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An Evaluation of Electrochemical Concentration Cell (ECC) Sonde Measurements of Atmospheric Ozone

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AN EVALUATION OF ELECTROCHEMICAL CONCENTRATION CELL (ECC) SONDE MEASUREMENTS OF ATMOSPHERIC OZONE

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SUMMARY

An evaluation of Electrochemical Concentration Cell (ECC) sonde performance has shown it to provide a reliable measurement of seasonal and annual trends in total ozone, variability in ozone versus altitude and season, altitude of peak ozone concentration, and other important ozone parameters. An analysis of ECC profiles from 1970-1976 provided consistent results with that obtained from other studies. A study of very short period (two to four hours) variations in Dobson measurements of total ozone provided unexpected results. The maximum total ozone consistently occurred at noon during the fall and winter months and the minimum occurred at noon during the spring and summer. A further study of this phenomena is recommended.

INTRODUCTION

A program of regular observations of atmospheric ozone has been in operation at NASA-Wallops Island since 1967. Since that time, vertical profiles of ozone have been measured on scheduled one observation per week basis using the Electrochemical Concentration Cell (ECC) ozonesonde. Throughout this observational period, various factors have influenced the attempted weekly launch of ECC sondes so that the total observations are considerably less than one per week. In addition to vertical profiles

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of ozone, Dobson Spectrophotometer observations of total ozone have been made daily at 10 AM, noon, and 2 PM. The Dobson observations have been made whenever weather conditions are such that the "direct sun technique" can be used. In nearly all cases, Dobson total ozone observations were made on the same day as that of an ECC ozonesonde release. These days of conjunctive ECC-Dobson total ozone observations form the data set from which an in-depth study of the ECC ozonesonde has been made.

SECTION 1
SYSTEMS COMPARISON

1.1 DOBSON SPECTROPHOTOMETER (OPTICAL METHOD)

The total amount of ozone has been measured since the early 1930's by the Dobson Spectrophotometer. This instrument is a specialized double-beam monochromater which measures the ratio of the intensities of ultraviolet light at two neighboring wavelengths in the solar spectrum (around 3000 Å). The wavelength pair is carefully chosen so that one wavelength is much more strongly absorbed by ozone than the other. The intensity ratio, therefore, can be used to estimate the total amount of ozone in the optical path from the sun to the instrument. A complete description of the Dobson technique is given in Reference 1.

The Dobson measurements taken at NASA-Wallops Island use the direct sunlight technique with the A-D wavelength pair to obtain the most reliable readings. These preferred modes of detection were used in all observations considered in this analysis.

1.2 ELECTROCHEMICAL CONCENTRATION CELL (CHEMICAL METHOD)

The most valuable use of a chemical method of ozone detection is in the determination of the vertical distribution of the ozone in the atmosphere. The ECC apparatus gives the concentration of ozone in the air at differenct heights by employing the chemical reaction in which ozone liberates iodine from a solution of potassium iodide, the amount of iodine freed being proportional to the amount of ozone passed through the solution. A further description of the ECC ozonesonde technique can be found in References 2 and 3.

The ECC ozonesonde which was developed by the Atmospheric Physics and Chemistry Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, and is flown in conjunction with a standard National Weather Service meteorological radiosonde, has been used in a regularly scheduled program of ozone soundings since 1967 at NASA-Wallops Island.

SECTION 2
DATA REDUCTION

Examples of reduced data received by the University of Dayton Research Institute (UDRI) from NASA-Wallops Island are presented in Tables 1 and 2 along with a typical ECC ozonagram featured in Figure 1. Table 1 shows the format of the Dobson Ozone Data Reduction Form. (This is a Wallops Flight Center form and is not used at other Dobson sites.) Direct sun measurements are taken three times a day with manual reduction of the data being performed by personnel at NASA-Wallops Island. The reduction involves a step-by-step process which results in total ozone values (m atm-cm) recorded in column #26. Table 2 reveals pertinent data from a typical ECC ozonesonde data sheet. Numerous atmospheric and sensor parameters are

TABLE 1

Ozone Data Reduction Form

Manual Data Reduction From AD or CD Direct Sun

Measurements by Dobson Spectrophotometer

Col. #	Name or Operation	NASA - Wallops Flight Center Wallops Island, Virginia 23337		
1	Date	1-1-73	1-1-73	1-1-73
2	Time GMT	1536	1728	1917
3	Wavelength	AD	AD	AD
4	R_A or R_C	125.2	114.6	178.6
5	R_o	125	114	178
6	ΔR	.2	.6	.6
7	N_o	118.7	108.3	169.3
8	ΔN	.2	.5	.6
9	$N_{A,C}$= (7) + (8)	118.9	108.8	169.9
10	R_D	27.7	25.7	65.6
11	R_o	27	25	65
12	ΔR	.7	.7	.6
13	N_o	18.7	16.7	55.6
14	ΔN	.7	.7	.5
15	N_D = (13) + (14)	19.4	17.4	56.1
16	(9) - (15)	99.5	91.4	113.8
17	T_o	1530	1724	1912
18	ΔT = (2) - (17)	6	4	5
19	μ_o	2.317	2.038	2.580
20	$\Delta\mu$	- 0.039	0.007	0.068
21	$\Delta T * \Delta\mu/6$	- 0.039	0.005	0.057
22	μ= (19) + (21)	2.278	2.043	2.637
23	C_1 * (16)	71.7	65.9	82.0
24	(23)/μ	31.5	32.2	31.1
25	(24) - C_2	30.6	31.3	30.2
26	X = (25)/100	.306	.313	.302

TABLE 2

Ozonesonde Data Sheet

STATION	NASA - Wallops Flight Center Wallops Island, Virginia 23337
DATE	7-24-75 GMT
TIME OF RELEASE	0057 GMT

LEVEL	Pa(mb)	Ta(°C)	P3	C.F.	Corr. P3
1	1017.2	25.6	82		
2	1000	24.5	86		
3	850	20.3	31		
4	700	8.6	26		
5	500	-8.3	7		
6	400	-17.8	16		
7	300	-34.7	13		
8	250	-43.7	8		
9	200	-55.3	8		
10	164	-62.4	3		
11	150	-62.2	8		
12	120	-68.3	8		
13	100	-65.0	31		
14	88	-65.7	45		
15	70	-59.3	79		
16	57	-60.7	81		
17	50	-57.3	110		
18	41	-54.3	122	1.003	122
19	30	-53.3	128	1.011	129
20	20	-48.6	137	1.028	140
21	17	-46.7	124	1.037	128
22	13	-43.0	122	1.053	129
23	10	-44.4	79	1.072	85
24	7	-39.7	50	1.104	56
25	5	-30.2	33	1.140	37

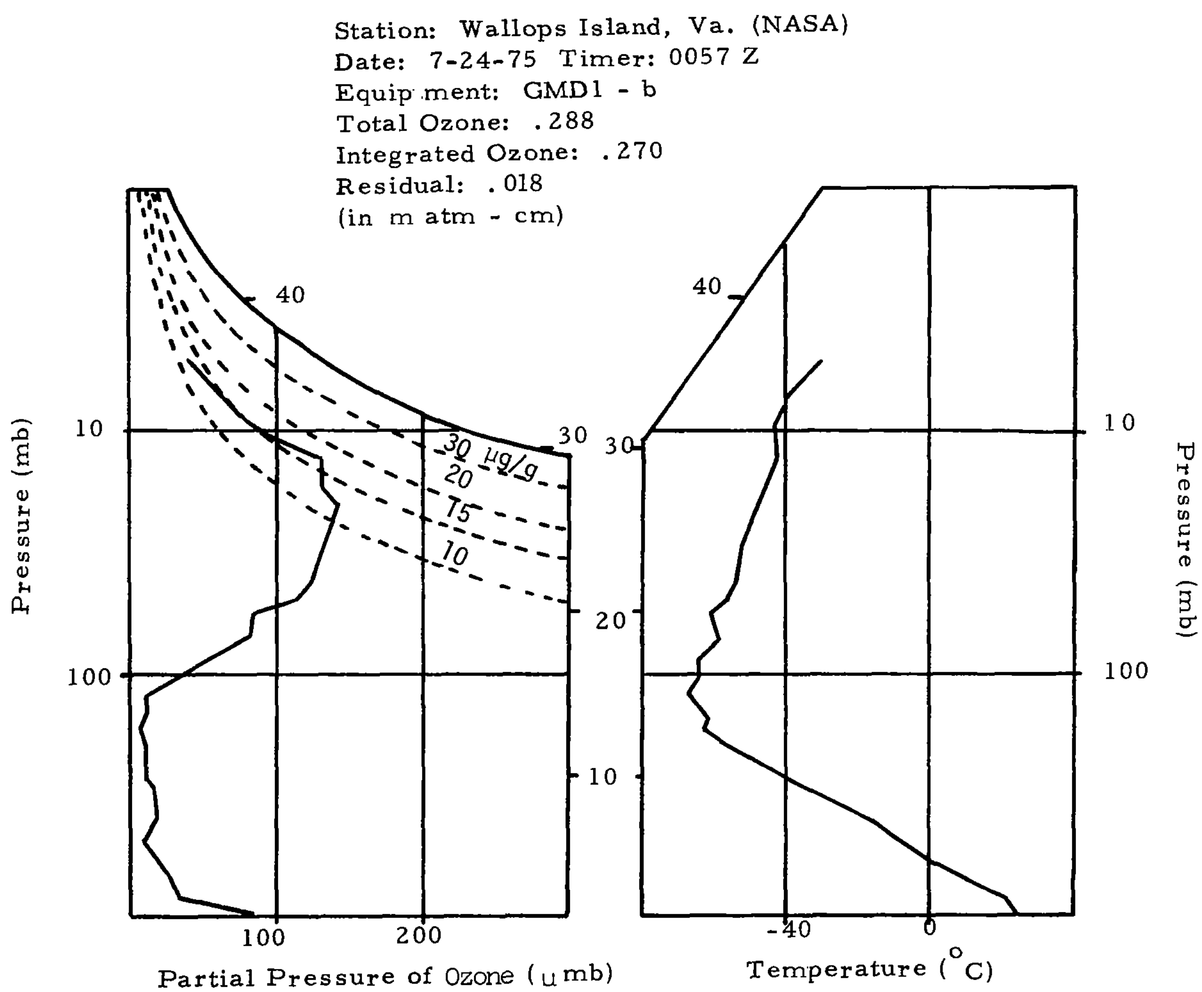

Figure 1. Ozonagram

recorded including atmospheric pressure (Pa) and temperature (Ta), and most importantly, the ozone partial pressure (P3). These ozone concentration values are used to plot the vertical distribution profile of ozone. Examination of the data sheet reveals that these ozone values are corrected for the variation of sonde pump efficiency at reduced ambient pressure (References 4 and 5).

Figure 1 shows the ozonagram for the associated data sheet presented in Table 2. Both ozone and temperature profiles are plotted up to burst height of the balloon. Graphical integration of the ozone profile using a planimeter provides a value of "Integrated Ozone" (.270 m atm-cm for this example). Above the burst height the partial pressure of ozone is assumed to follow a line of constant missing ratio. Integration of the constant mixing ratio line above burst provides the "Residual Ozone" (.018 m atm-cm). The addition of these two ozone values results in the "Total Ozone" figure (.288 m atm-cm).

SECTION 3
SAMPLE SET DETERMINATION

An abundance of both ECC and Dobson data was provided by NASA-Wallops Island for the investigation. The first task was to establish a credible sample set of comparable data from which meaningful inferences about ozone measurement differences could be made. Comparable total ozone data came from Dobson readings (weather permitting - three per day) and ECC flights (scheduled weekly) made from January 1970 to December 1976. Available ECC and Dobson data were arranged chronologically and dates, as well as times (closest), of measurement were used to match corresponding total ozone values. Careful investigation of this table of comparisons prompted removal of certain readings for various reasons. Four comparisons were disregarded because of instrumentation failure or abnormal termination of an ECC flight at a low altitude (< 25 Km). Five sets of observations were disregarded because of a large time difference between ECC and associated Dobson readings (> 3 hours). The remaining set of 123 comparisons were used to provide correlation statistics.

Data organization was also considered to be an important factor in the analysis. The 123 observations contained 28 from the year 1976. These 28 observations were treated as a subset of the total data set for two reasons. First, only a few of these flights were available when the analysis began. Second, the ECC sondes in 1976 underwent a pre-flight calibration not performed on earlier sondes. Even though these calibrations were **not** applied to the data at that time (the post-flight analysis using the calibrations is presently being studied by Bandy of Drexel University under a Wallops contract), a separate analysis of the subset was made for future comparison.

It should also be noted that all ECC data presented in this report was not normalized to match the total ozone of the Dobson Spectrophotometer as recommended by the International Ozone Commission (IOC) and the World Meteorological Organization (WMO) - this normalization process would defeat the purpose of the study.

SECTION 4
COMPARISON STATISTICS

4.1 1970-1975 DATA

Table 3 lists the 95 comparisons of total ozone values in chronological order and pertinent statistics such as differences (ECC-Dobson) and percentage differences ((DIFF/Dobson) X 100). Soundings that showed a large percentage difference (greater than 15%) were carefully scrutinized to assure that no cause for removal of

TABLE 3

Comparison Statistics (1970-1975 Data)

DATE	Ω ECC	Ω DOBSON	Ω DIFF	% DIFF
5-20-70	0.329	0.371	-0.042	-11.3
5-27-70	0.327	0.362	-0.035	- 9.7
10-7-70	0.258	0.290	-0.032	-11.0
10-14-70	0.232	0.270	-0.038	-14.1
10-29-70	0.179	0.267	-0.088	-33.0
11-4-70	0.322	0.316	0.006	1.9
11-19-70	0.416	0.293	0.123	42.0
11-25-70	0.345	0.362	-0.017	- 4.7
12-9-70	0.268	0.310	-0.042	-13.5
4-22-71	0.367	0.412	-0.045	-10.9
5-5-71	0.365	0.373	-0.008	- 2.1
5-19-71	0.312	0.309	0.003	1.0
5-27-71	0.336	0.291	0.045	15.5
6-3-71	0.300	0.342	-0.042	-12.3
6-9-71	0.370	0.372	-0.002	- 0.5
6-16-71	0.321	0.357	-0.036	-10.1
6-23-71	0.381	0.345	0.036	10.4
7-7-71	0.316	0.346	-0.030	- 8.7
7-14-71	0.318	0.319	-0.001	- 0.3
7-21-71	0.273	0.275	-0.002	- 0.7
7-28-71	0.356	0.316	0.040	12.7
8-11-71	0.294	0.317	-0.023	- 7.3
8-25-71	0.318	0.296	0.022	7.4
9-16-71	0.300	0.299	0.001	0.3
9-23-71	0.257	0.281	-0.024	- 8.5
9-30-71	0.233	0.286	-0.053	-18.5
10-7-71	0.275	0.310	-0.035	-11.3
11-4-71	0.229	0.289	-0.060	-20.8
11-11-71	0.328	0.335	-0.007	- 2.1
11-18-71	0.243	0.260	-0.017	- 6.5
12-16-71	0.308	0.284	0.024	8.5
12-30-71	0.265	0.301	-0.036	-12.0
1-6-72	0.295	0.290	0.005	1.7
1-13-72	0.243	0.274	-0.031	-11.3
1-20-72	0.294	0.323	-0.029	- 9.0
2-10-72	0.351	0.376	-0.025	- 6.6
2-25-72	0.336	0.358	-0.022	- 6.1
5-4-72	0.341	0.348	-0.007	- 2.0
5-18-72	0.441	0.391	0.050	12.8
6-1-72	0.344	0.367	-0.023	- 6.3
6-9-72	0.386	0.363	0.023	6.3
6-16-72	0.253	0.357	-0.104	-29.1
8-3-72	0.248	0.309	-0.061	-19.7
8-10-72	0.304	0.304	0.000	0.0

TABLE 3. Concluded

DATE	Ω ECC	Ω DOBSON	Ω DIFF	% DIFF
9-14-72	0.349	0.311	0.038	12.2
9-21-72	0.294	0.314	-0.020	- 6.4
9-29-72	0.297	0.353	-0.056	-15.9
10-5-72	0.350	0.308	0.042	13.6
10-12-72	0.328	0.302	0.026	8.6
10-20-72	0.377	0.329	0.048	14.6
10-26-72	0.289	0.317	-0.028	- 8.8
11-10-72	0.262	0.291	-0.029	-10.0
11-16-72	0.321	0.322	-0.001	- 0.3
11-24-72	0.397	0.353	0.044	12.5
12-1-72	0.374	0.336	0.038	11.3
12-7-72	0.225	0.261	-0.036	-13.8
12-21-72	0.341	0.322	0.019	5.9
1-26-73	0.356	0.335	0.021	6.3
2-1-73	0.335	0.322	0.013	4.0
2-15-73	0.351	0.327	0.024	7.3
3-15-73	0.316	0.292	0.024	8.2
3-23-73	0.460	0.382	0.078	20.4
6-7-73	0.330	0.307	0.023	7.5
6-14-73	0.357	0.331	0.026	7.9
6-30-73	0.344	0.334	0.010	3.0
8-16-73	0.324	0.329	-0.005	- 1.5
9-7-73	0.347	0.327	0.020	6.1
9-20-73	0.334	0.333	0.001	0.3
9-27-73	0.294	0.297	-0.003	- 1.0
10-4-73	0.274	0.272	0.002	0.7
10-18-73	0.363	0.330	0.033	10.0
11-15-73	0.353	0.300	0.053	17.7
12-13-73	0.269	0.309	-0.040	-12.9
1-10-74	0.286	0.252	0.034	13.5
1-17-74	0.346	0.301	0.045	15.0
4-18-74	0.363	0.377	-0.014	- 3.7
6-29-74	0.396	0.363	0.033	9.1
6-30-74	0.412	0.340	0.072	21.2
8-15-74	0.329	0.334	-0.005	- 1.5
8-29-74	0.297	0.306	-0.009	- 2.9
9-12-74	0.260	0.294	-0.034	-11.6
9-26-74	0.332	0.309	0.023	7.4
10-18-74	0.326	0.296	0.030	10.1
1-10-75	0.288	0.276	0.012	4.3
1-23-75	0.379	0.306	0.073	23.9
2-27-75	0.304	0.338	-0.034	-10.1
3-6-75	0.396	0.365	0.031	8.5
3-27-75	0.250	0.304	-0.054	-17.8
4-10-75	0.329	0.401	-0.072	-18.0
7-29-75	0.297	0.300	-0.003	- 1.0
7-29-75	0.308	0.322	-0.014	- 4.3
10-23-75	0.280	0.288	-0.008	- 2.8
11-19175	0.262	0.280	-0.018	- 6.4
12-2-75	0.340	0.323	0.017	5.3
12-12-75	0.352	0.283	0.069	24.4
Mean	0.319	0.320	-0.001	- 0.3
St Dev	0.050	0.034	0.038	12.19

the soundings from the sample set existed. Means and standard deviations were also computed for the data set with the following results being observed.

1) Both detection systems measure virtually the same mean total ozone over the time period under consideration (ECC - .319 versus Dobson - .320). Thus, no bias exists between ECC and Dobson readings.

2) ECC observations exhibit more variability over the sample than Dobson readings. The variability in total ozone for ECC sondes as measured by the standard deviation of 95 observations is $\sigma_{ECC} = .050$ units as compared to $\sigma_{Dobson} = .034$ for the corresponding 95 Dobson observations.

3) The standard deviation of the percentage differences is 12.19%. This can be interpreted as a 12.19% total measurement error between the systems. It cannot be determined what proportion of the total error is contributed by each sensor. Item (2) indicates much of the total error occurs because of the large variability observed by the ECC sonde. This implies either the ECC sonde is contaminated by a rather large random flight-to-flight error, or that the Dobson technique is not sensitive to measurement of all ozone fluctuations.

To obtain a graphical representation of the ECC-Dobson total ozone comparison, Figure 2 was produced. Total ozone values from each system were averaged over seasons. The ECC plot shows rather good agreement with the Dobson measurement of seasonal fluctuations. Average maximum total ozone values occur during the spring with minimum values being realized during the autumn months (Reference 6). This variation is accurately noted by the ECC plot except for some reasons where the number of observations is too small to infer disagreement with Dobson measurements.

4.2 1976 DATA

Availability of data and different pre-flight preparations and calibration techniques on ECC sondes flown in 1976 prompted a separate analysis of data recorded during that year. Table 4 records the 1976 ECC and Dobson total ozone data with

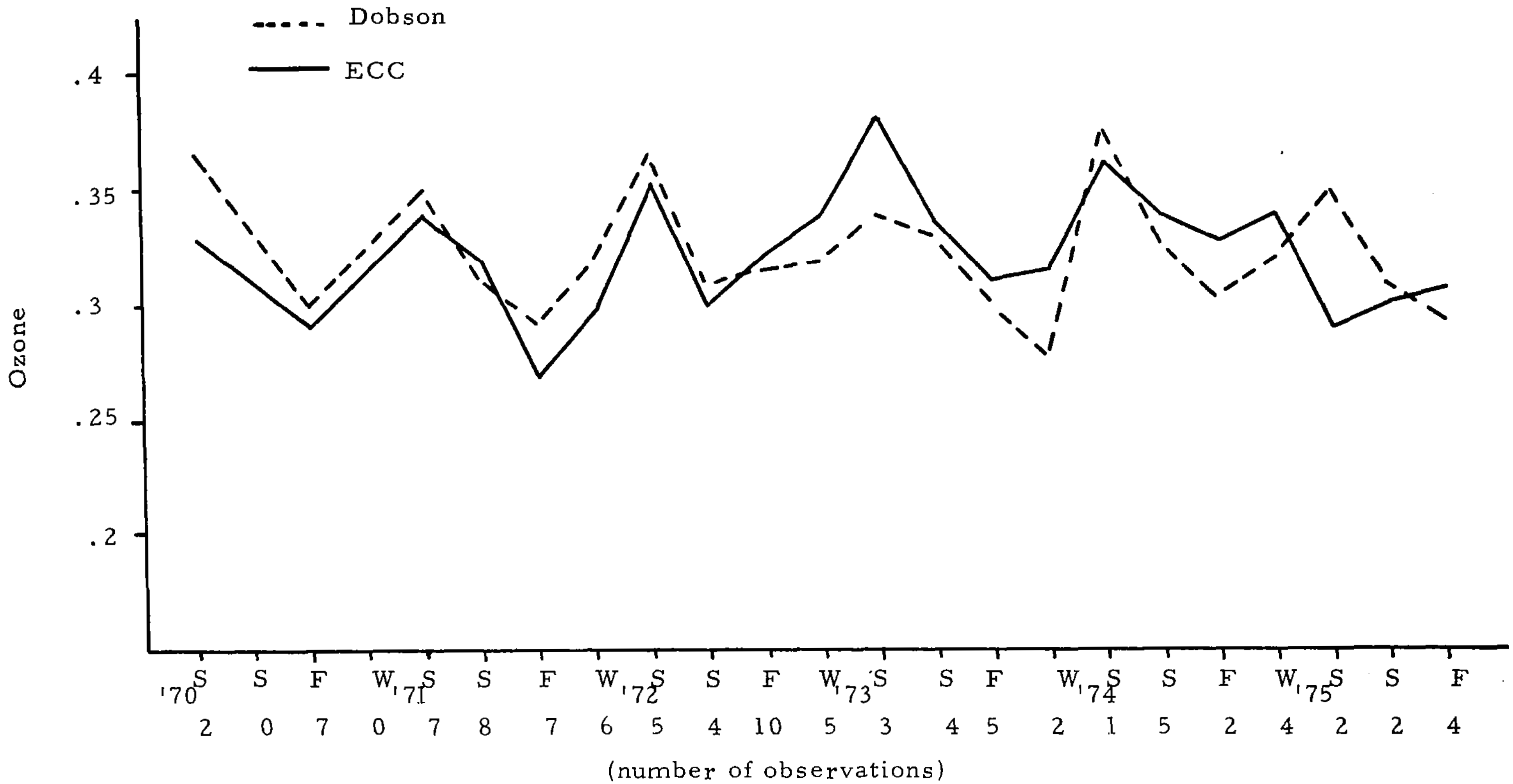

Figure 2. Mean Seasonal Total Amount of Ozone

TABLE 4

Comparison Statistics (1976 Data)

DATE	ECC	DOBSON	DIFF	% DIFF
4-7	0.324	0.324	0.000	0.0
4-14	0.344	0.363	-0.019	-5.2
4-22	0.333	0.312	0.021	6.7
5-5	0.459	0.366	0.093	25.4
5-20	0.361	0.356	0.005	1.4
5-26	0.446	0.431	0.015	3.5
6-3	0.351	0.391	-0.040	-10.2
6-9	0.433	0.358	0.075	20.9
6-16	0.288	0.303	-0.015	-5.0
6-23	0.333	0.332	0.001	0.3
6-30	0.335	0.324	0.011	3.4
7-7	0.326	0.321	0.005	1.6
7-14	0.359	0.344	0.015	4.4
7-21	0.308	0.317	-0.009	-2.8
7-28	0.351	0.325	0.026	8.0
8-11	0.277	0.328	-0.051	-15.5
8-18	0.317	0.339	-0.022	-6.5
9-1	0.350	0.319	0.031	9.7
9-8	0.281	0.311	-0.030	-9.6
9-22	0.266	0.331	-0.065	-19.6
10-6	0.267	0.281	-0.014	-5.0
10-13	0.343	0.297	0.046	15.5
10-27	0.368	0.330	0.038	11.5
11-10	0.335	0.345	-0.010	-2.9
11-11	0.397	0.306	0.091	29.7
11-18	0.323	0.309	0.014	4.5
11-24	0.370	0.333	0.037	11.1
12-1	0.267	0.291	-0.024	-8.2
Mean	0.340	0.332	0.008	2.4
St. Dev.	0.051	0.031	0.038	11.55

appropriate sample set statistics computed. No comparable data was available for January, February, and March of 1976. The following points summarize results obtained.

1) The lack of winter data, when total ozone values are generally below the yearly average, is reflected by higher mean total ozone values (ECC - .340, Dobson - .332) than found in the 1970-1975 data. There is no detectable bias between measurements from the two systems. The mean percentage difference of 2.4% is not significant for the small sample size.

2) Systems measurement variability over the sample set compare almost identically with the corresponding 1970-1975 values (σ_{ECC76} = .051, $\sigma_{ECC70-75}$ = .050, σ_{DOB76} = .031, $\sigma_{DOB70-75}$ = .034).

3) The one sigma percentage difference between total ozone values for the 1976 data is 11.6% as compared to 12.2% for the 1970-75 data.

4) The 1976 observations indicate that the performance of the ECC and Dobson systems during this period were statistically homogeneous with the pre-1976 data.

SECTION 5
ERROR ANALYSIS

The approximate 12% difference between ECC and Dobson measurements is in excess of the estimate errors found in the estimate errors found in the literature for each system. Reference 7 indicates a Dobson measurement error of less than 5%. Reference 8 gives the ECC calculated sonde error as ≈5%. In an attempt to explain discrepancies between observed differences in measurements and error estimates, an analysis was made of the various factors that were believed to be contributing causes. Time separation between Dobson and ECC observation, data processing errors, and residual ozone estimations were some of the factors analyzed. The following section describes these analyses and the results they provided.

5.1 TIME DIFFERENCE

It was thought that the difference in times between ECC and associated Dobson observations could be a factor in the total ozone differences noted. Dobson observations were made three times per day at approximately 10 AM, noon, and 2 PM local time. ECC observations in nearly all cases were made within the range of 10 AM to 2 PM. To provide a Dobson observation that corresponds exactly with the ECC launch value, a linear interpolation between observations was made. Table 5 provides the mean statistics generated by the comparison of this "interpolated" Dobson value with the associated ECC total ozone value. A simple comparison between the mean values and those generated by the original ECC-Dobson comparison (where the closest Dobson observation in time was used) reveals that a small time difference (< two hours) between ECC and Dobson measurement readings does not really affect the pertinent statistics over the entire data set.

A graphical insight of the time difference aspect of the data is provided in Figure 3 which plots the percentage difference (between ECC and Dobson total ozone values) versus the time difference between associated readings (min.). If percentage differences increased as the time differences increased, it might be assumed that the time between ECC and Dobson observations was a significant factor. However, the almost random scattering of points on the graph, along with the interpolation study mentioned above, led to the conclusion that the time differences between observations was not a contributing factor to the discrepancy in total ozone values between the two systems.

TABLE 5

Time Difference - Interpolation Effect

		ECC - Dobson		
	ECC	Dobson	Diff.	% Diff.
Mean	.326	.320	.007	2.2
Std. Dev.	.047	.030	.038	11.55

		ECC - Revised Dobson		
	ECC	Dobson	Diff.	% Diff.
Mean	.326	.321	.006	1.9
Std. Dev.	.047	.031	.038	11.72

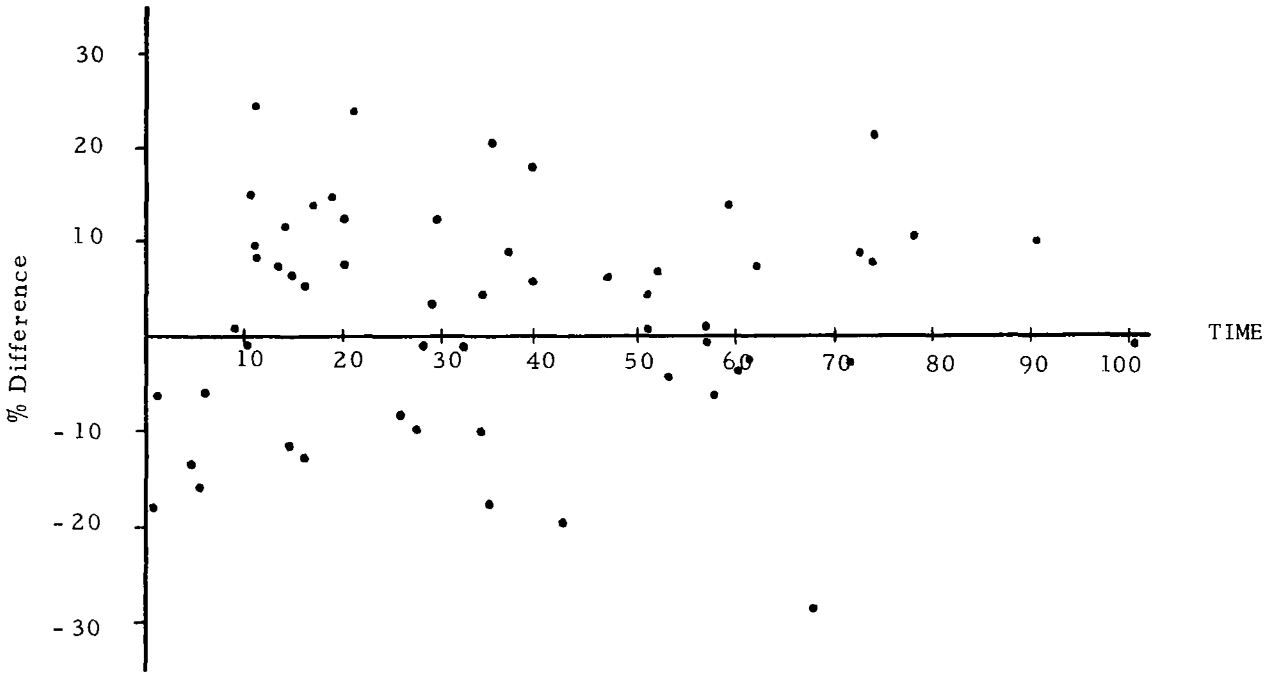

Figure 3. Time Difference vs. Percentage Difference

5.2 GRAPHICAL VS. NUMERICAL INTEGRATION

Another source of differences in total ozone observations from the sensor was thought to arise from the method that was used to calculate total integrated ozone for the ECC ozonesonde. Planimeter integration of ozone partial pressure versus log pressure was performed by personnel at NASA-Wallops Island giving a graphical representation of the integration process. Numerical integration as discussed in Reference 9 has also been used to derive total ozone from the ECC sonde. It was thought that discrepancies in ozone values might be due to differences between numerical and graphical integration. (Reference 10 provides a general comparison of the two techniques). Ozone partial pressure and atmospheric pressure data from individual ECC flights were tabulated and used as input to a numerical integration computer program. The total integrated ozone values generated by this numerical process were compared with the values obtained graphically (planimeter measurements) by personnel at NASA-Wallops Island. Table 6 provides a comparison of ECC total ozone values resulting from the two methods mentioned. The pertinent statistics computed reveal no bias. The standard deviation of the percentage difference in total ozone using the two integration method is 2.65%.

The table below shows the comparison between Dobson measurements and associated ECC values (numerically computed). Total means and standard deviations remain

Numerical vs. Graphical Integration

	ECC (Numerical) - Dobson			
	ECC	Dobson	Diff.	% Diff.
Mean	.321	.320	.000	.2
Std. Dev.	.051	.034	.040	12.59

	ECC (Graphical) - Dobson			
	ECC	Dobson	Diff.	% Diff.
Mean	.319	.320	-.001	-.3
Std. Dev.	.050	.034	.038	12.19

TABLE 6

Comparison of Dobson Total Ozone by Numerical and Graphical Integration Techniques

DATE	Ω GRAPH.	Ω NUM.	Ω DIFF	% DIFF
5-20-70	0.329	0.332	- 0.003	- 0.9
5-27-70	0.327	0.333	- 0.006	- 1.8
10-7-70	0.258	0.260	- 0.002	- 0.8
10-14-70	0.232	0.235	- 0.003	- 1.3
10-29-70	0.179	0.179	0.000	0.0
11-4-70	0.322	0.324	- 0.002	- 0.6
11-19	0.416	0.422	- 0.006	- 1.4
11-25-70	0.345	0.350	- 0.005	- 1.4
12-9-70	0.268	0.269	- 0.001	- 0.4
4-22-71	0.367	0.374	- 0.007	- 1.9
5-5-71	0.365	0.371	- 0.006	- 1.6
5-19-71	0.312	0.311	0.001	0.3
5-27-71	0.336	0.334	0.002	0.6
6-3-71	0.300	0.303	- 0.003	- 1.0
6-9-71	0.370	0.370	0.000	0.0
6-16-71	0.321	0.324	- 0.003	- 0.3
6-23-71	0.381	0.386	- 0.005	- 1.3
7-7-71	0.316	0.320	- 0.004	- 1.3
7-14-71	0.318	0.323	- 0.005	- 1.5
7-21-71	0.273	0.275	- 0.002	- 0.7
7-28-71	0.356	0.351	0.005	1.4
8-11-71	0.294	0.274	0.020	7.3
8-25-71	0.318	0.323	- 0.005	- 1.5
9-16-71	0.300	0.280	0.020	7.1
9-23-71	0.257	0.256	0.001	0.4
9-30-71	0.233	0.244	- 0.011	- 4.5
10-7-71	0.275	0.296	- 0.021	- 7.1
11-4-71	0.229	0.228	0.001	0.4
11-11-71	0.328	0.332	- 0.004	- 1.2
11-18-71	0.243	0.246	- 0.003	- 1.2
12-16-71	0.308	0.310	- 0.002	- 0.6
12-30-71	0.265	0.266	- 0.001	- 0.4
1-6-72	0.295	0.298	- 0.003	- 1.0
1-13-72	0.243	0.245	- 0.002	- 0.8
1-20-72	0.294	0.301	- 0.007	- 2.3
2-10-72	0.351	0.355	- 0.004	- 1.1
2-25-72	0.336	0.341	- 0.005	- 1.5
5-4-72	0.341	0.343	- 0.002	- 0.6
5-18-72	0.441	0.447	- 0.006	- 1.3
6-1-72	0.344	0.349	- 0.005	- 1.4
6-9-72	0.386	0.394	- 0.008	- 2.0
6-16-72	0.253	0.251	0.002	0.8
8-3-72	0.248	0.250	- 0.002	- 0.3
8-10-72	0.304	0.315	- 0.011	- 3.5

TABLE 6. Concluded

DATE	Ω GRAPH.	Ω NUM.	Ω DIFF	% DIFF
9-14-72	0.349	0.350	-0.001	-0.3
9-21-72	0.294	0.289	0.005	1.7
9-29-72	0.297	0.295	0.002	0.7
10-5-72	0.350	0.365	-0.015	-4.1
10-12-72	0.328	0.332	-0.004	-1.2
10-20-72	0.377	0.346	0.031	9.0
10-26-72	0.289	0.290	-0.001	-0.3
11-10-72	0.262	0.263	-0.001	-0.4
11-16-72	0.321	0.328	-0.007	-2.1
11-24-72	0.397	0.407	-0.010	-2.5
12-1-72	0.374	0.378	-0.004	-1.1
12-7-72	0.225	0.235	-0.010	-4.3
12-21-72	0.341	0.338	0.003	0.9
1-26-73	0.356	0.356	0.000	0.0
2-1-73	0.335	0.308	0.027	8.8
2-15-73	0.351	0.374	-0.023	-6.1
3-15-73	0.316	0.317	-0.001	-0.3
3-23-73	0.460	0.458	0.002	0.4
6-7-73	0.330	0.336	-0.006	-1.8
6-14-73	0.357	0.357	0.000	0.0
6-30-73	0.344	0.348	-0.004	-1.1
8-16-73	0.324	0.328	-0.004	-1.2
9-7-73	0.347	0.344	0.003	0.9
9-20-73	0.334	0.338	-0.004	-1.2
9-27-73	0.294	0.295	-0.001	-0.3
10-18-73	0.363	0.370	-0.007	-1.9
11-15-73	0.353	0.360	-0.007	-1.9
12-13-73	0.269	0.255	0.014	5.5
1-10-74	0.286	0.274	0.012	4.4
1-17-74	0.346	0.339	0.007	2.1
4-18-74	0.363	0.379	-0.016	-4.2
6-29-74	0.396	0.383	0.013	3.4
6-30-74	0.412	0.393	0.019	4.8
8-15-74	0.329	0.333	-0.004	-1.2
8-29-74	0.297	0.298	-0.001	-0.3
9-12-74	0.260	0.261	-0.001	-0.4
9-26-74	0.332	0.337	-0.005	-1.5
10-18-74	0.326	0.322	0.004	1.2
1-10-75	0.288	0.291	-0.003	-1.0
1-23-75	0.379	0.382	-0.003	-0.8
2-27-75	0.304	0.293	0.011	3.8
3-6-75	0.396	0.388	0.008	2.1
3-27-75	0.250	0.244	0.006	2.5
4-10-75	0.329	0.324	0.005	1.5
7-29-75	0.297	0.301	-0.004	-1.3
7-29-75	0.308	0.303	0.005	1.7
10-23-75	0.280	0.276	0.004	1.4
11-19-75	0.262	0.261	0.001	0.4
12-2-75	0.340	0.341	-0.001	-0.3
12-12-75	0.352	0.344	0.008	2.3
Mean	0.320	0.320	-0.001	-0.2
St Dev	0.050	0.051	0.008	2.65

virtually unchanged from the graphically integrated ECC measurements comparison. Therefore, graphical integration of the profiles to determine integrated ozone is a source of a small measurement variation (σ = 2.65%) but does not significantly contribute to the 12% difference between ECC and Dobson values.

5.3 TOTAL OZONE AND SEASONAL ANALYSIS

Another factor considered to be important in the study was whether the differences between ECC and associated Dobson readings were a function of the total amount of ozone measured. If one of the sensors accuracy is dependent upon the amount of ozone present in the atmosphere, then this effect can be observed statistically as a function of total ozone. Figure 4 graphically shows a plot of the percentage differences in total ozone versus the associated total ozone measured (Dobson value). This graph shows that varying degrees of percentage differences occur almost randomly over the entire range of total ozone values. Thus, it was concluded that sensor accuracy is not a function of the amount of ozone present.

Since ozone exhibits a rather well-defined annual trend, a seasonal analysis of total ozone can also indicate sensor accuracy with respect to the amount of ozone present in the atmosphere. With this in mind, a study of seasonal ozone characteristics as well as systems measurement comparison was undertaken. Table 7 provides the sample statistics according to season with the following aspects being noted.

1) Spring and Fall measurements provide the maximum and minimum mean total ozone values throughout the year.

2) Summer observations appear to be the most consistent (less variable) values, σ_{ECC} = .040, σ_{Dobson} = .020).

3) ECC-Dobson total ozone agreement remains relatively constant from season to season.

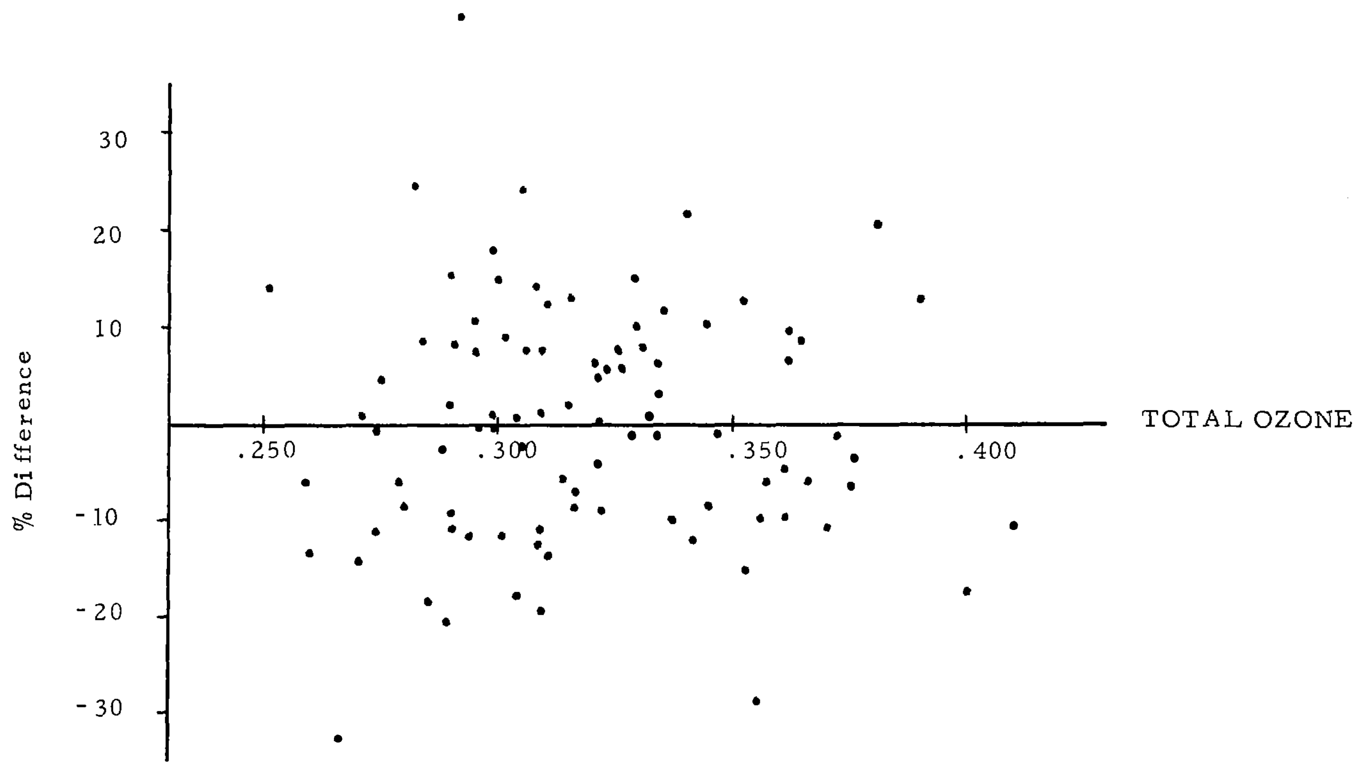

Figure 4. % Difference Between Dobson and Ecc Total Ozone vs. Dobson Total Ozone

TABLE 7

Seasonal Analysis

		ECC	Dobson	Diff.	% Diff.
Spring (n = 20)	Mean	.344	.356	-.012	-3.1
	Std. Dev.	.050	.033	.044	12.41
Summer (n = 23)	Mean	.322	.319	.003	.7
	Std. Dev.	.040	.020	.029	8.96
Fall (n = 35)	Mean	.302	.303	-.002	-.8
	Std. Dev.	.055	.026	.043	14.59
Winter (n = 17)	Mean	.322	.315	.007	2.6
	Std. Dev.	.041	.034	.032	10.32

Although these observations reveal meaningful seasonal characteristics of ozone measurement, seasonal influences do not seem to be a major reason for measurement differences.

5.4 RESIDUAL ANALYSIS

In the derivation of the total ozone from ECC ozonesonde observations, the partial pressure of ozone can only be calculated to the collapse altitude of the balloon (approximately 30 Km). To obtain the total ozone, ozone partial pressure is integrated to the collapse altitude and a residual amount estimated for the region of the atmosphere above collapse. The residual amount is estimated by assuming the partial pressure above collapse altitude follows a line of constant mixing ratio that is determined by the partial pressure profile immediately below collapse.

It is possible that the assumptions used in determining the residual ozone result in a significant error in the total ozone. If such is the case, it was thought that if this residual value was a large percentage of the total ozone, large differences between ECC and Dobson readings would be observed. Figure 5 plots the percentage residual value versus the associated percentage difference. If percentage residual increased as percentage difference increased, it might be expected that this was a significant source of measurement differences. However, the almost random scattering of points indicates no real significant effect.

5.5 GOODNESS-OF-FIT

Finally, an analysis of the distribution of percentage differences was made. Figure 6 provides a histogram of this distribution. A goodness-of-fit test was performed on the data and the null hypothesis (data from a Normal Distribution) could not be

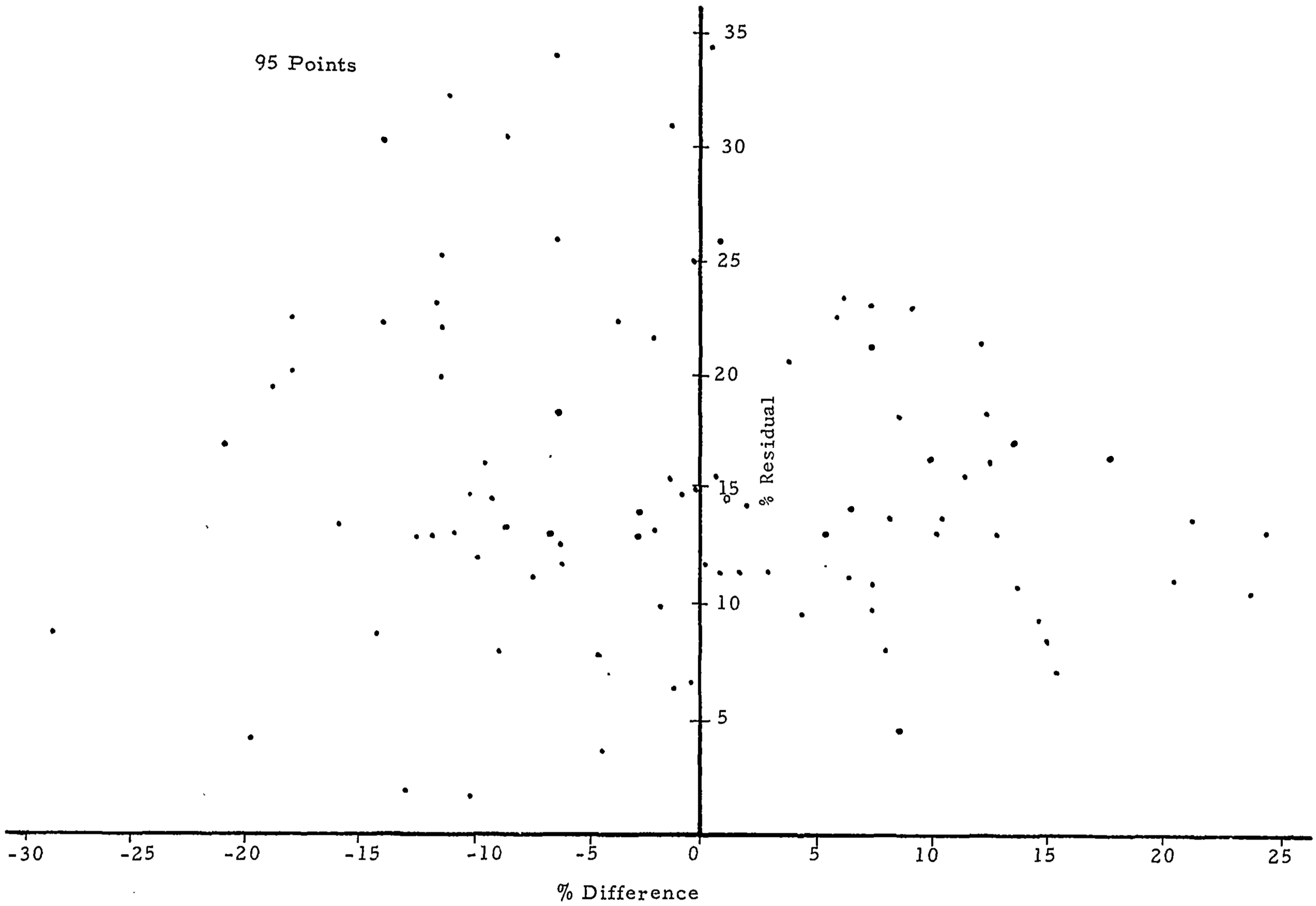

Figure 5. % Residual - % Difference

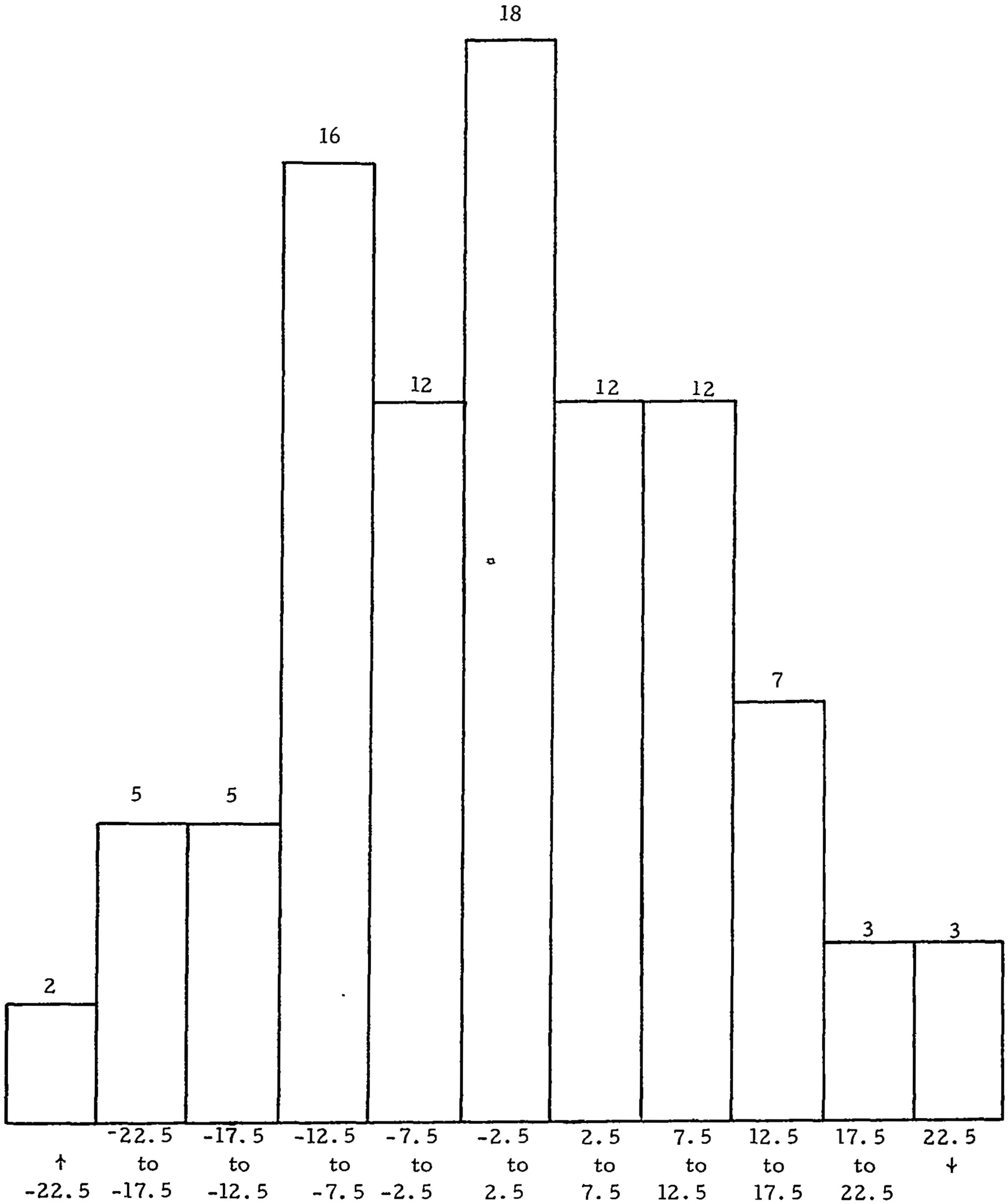

Figure 6: Histogram of Percentage Difference

rejected at the α =.05 level. Thus, the conclusion that can be made is that the differences between systems follows the type of distribution that one would expect for sensors performing as designed. It does not appear that the differences are caused by a system or hardware malfunction since this would tend to bias results and thus skew the distribution away from normal.

SECTION 6
CONCLUSIONS

6.1 ERROR ANALYSIS

The previous section provided an in-depth study of the factors which were believed to contribute to the observed 12% RMS difference between total ozone values obtained from the ECC and Dobson sensors. None of the factors were found to significantly contribute to the 12% difference. A summary of pertinent results from the previous section are as follows.

1) Large time differences (> two hours) between ECC and associated Dobson total ozone measurements do not account for the discrepancies between measured total ozone values.

2) Graphical integration of the ECC profiles to determine integrated ozone is a source of a small measurement variation but does not significantly contribute to the percentage difference between ECC and Dobson total ozone values.

3) Sensor accuracy is not a function of the amount of ozone present in the atmosphere.

4) Seasonal influences are not a major reason for total ozone measurement differences.

5) The set of percentage differences between ECC and Dobson total ozone measurements comes form a population having a Normal Distribution.

Data processing and time differences make a total contribution of 2-3% (other factors negligible) to the 12% difference between the sensors. Inherent sensor accuracy documented in Reference 7 is less than 5% RMS error for the Dobson sensor and approximately 5% for the ECC sonde. Thus, 5-7% of the 12% difference remains unexplained. Since the unexplained difference could not be attributed to a specific sensor, it could not be determined which, if any of the sensors, was performing in conformance with the Reference 8 accuracy figures. The conclusions that can be drawn are as follows.

a) There is no bias between the sensors.

b) Approximately 5-7% of the RMS difference between the sensors remains unexplained.

c) The ECC sonde shows considerably more variability in total ozone (σ ECC=.051) than the Dobson (σDobson=.034). Whether this variability is real or due to sensor inaccuracy has not been established.

The following sections analyze data from the ECC sonde and Dobson spectrophotometer to establish sensor validity by evaluating sensor observations relative to known ozone behavior

6.2 ANALYSIS OF ECC VERTICAL PROFILE OF OZONE

An analysis was made of the 123 ECC ozone profiles to determine seasonal variation, altitude of peak ozone concentration, and other properties of the ozone in the troposphere and lower statosphere.

Mean seasonal ozone profiles (one-sigma band included) as well as mean temperature profiles are illustrated for the years 1970-1976 in Figure 7. The profiles were obtained for each season by averaging the ozone partial pressure values and temperatures at various levels (1000, 700, 500, 300, 250, 200, 150, 100, 70, 50, 30, 20, 10 millibars). Standard deviations of the ozone partial

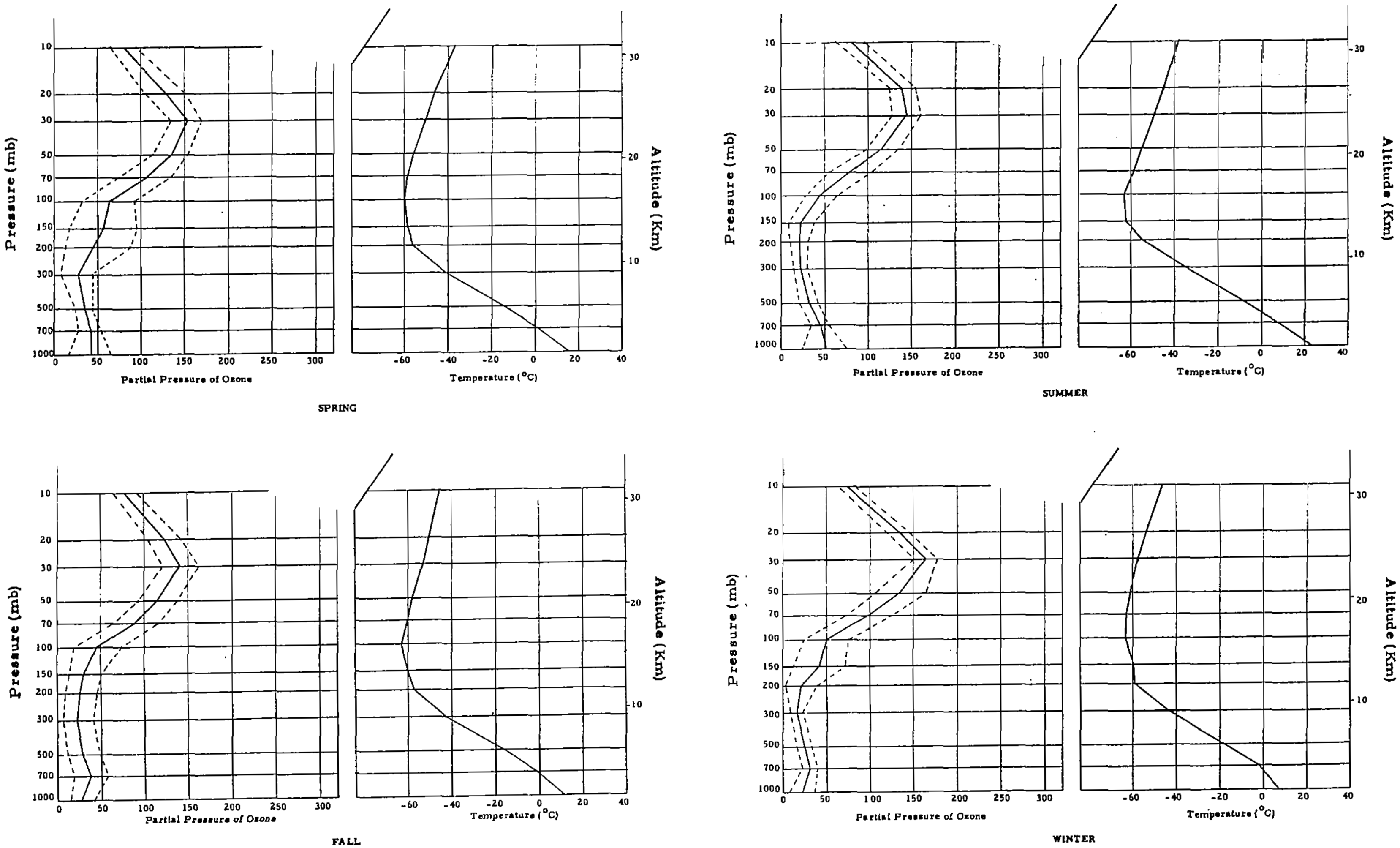

Figure 7. Mean Seasonal Ozone and Temperature Profiles

pressures at each level were also evaluated to determine at what altitudes the ozone variability was the greatest.

Figure 8 shows the mean seasonal build up and decay of ozone. In the lower stratosphere where the peak ozone occurs, a rapid rise in ozone occurs during the winter months. From the winter maximum, a decay gradually takes place through the remainder of the year. Reference 11 suggests the winter maximum results from ozone transport from the upper stratosphere at low or middle latitudes. Near the tropopause the maximum occurs in the spring and is rapidly removed by summer. Transport to the surface during the summer months probably account for the minimum ozone at the tropopause in summer and maximum at the surface. During the fall and winter months, ozone at the tropopause continues to build. At the surface the minimum is reached in winter and rapidly increases in spring and summer.

A study of the statistics and the general characteristics of the profiles shown in Figures 7 and 8 yielded the following results.

1) The profiles substantiate the known seasonal variation of total ozone (Spring - maximum, Fall - minimum).

2) Peak ozone concentration generally occurs around 23-24 Km throughout the year.

3) A relatively small proportion of the total ozone is found in the troposphere (below 10 Km). Most of the ozone in a vertical column is found in the lower stratosphere.

4) Variations from the mean profile are greatest around the level of the tropopause (especially during winter and spring).

5) Ozone profiles can reveal ozone transport and general circulation throughout the year.

Thus, this ECC method provides ozone measurement accuracy which is sufficient to observe seasonal trends, ozone variability, and other important ozone characteristics.

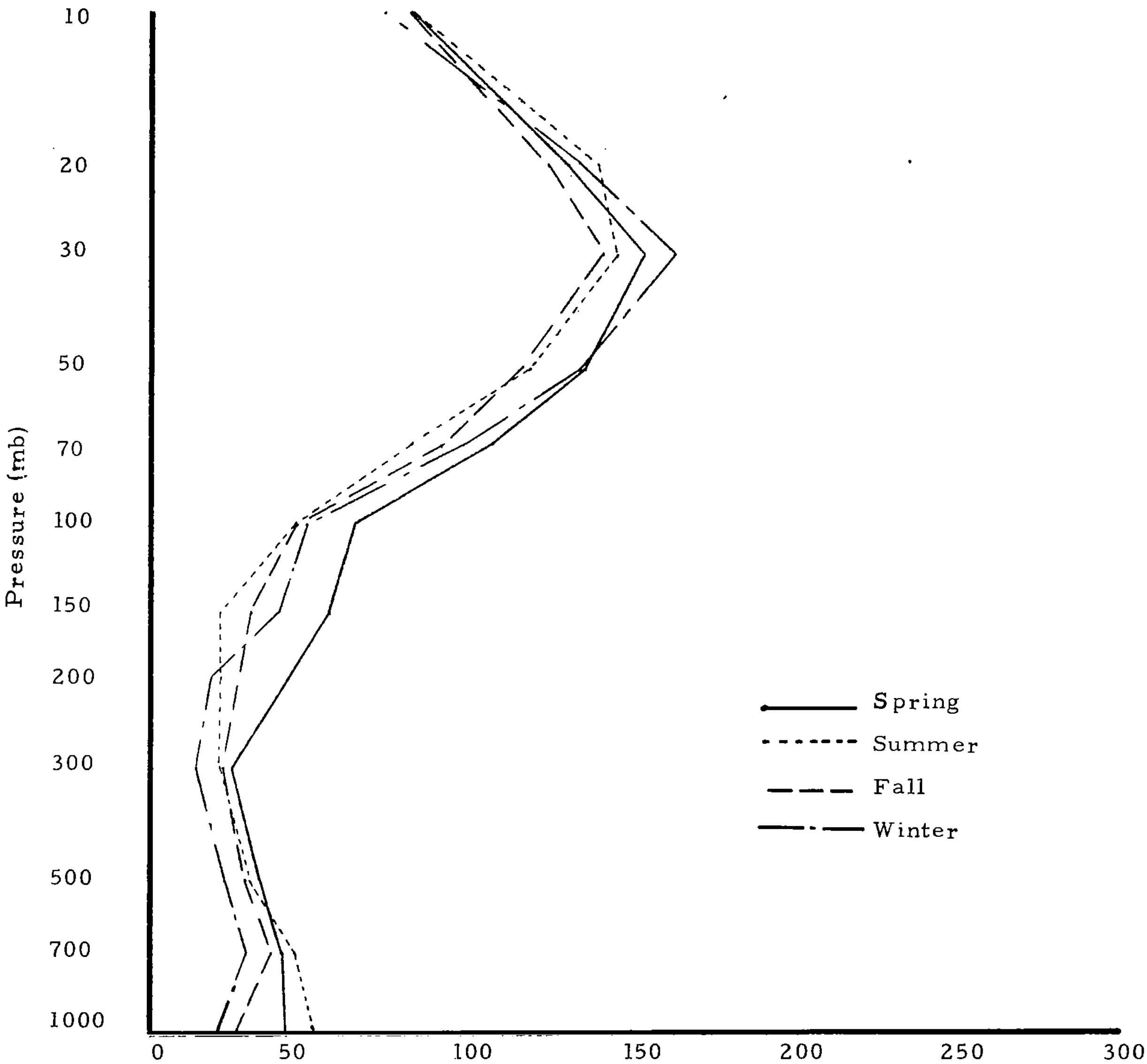

Figure 8. Mean Seasonal Ozone Profiles Comparison

6.3 ANALYSIS OF DOBSON TOTAL OZONE MEASUREMENTS

A study of Dobson measurements over the years of concern (1972-1976) was performed to gain a better understanding of short- and long-period total ozone fluctuations which could prove to be valuable in explaining differences between, and variations within, systems of ozone detection. The sample set of total ozone values used for this analysis consisted of the available daily Dobson measurements (weather permitting - 10 AM, noon, 2 PM) made from June 1972 to August 1976. This large sample set (≈3, 000 observations) provided a statistically sound population of values from which meaningful inferences were made.

6.3.1 Short-Period Changes

Three daily Dobson readings at Wallops Island provide data to observe very short-period variations of total ozone. Figure 9 presents mean monthly values of total ozone at 10 AM, noon, and 2 PM, averaged over the years under consideration. A very definite trend seems to exist upon examination of the graph produced. Generally, during the summer months (April through September) the noon observations appear to be approximately 2-3% lower than the associated morning and afternoon measurements. The months of March and October act as "transition periods" with the winter months (November through February) producing a daily maximum total ozone at noon. A similar trend in the data for the individual years under consideration can be observed in Figure 10. Whether this short term oscillation is real or artifically induced has not yet been determined. Since the oscillation changes in sign near the spring and fall equinox, an analysis was made to verify the calculation of the solar zenith angle used in deriving total ozone. No error was found that could cause the short-term oscillation. Further study of other possible causes is recommended. It is also recommended that Dobson measurements from other sites be analyzed for the presence of this short-term oscillation.

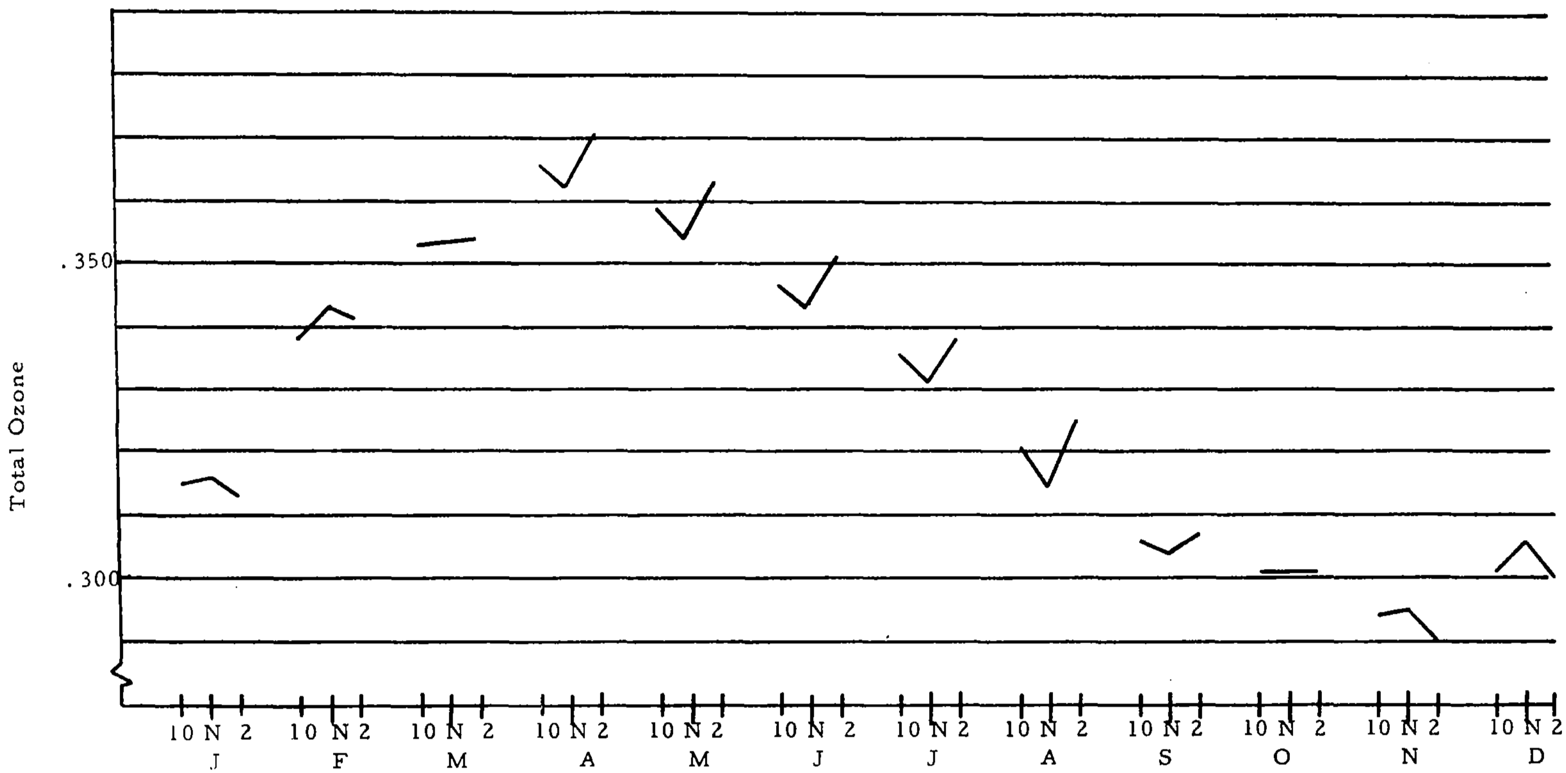

Figure 9. Mean Monthly Total Ozone (Dobson) at 10 AM, Noon and 2 PM-
Years 1972- 1976 Combined.

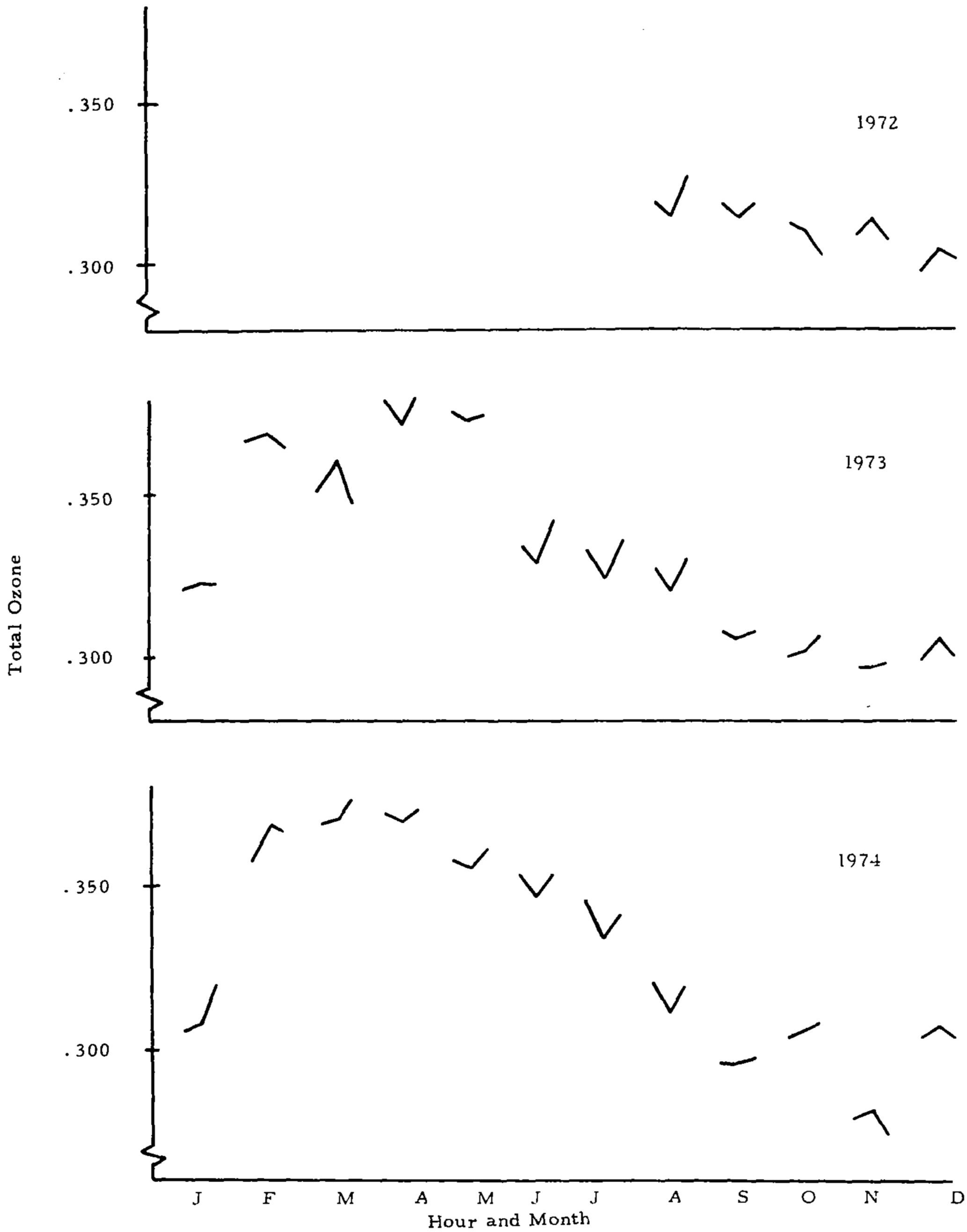

Figure 10. Mean Monthly Total Ozone (Dobson) at 10 AM, Noon and 2 PM - Years 1972, 1973, 1974

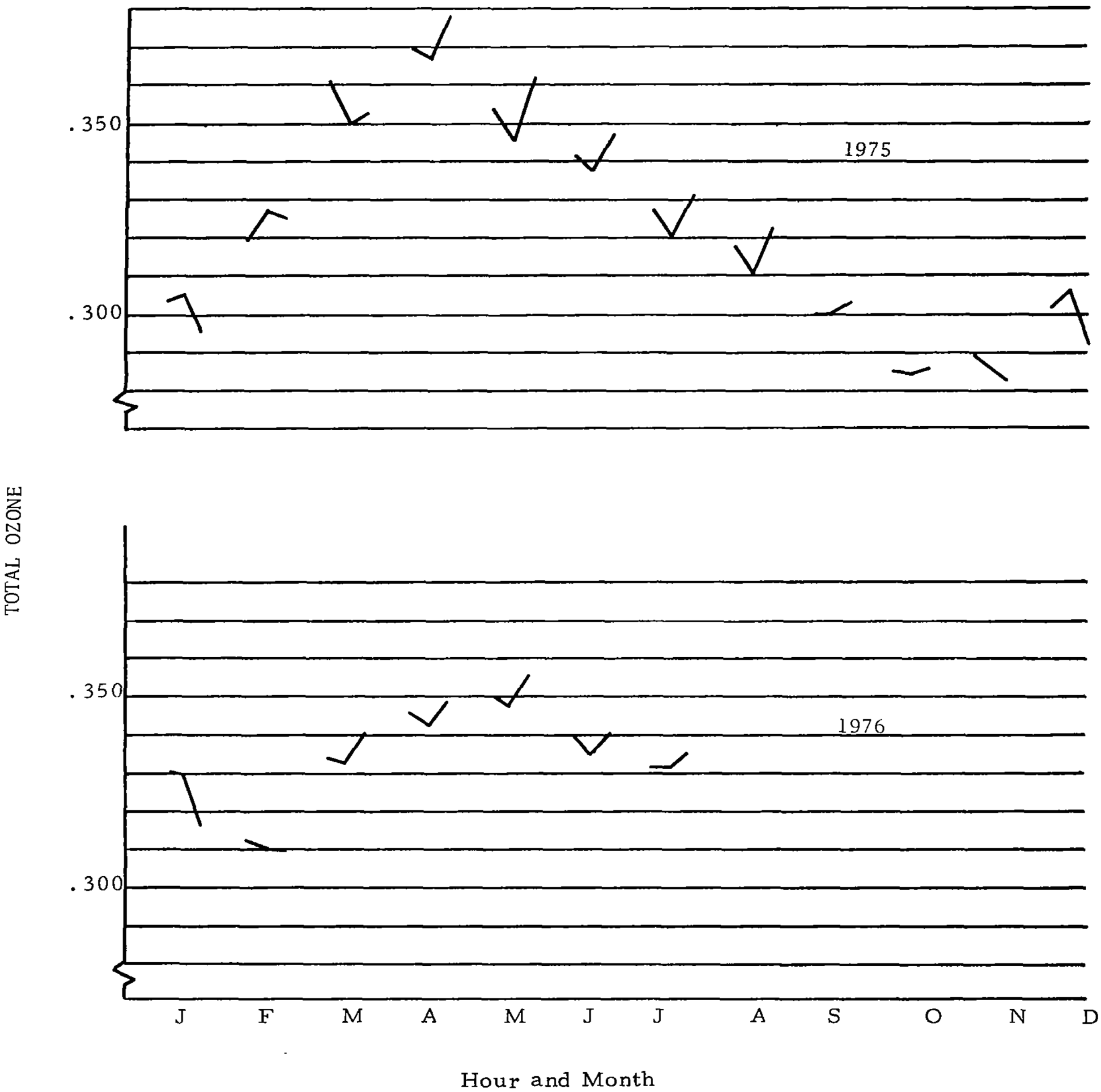

Figure 10. Concluded. Mean Monthly Total Ozone (Dobson) at 10 AM, Noon and 2 PM - Years 1975, 1976

SECTION 7

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16. Abstract

Using Dobson Spectrophotometer measurements of total ozone as a comparison, an analysis of the Electrochemical Concentration Cell (ECC) ozonesonde's measurement accuracy is presented. Days of conjunctive ECC-Dobson observations (from 1970 to 1976 at Wallops Flight Center) provide a set of 123 pairs of total ozone values. Sample set statistics are generated with means and standard deviations of total ozone values and differences being noted. An in-depth study of factors such as time assumptions used in calculating residual ozone, and other possible sources of errors are examined.

A study of ECC ozone profiles is also presented with an evaluation of sonde measurement of seasonal trends, altitude or peak ozone concentration, and other important ozone parameters. Short-period changes in total ozone using Dobson data during the observational period are also described.

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