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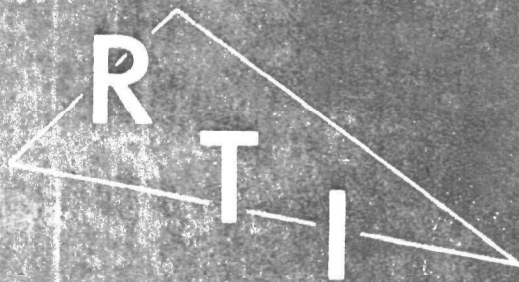
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FINAL REPORT

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A STUDY OF CORRELATIONS OF
OZONE AND SULFUR DIOXIDE

by

L. F. Ballard

L. K. Matus

Prepared for

Environmental Protection Agency
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N O T I C E

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A STUDY OF CORRELATIONS OF OZONE AND SULFUR DIOXIDE

This report describes the results of a data analysis study to determine the correlation between ozone (O_3) and sulfur dioxide (SO_2) concentrations in ambient air using data that had been obtained previously in Los Angeles and St. Louis (Refs. 1-3). Sulfur dioxide concentrations were determined by the flame photometric detector method. Ozone concentrations were determined by the chemiluminescent reaction between ozone and ethylene. These methods are assumed to have a high degree of specificity under the prevailing ambient air conditions and no corrections for instrument interferences are applied.

Wilson et al. (Ref. 4) demonstrated the effect of SO_2 on oxidant formation in environmental chambers. The effect was small but statistically significant. The mechanism was postulated to be the slow reaction involving SO_2 and oxides of nitrogen.

Not having an established gas phase reaction model as a basis for relating SO_2 and O_3 in this study, a series of simple linear regressions were performed to test or determine the significance of a relationship if it exists. Data sets consisted of hourly averages obtained at the same time each day. A normal distribution of error was assumed.

Results of a linear correlation of the form

$$[SO_2] = a_1[O_3] + a_2$$

are shown in Tables I-III for data obtained in Los Angeles and St. Louis, Phase I and St. Louis, Phase II. The upper part of the tables includes each of the 24 hourly averages using all the data with no constraints. The lower part includes data for 1000 to 1700 hours only when the

TABLE I

CORRELATION BETWEEN SULPHUR DIOXIDE AND OZONE

$$\text{IN LOS ANGELES: } [\text{SO}_2] = a_1[\text{O}_3] + a_2$$

4 SEP 70 TO 1 DEC 70

Hour	Correlation Coefficient	Slope	Intercept (ppm · ozone)	Case Count
NO STIPULATIONS:				
0000	.103	.128	.006	73
0100	.017	.019	.007	73
0200	-.060	-.061	.007	73
0300	-.041	-.033	.007	73
0400	-.044	-.034	.007	73
0500	-.103	-.094	.007	72
0600	-.104	-.162	.008	72
0700	-.110	-.293	.009	72
0800	-.238	-.677*	.011	71
0900	-.284	-.402*	.013	66
1000	.102	.056	.008	56
1100	.406	.165*	.005	56
1200	.398	.142*	.004	56
1300	.241	.110	.008	57
1400	.463	.166*	.004	58
1500	.449	.134*	.003	68
1600	.377	.097*	.004	72
1700	.420	.142*	.002	73
1800	.277	.129*	.003	73
1900	.342	.242*	.003	73
2000	.280	.259*	.004	73
2100	.215	.176	.004	73
2200	.128	.133	.005	73
2300	.153	.183	.005	73
STIPULATIONS - .020<NO2<.040, and RH<70:				
1000	-.981	-.369	.001	3
1100	.227	.054	-.004	5
1200	.084	.036	-.005	5
1300	.169	.022	-.005	6
1400	.934	.349*	-.009	5
1500	.878	.107*	-.004	5
1600	.544	.130	-.005	7
1700	.769	.329	-.004	6

* Significant at the 5% level.

TABLE II
 CORRELATION BETWEEN SULPHUR DIOXIDE AND OZONE
 IN ST LOUIS I: $[SO_2] = a_1[O_3] + a_2$
 13 MAY 71 TO 17 AUG 71

HOUR	CORRELATION COEFFICIENT	SLOPE	INTERCEPT (ppm · ozone)	CASE COUNT
NO STIPULATIONS:				
0000	.037	.024	.003	85
0100	-.020	-.009	.002	85
0200	.169	.080	.000	85
0300	.076	.047	.002	85
0400	.172	2.343	-.056	85
0500	.099	.063	.002	85
0600	.070	.059	.002	85
0700	-.231	-.255	.008	72
0800	-.330	-3.903*	.067	81
0900	-.268	-.270*	.018	76
1000	-.138	-.180	.021	74
1100	-.130	-.175	.023	76
1200	-.011	-.010	.010	79
1300	-.101	-.080	.011	79
1400	.015	.011	.007	77
1500	.203	.078	.000	79
1600	.294	.133*	-.002	81
1700	.172	.108	.001	84
1800	.101	.074	.004	85
1900	.066	.051	.005	85
2000	.040	.036	.005	85
2100	.149	.116	.004	84
2200	.055	.047	.005	84
2300	-.020	-.020	.006	84
STIPULATIONS - .020 < NO2 < .040. and RH < 70:				
1000	.849	.677	-.016	5
1100	.071	.304	.025	3
1200	1.000	1.182	.046	2
1300	-.866	-3.181	.161	4
1400	-.119	-.040	.013	6
1500	.554	.156	-.005	5
1600	.375	.048	.001	9
1700	.048	.026	.004	13

* Significant at the 5% level.

TABLE III

CORRELATION BETWEEN SULPHUR DIOXIDE AND OZONE

$$\text{IN ST. LOUIS II: } [\text{SO}_2] = a_1[\text{O}_3] + a_2$$

7 OCT 71 TO 20 DEC 71

HOUR	CORRELATION COEFFICIENT	SLOPE	INTERCEPT	CASE COUNT
NO STIPULATIONS:				
0000	-.046	-.079	.007	64
0100	-.112	-.188	.007	64
0200	-.124	-.129	.005	64
0300	-.185	-.180	.005	64
0400	-.119	-.110	.004	64
0500	-.203	-.149	.005	64
0600	-.185	-.406	.007	64
0700	-.159	-.322	.005	59
0800	-.165	-.374	.007	55
0900	-.150	-.373	.011	51
1000	-.252	-.590	.019	55
1100	-.286	-.591*	.022	62
1200	-.184	-.216	.014	63
1300	-.072	-.085	.012	63
1400	-.288	-.271*	.015	63
1500	-.333	-.342*	.015	63
1600	-.284	-.280*	.012	64
1700	-.227	-.225	.008	64
1800	-.146	-.203	.006	64
1900	-.173	-.275	.006	64
2000	-.146	-.130	.005	64
2100	.003	.004	.005	64
2200	-.038	-.043	.005	64
2300	.131	.174	.004	64
STIPULATIONS - .020<NO2<.040, and RH<70:				
1000	-.726	-.940*	.025	11
1100	-.344	-.333	.015	10
1200	.109	.070	.006	9
1300	-.380	-.285	.016	15
1400	-.130	-.090	.013	19
1500	-.303	-.271	.010	22
1600	-.289	-.210	.009	22
1700	-.126	-.050	.002	16

* Significant at the 5% level.

relative humidity was less than 70 percent and the NO₂ concentration was between 0.02 and 0.04 ppm. These added constraints increase the correlation coefficient, but the reduction in the number of cases gives a net loss of significance. Asterisks are placed beside those coefficients significantly different from zero at the 5% level. The relatively poor reliability of the SO₂ instrument response during the St. Louis operation would be expected to limit the maximum correlation that could be observed (Ref. 3). High correlation requires that the variability due to instrument error be small compared to the average value and range of SO₂ concentration. In Appendices A, B, and C the hourly averages and standard deviations are given for O₃, SO₂, NO₂, solar radiation, and relative humidity. SO₂ averages are in the neighborhood of 0.01 ppm. The instrument reproducibility as determined by calibrations at two-day intervals was much greater than 0.01 ppm so that low correlations can be expected.

The marginal significance of the correlation and the difference in the sign of the coefficient from morning to afternoon are the dominant features of Tables I-III. To provide additional insight into this correlation a multiple linear regression analysis was performed including the five variables indicated above. The regression equation is written as a linear prediction model for O₃ using these variables

$$[O_3] = a_1[SO_2] + a_2[NO_2] + a_3[R.H.] + a_4[Sol.Rad.] + a_5 .$$

The multiple correlation coefficients and standard error of estimates for this predictor are given in Table IV. The highest correlation and the lowest prediction error are obtained for the St. Louis II data.

This is largely attributed to improved measurements of NO_2 concentration by the chemiluminescent method. In this case the error of estimate varies from .006 to .014 ppm which is comparable to the reproducibility of many ozone instruments.

The correlation of this predictor with ozone concentrations is significant in most cases at the 1% level (indicated by two asterisks in Table IV). The solar radiation coefficient is the most significant term, achieving the 1% level in all cases. The SO_2 coefficient is not significantly different from zero at the 5% level in any of the St. Louis data. In Los Angeles the SO_2 coefficient is significant at the 5% level at 1200, 1400, 1500, and 1700 hours; the coefficient ranges between 0.33 and 0.68.

Several other prediction models were tested as indicated in Table V and Table VI. In model II the SO_2 term was removed. In model III the NO_2 term was removed. Models IV and V make use of the ratios SO_2/NO_2 and SO_2/RH . None of these variations in the model form resulted in a significantly better predictor of the O_3 concentrations. Individual regression coefficients other than solar radiation were significant at the 5% level at only one or two hours of the day. Greatest significance was usually found near the middle of the day.

In summary, a linear relation between the concentration of O_3 and SO_2 in ambient air is suggested by the LA data only. The multiple correlations attempted are not consistently significant. Interpretation of the relation is difficult because of the dependence of these variables upon gas phase reactions involving NO_2 , water vapor and other gases as well as the variability of instrumentation response and the uncertainty of SO_2 emission source distribution effects.

TABLE IV

MULTIPLE CORRELATION ANALYSES

$$O_3 = a_1[SO_2] + a_2[NO_2] + a_3[RH] + a_4[SOL RAD] + a_5$$

CORRELATION COEFFICIENT

HOUR	LOS ANGELES	ST. LOUIS I	ST. LOUIS II
	4 SEP 70 TO 1 DEC 70	13 MAY 71 TO 17 AUG 71	7 OCT 71 TO 20 DEC 71
1000	.459	.449*	.725**
1100	.561*	.506**	.749**
1200	.709**	.393	.741**
1300	.724**	.444*	.719**
1400	.717**	.305	.715**
1500	.738**	.428*	.836**
1600	.746**	.502**	.832**
1700	.740**	.494**	.774**

STANDARD ERROR OF ESTIMATE

1000	.017	.015	.006
1100	.025	.014	.008
1200	.029	.017	.012
1300	.029	.017	.012
1400	.032	.021	.014
1500	.027	.021	.010
1600	.024	.019	.010
1700	.015	.018	.009

* Significant at the 5% level.

** Significant at the 1% level.

TABLE V
 MULTIPLE CORRELATION ANALYSES
 ST. LOUIS II
 7 OCT 71 TO 29 DEC 71
 CORRELATION COEFFICIENT*

HOUR	I	II	III	IV	V
1000	.725	.607	.609	.573	.587
1100	.749	.754	.792	.771	.700
1200	.741	.840	.733	.750	.700
1300	.719	.891	.791	.753	.768
1400	.715	.750	.704	.731	.730
1500	.836	.816	.785	.794	.818
1600	.832	.782	.781	.792	.796
1700	.775	.728	.728	.728	.711

- * I: $O_3 = a_1[SO_2] + a_2[NO_2] + a_3[RH] + a_4[SOL\ RAD] + a_5$
 II: $O_3 = a_1[NO_2] + a_2[RH] + a_3[SOL\ RAD] + a_4$
 III: $O_3 = a_1[SO_2] + a_2[RH] + a_3[SOL\ RAD] + a_4$
 IV: $O_3 = a_1[SO_2/NO_2] + a_2[RH] + a_3[SOL\ RAD] + a_4$
 V: $O_3 = a_1[SO_2/NO_2] + a_2[SO_2/RH] + a_3[SOL\ RAD] + a_4$

TABLE VI
 MULTIPLE CORRELATION ANALYSES
 ST. LOUIS II
 7 OCT 71 TO 20 DEC 71
 STANDARD ERROR OF ESTIMATE*
 (ppm . ozone)

HOUR	I	II	III	IV	V
1000	.006	.008	.007	.007	.007
1100	.008	.008	.007	.008	.009
1200	.011	.009	.012	.012	.013
1300	.012	.008	.011	.012	.011
1400	.014	.013	.014	.014	.014
1500	.010	.010	.012	.012	.011
1600	.010	.011	.011	.011	.011
1700	.009	.009	.010	.010	.010

- * I: $O_3 = a_1[SO_2] + a_2[NO_2] + a_3[RH] + a_4[SOL\ RAD] + a_5$
 II: $O_3 = a_1[NO_2] + a_2[RH] + a_3[SOL\ RAD] + a_4$
 III: $O_3 = a_1[SO_2] + a_2[RH] + a_3[SOL\ RAD] + a_4$
 IV: $O_3 = a_1[SO_2/NO_2] + a_2[RH] + a_3[SOL\ RAD] + a_4$
 V: $O_3 = a_1[SO_2/NO_2] + a_2[SO_2/RH] + a_3[SOL\ RAD] + a_4$

Future efforts to understand this relationship should include the development of a prediction model based on postulated gas phase reactions. Recognizing that ambient air data is the true test for such a model, field data such as that in this study should be utilized. High correlation is not to be expected if the variability due to instrument error is large relative to the average value and range of SO₂ and O₃ concentrations. Significance of the statistical comparison of the model and instrumental data would be enhanced by independent tests indicating both the nature of the distribution function and magnitude of the expected deviation attributable to the error in instrument output.

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APPENDIX A
 STATISTICAL AIR QUALITY DATA IN LOS ANGELES
 4 SEP 70 TO 1 DEC 70

HOURS --		0000	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100
OZONE	AVERAGE (PPM)	.002	.002	.003	.003	.003	.001	.000	.001	.006	.018	.038	.058
	STANDARD DEVIATION	.007	.008	.009	.010	.009	.005	.003	.003	.007	.016	.029	.039
	CASE COUNT	76	76	76	76	75	75	75	73	70	63	65	65
SO2	AVERAGE (PPM)	.007	.007	.007	.007	.007	.007	.009	.011	.011	.010	.012	.013
	STANDARD DEVIATION	.008	.008	.008	.008	.008	.008	.008	.009	.009	.009	.012	.014
	CASE COUNT	82	82	82	82	81	81	81	80	79	74	74	71
NO2	AVERAGE (PPM)	.085	.084	.082	.079	.077	.083	.100	.121	.125	.127	.112	.094
	STANDARD DEVIATION	.046	.046	.045	.045	.043	.043	.052	.064	.078	.084	.089	.054
	CASE COUNT	70	70	70	70	69	69	69	64	58	61	58	56
SOL. RAD.	AVERAGE (LANGLEYS)	.001	.000	.000	.000	.000	.004	.083	.255	.439	.588	.699	.746
	STANDARD DEVIATION	.003	.003	.002	.002	.003	.008	.059	.128	.173	.199	.210	.220
	CASE COUNT	86	86	86	86	85	85	85	84	86	87	87	87
RH	AVERAGE (PERCENT)	57.950	58.124	58.111	57.530	57.832	57.974	57.956	56.284	52.125	47.793	43.714	40.735
	STANDARD DEVIATION	18.121	17.630	17.720	18.642	18.845	18.493	18.455	18.725	19.431	19.380	17.793	17.250
	CASE COUNT	86	86	86	86	85	85	85	84	86	87	87	87

HOURS --		1200	1300	1400	1500	1600	1700	1800	1900	2000	2100	2200	2300
OZONE	AVERAGE (PPM)	.066	.061	.049	.033	.020	.014	.007	.005	.004	.004	.003	99.999
	STANDARD DEVIATION	.047	.045	.040	.035	.025	.020	.013	.017	.009	.008	.007	99.999
	CASE COUNT	66	69	72	75	76	76	76	76	76	76	76	76
SO2	AVERAGE (PPM)	.016	.014	.010	.008	.006	.005	.004	.005	.005	.005	.006	99.999
	STANDARD DEVIATION	.021	.016	.012	.010	.008	.007	.008	.008	.008	.008	.008	99.999
	CASE COUNT	73	74	81	82	82	82	83	83	82	82	82	82
NO2	AVERAGE (PPM)	.087	.080	.080	.086	.083	.083	.080	.080	.081	.081	.083	99.999
	STANDARD DEVIATION	.055	.044	.039	.040	.040	.040	.036	.039	.042	.040	.041	99.999
	CASE COUNT	59	63	66	70	71	71	71	70	70	70	70	70
SOL. RAD.	AVERAGE (LANGLEYS)	.696	.614	.463	.277	.109	.022	.001	.001	.001	.001	.001	99.999
	STANDARD DEVIATION	.245	.248	.238	.215	.105	.034	.003	.004	.004	.003	.003	99.999
	CASE COUNT	87	87	87	87	87	87	87	87	86	86	86	86
RH	AVERAGE (PERCENT)	41.493	42.406	44.303	46.703	49.416	51.805	53.840	55.107	56.742	57.278	57.592	99.999
	STANDARD DEVIATION	15.913	16.078	16.475	16.769	17.605	18.232	18.861	19.077	18.592	18.114	18.422	99.999
	CASE COUNT	87	87	87	87	87	87	87	87	86	86	86	86

