	293.	1.04		1530	
B186	2104	2103	080784		3.72	4.93	46.1	218.	.599	290.	.962		6395	
B187	2204	2202 2302	080784		3.72	3.20	27.3	179.	.532	201.	.842		0617	
B188	1913	1955	080784		3.74	2.55	32.7	128.	.421	131.	.681	7.9	9604	
B189	1956	2026	080984		3.00		287.	592.	8.75	368.	5.41			
B107	2027	2026	080984		3.07		254.	504.	6.12	238.	2.78		7142	
B191	2027	2117	080984 080984		3.14		231.	418.	3.50	172.	1.54		2301	
B192	2119	2117	080784		3.11		262.	447.	3.93	194.	1.54		3688	
B193	2144	2143	080784		3.13		233.	424.	3.31	240.	1.07		5079	
B194	2218	2216			3.17		192.	363.	2.92	207.	1.07		9523	
B174 B195	2218	2317	080784		3.20		194.	345.	2.77	198.	.714		1507	
B175	2319	2317	080984 080984		3.17		212.	357.	3.12	204.	< 1.0		0463	
B178	2317	2347			3.18		222.	339.	3.25	194.	<.863		2450	
B172 B198	0020	0018	080984		3.22		220.	294.	3.03	164.	< .90		B410	
B170	0020	0118	081084		3.19		239.	315.	3.40	169.	< .82		3245	
B177 B200	0120	0147	081084 081084		3.20		234.	304.	3.62	160.	.758		B013	
9744	4124	VI4/	001004		3.24		216.	292.	3.53	151.	.910	5.8	8013	

SHP #	START	END	BATE	pH-F	pH-L	C1	NO3	S04	Na	NH4	к	HSO3	HCHO	H202
B201	0149	0216	081084		3.23		202.	300.	3.45	154.	< .75		5.7218	HEUK
B202	0219	0246	081084		3.27		179.	284.	2.96	137.	<1.09		5.2847	
B203	0249	0318	081084		3.22		185.	301.	3.02	145.	(1.13		5.0066	
B204	0320	0347	081084		3.10		259.	418.	4.26	218.	<1.91		5.3245	
B205	0348	0415	081084		3.15		227.	380.	3.54	196.	<1.79		4.5547	
B206	0416	0445	081084		3.14		242.	394.	4.02	203.	< 1.1		.46476	
B207	0446	0516	081084		3.22		197.	317.	3.10	161.	< .94		5.2054	
B208	0537	0543	081084		3.24		180.	292.	3.34	153.	< .90		4.6476	
B209	0544	0610	081084		3.27		173.	294.	3.19	145.	< 1.4		5.2054	
B210	0611	0810	081084		3.22		176.	309.	3.38	167.	.665		4.7871	
B211	0815	0853	081084		3.24		171.	308.	2.77	178.	< .78		5.1124	
B212	0855	0937	081084		3.27	7.93	141.	282.	2.38	147.	< .90		5.3448	
B213	0940	1013	081084		3.26	8.28	144.	289.	2.57	158.	1.38		4.0079	
B214	1015	1041	081084		3.22	9.16	147.	289.	2.65	158.	1.38		5.3968	
B215	1043	1235	081084		3.02		249.	475.	3.94	255.	1.53		4.4841	

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SMP N	START	END	DATE	pH-F	pH-L	C1	NO3	504	Na	NH4	к	HSO3	нсно	H202
C127	1259	1333	072784		4.04	11.7	79.0	62.6	12.2	63.7	1.98			
C128	1334	1405	072784		4.06	4.27	58.2	51.2	3.47	53.8	.410			
C129	1407	1435	072784		3.96	3.17	61.7	57.8	1.19	55.0	.473			
C130	1436	1505	072784		3.86	3.79	75.2	67.5	1.53	63.5	.074			
C131	1508	1536	072784		3.83	4.60	88.3	70.6	1.74	68.1	.331			
C132	1537	1805	072784		3.77	4.21	85.4	76.8	1.46	59.4	.405			
C133	1823	1855	072784		3.70	14.2	83.0	93.9	11.2	47.6	< .33			
C134	1856	1922	072784		3.78	2.43	65.3	71.5	.955	39.0	< .33			
C135	1927	2007	072784		3.75	2.31	73.7	76.7	.955	34.8	.337			
C136	2305	0611	072784		3.21		204.	278.			2.29			
C138	0656	0734	072884		3.77	3.80	94.3	65.8	3.45	50.0	.375			
C139	0735	0808	072884		3.90	2.45	79.7	48.2	2.28	39.4	.520			
C140	0807	0845	072884		3.71	3.80	135.	77.4	2.31	73.1	.052			
C141	0846	0920	072884		3.70	3.29	123.	75.7	1.97	74.5	.364			
C142	0920	1000	072884		3.74	3.03	114.	81.6	1.88	78.5	.468			
C143	1346	1418	080184		3.21	0.00	171.	495.	4.56	474.	2.43			
C144	1419	1546	080184		3.26		164.	454.	3.47	448.	1.14			
								1011	5.4/	110.	1			
C146	1548	1612	080184		3.26		143.	381.	2.23	356.	1.14			
C147	1613	1757	080184		3.46	5.92	88.	263.	.881	230.	.451		3.9549	
C148	1759	1820	080184		3.83	1.25	28.5	118.	. 473	115.	1.02		4.6302	
C149	1825	1854	080184		3.93	.353	15.5	93.6	.322	85.1	<.5		3.7876	
C150	1900	1930	080184		3.94	.353	16.4	93.5	.322	91.6	.410		3.7234	
													.77170	
C152	2005	2032	080184		4.03	.223	9.87	71.7	4.28	90.6	3.28		3.5950	
C153	2035	2110	080184		3.75	.670	17.5	119.	.257	56.5	.416		3.3382	
C154	2113	2154	080184		3.76	.618	20.0	116.	.220	60.9	<.5		3.0615	
C155	2157	2231	080184		3.47	.764	26.5	182.	.216	64.8	.729		2.8428	
C156	2235	0119	080184		3.46	1.80	37.0	209.						
C157	0120	0154	080284		3.71	.927	24.4	131.	.277	84.2	.683		3.1708	
C158	0156	0234	080284		3.77	1.10	25.4	111.	.386	77.6	.135			
C159	0236	0305	080284		3.65	2.59	54.3	133.	.438	103.	.630			
C160	0307	0336	080284		3.71	1.81	39.3	120.	.490	82.0	.225			
C161	0338	0405	080284		3.69	2.35	46.0	126.	. 468	79.9	.379		3.8585	
C162	0407	0436	080284		3.61	3.6	65.7	140.	.632	92.9	. 427		3.7175	
C163	0437	0504	080284		3.55	4.07	75.9	155.	.772	114.	.617		3.6628	
C164	0505	0605	080284		3.46		90.8	205.					4.3735	
C165	0607	0633	080284		3.60	2.36	43.1	152.	.462	105.	1.04			
C166	0634	0820	080284		3.47		79.6	228.	1.40	175.	1.18		4.1479	

SMP #		END	DATE	pH-F	pH-L	C1	NO3	504	Na	NHA	к	HSO3	нсно	H202
D126	1210	1255	072784		4.45	15.2	213.	49.7	5.36	41.9	1.09			
D127	1255	1330	072784		4.40	19.3	286.	70.2	6.27	73.1	1.57			
D128	1330	1403	072784		4.31	12.9	201.	60.5	4.77	89.3	< .61			
D129	1403	1433	072784		4.30	8.56	158.	56.6	3.45	58.4	.730			
D130	1433	1504	072784		4.24	9.73	155.	63.4	3.96	69.2	1.31			
D131	1504	1533	072784		4.14	9.50	152.	68.5	3.68	72.6	1.08			
D132	1533	1819	072784		3.90	9.49	154.	86.4	3.79	80.4	1.68			
D133	1819	1921	072784		3.76	5.51	112.	88.0	2.32	60.2	.607			
D134	1921	2005	072784		3.76	4.44	101.	89.9	1.78	53.2	.675			
D136	2303	0619	072784		3.41	9.11	154.	178.	6.25	85.7	.891			
D137	0619	0654	072884		3.68	4.58	99.6	88.7	5.13	56.8	.375			
D138	0654	0726	072884		3.73	3.95	96.6	71.2	4.62	48.0	.422			
D139	0726	0806	072884		3.85	3.48	93.9	59.3	3.36	41.3	0			
D140	0806	0845	072884		3.77	3.89	113.	71.9	2.86	56.0	.104			
D141	0845	0920	072884		3.75	3.95	133.	82.7	2.52	71.4	.208			
B142	0920	1000	072884		3.72	3.73	129.	83.7	2.20	76.6	.364			
D143	1344	1416	080184		2.98		398.	803.	13	708.	9.73			
D144	1416	1516	080184		3.12		223.	597.	4.76	587.	2.84			
D145	1516	1545	080184		3.20		176.	463.	4.86	435.	1.58			
D146	1545	1610	080184		3.23		166.	435.	3.71	401.	1.30			
D147	1610	1759	080184		3.36	8.73	123.	349.	1.78	285.	.410		3.2740	
D148	1759	1831	080184		3.72	2.26	40.0	152.	-645	143.	. 656		4.5337	
B149	1831	1858	080184		3.85	.987	18.7	107.	.365	95.9	<.5		3.5308	
D150	1900	1938	080184		3.90	.515	17.1	102.	.322	95.8	.697		4.4373	
D151	1938	2004	080184		4.02	2.92	12.1	80.7	2.76	76.7	.416		4.4373	
D152	2004	2029	080184		3.98	.989	7.85	77.6	.836	53.5	.323		3.9160	
D153	2029	2106	080184		3.81	.430	13.2	103.	.321	52.8	.369		3.3382	
D154	2106	2150	080184		3.69	1.23	20.3	128.	.498	66.0	.469		2.4874	
D155	2150	2231	080184		3.69	1.05	20.1	119.						
D156	2231	0114	080184		3.41	6.18	35.1	214.	5.06	82.2	1.14			
D157	0114	0153	080284		3.61	1.85	28.9	151.	1.55	85.2	.677		3.3075	
B158	0153	0229	080284		3.70	1.28	26.0	136.	.515	79.6	. 495			
D159	0229	0303	080284		3.65	2.09	37.2	132.	.877	86.9	.495		3.1981	
D160	0303	0334	080284		3.66	2.43	44.6	132.	.954	83.8	.765		3.7620	
D161	0334	0403	080284		3.66	1.88	41.3	124.						
D162	0403	0434	080284		3.65	2.08	36.1	99.1	.819	62.3	.569			
D163	0434	0503	080284		3.58		62.0	143.						
D164	0503	0604	080284		3.47		81.2	191.	1.87	139.	.806			
<u>n+/</u> =	0404	.0471	080224		3.56		56.6	164.	2.14	114.	1.18			

WHITEFACE	CLOUD	WATER	\$

S04

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SMP # START

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	D188	1913	1949	080984	2.90	371.	758.	7.44	473.	3.86	5-3174
	D189	1949	2018	080784	3.01	304.	639.	6.47	341.	3.09	5.8333
	D190	2018	2041	080984	3.06	273.	539.	8.84	267.	3.71	6.3095
	D191	2041	2115	080984	3.12	254.	447.	4.90	200.	1.70	6.4285
	D192	2115	2141	080784	3.14	235.	425.	3.64	249.	1.22	
	D193	2141	2214	080784	3.17	199.	382.	5.78	219.	1.38	6.3888
	D194	2214	2245	080784	3.19	192.	357.	4.47	201.	1.11	6.9047
	B195	2245	2316	080984	3.20	198.	345.	4.12	197.	1.02	5.4834
	D196	2316	2345	080984	3.18	207.	340.	4.49	189.	< .B6	5.5231
	D197	2345	0015	080784	3.23	210.	305.	5.54	171.	1.29	6.2384
	D198	0015	0045	081084	3.20	218.	295.	5.46	163.	1.33	6.5960
	D199	0045	0116	081084	3.21	224.	300.	5.17	158.	1.51	6.5760
	D200	0116	0146	081084	3.23	217.	288.	3.88	149.	1.36	6.7152
	0201	0146	0214	081084	3.26	200.	284.	4.31	147.	1.51	6.9536
64	D202	0214	0244	081084	3.26	178.	273.	3.59	137.	<1.21	6.3178
88	D203	0244	0315	081084	3.25	178.	284.	4.23	135.	<1.40	5.7218
20	B204	0315	0345	081084	3.20	199.	325.	3.69	158.	<1.29	5.6423
lui in	2205	-A? 15-	A417	081084	7 15	2.26	770	3.59	192	<1.79	5.62

SMP #	START	END	DATE	ρ́Η-F	pH-L	C1	NO3	\$04	Na	NH4	К	HSO3	HCHO	H202
D206	0413	0443	081084		3.17		230.	381.	3.80	194.	< 1.1		4.9265	
D207	0443	0514	081084		3.23		201.	329.	3.39	169.	1.10		5.6701	
D208	0514	0539	081084		3.26	8.52	168.	277.	3.13	143.	< .78		5.5772	
D209	0539	0608	081084		3.24		178.	293.	3.05	148.	< .70		5.5772	
D210	0608	0815	081084		3.28	6.82	146.	257.	2.64	123.	< .82		5.1124	
B211	0815	0853	081084		3.19		192.	339.	4.63	194.	1.13		5.8096	
D212	0853	0937	081084		3.19		163.	309.	5.04	168.	1.52		4.8809	
D213	0937	1013	081084		3.23	8.83	153.	301.	2.65	158.	.767		5.3571	
D214	1013	1041	081084		3.20	12.0	163.	323.	5.14	169.	1.53		5.9523	
D215	1041		081084		3.15		194.	384.	6.25	202.	1.68		6.2301	

APPENDIX I

Daily weather readings from the summit of Whiteface, summer 1984.

STATE UNIVERSITY OF NEW YORK ATMOSPHERIC SCIENCES RESEARCH CENTER

DATA SHEET; HOURLY RECORDS

Station Whiteface Summit

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Data July - Temperatures - F - 1984

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<u> </u>	1	2	•	;	4	•	; •	,	•	•	30	i n	Num	1	2	3	4	6		,		•	10	n	Moda	TAX	MIN	194
1	63	67	167	1	65	59	58	60	56	56	56	56	54	54	53	5.3	54	Sr.	5.6	56	59	54	63	1 4		100	100	
2	68	6						54	55		58			<u> </u>	 	67		65	63	<u>به</u>		<u> </u>	<i></i>			26	23	
<u> </u>			:53		<u>24. </u>]	5.4	54	24	54	.53	52		1	60	41	64	63		-63		1	1	1	1	1	64	52	
							15.2	1.53		54.	55		. 55	56	55	5.5.	54	54	1.5%	52	57	57	57	57	151	57	152	l.
F	56	176	150		2	<u>5</u>	195	153	23	54	54	the second s	_	57	157	55		52	151	52	152	53	54	1 55	<u>54</u>	57	51	1
-t.	2.4.	24		÷	26	50	120	12.1	124	54	55 49		<u>. (.</u> .).	43.		<u>ماما ا</u>			:54	5.4	55	156	55		.53	66	50	į.
t	38	29			77	.37 37	1.36	137	37	37	38		42	49	50		53. 14E	52	150	45	143	40	39		139	53	39	
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STATE UNIVERSITY OF NEW YORK

ATMOSPHERIC SCIENCES RESEARCH CENTER

DATA SHEET; HOURLY RECORDS

Data

With the Summit

July - Wind Direction (X 10) Degrees - 1984

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STATE UNIVERSITY OF NEW YORK ATMOSPHERIC SCIENCES RESEARCH CENTER

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DATA SHEET; HOURLY RECORDS

Summit

Data July - Wind Speed - Rnots - 1984

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DATA SHEET; HOURLY RECORDS

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STATE UNIVERSITY OF NEW YORK ATMOSPHERIC SCIENCES RESEARCH CENTER

DATA SHEET; HOURLY RECORDS

Whiteface Summit Quation

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