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The Characterization of Pollutant Concentrations by a Relative Measure of Variability

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A general equation has been developed for determining the relative measure of variability of pollutant concentrations in air. From the general equation, specific equations can be developed for any set of time-averaging periods including the 5-min./1-hr., 5-min./24-hr., and 1-hr./24-hr. systems. From a continuous series of data over a long sampling period, the maximum concentration for the short time-averaging period and the average concentration for the longer time-averaging period are determined for use in calculating the relative measure of variability. The

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20. Abstract (Continued)

general equation is:

$$(P_e)_{t/T} = \frac{N \cdot (C_{avg})_T}{(C_{max})_t} . \qquad (1)$$

where $(P_e)_{t/T}$ is the relative measure of variability, t is the short time-averaging time at which the short time-averaging time at which the maximum concentration, C_{max}, is obtained, T is the long time-averaging time at which the average concentration, C_{avg}, is obtained, and N is a constant which acts on the system as a constraint in limiting values of P_e from one to N.

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The Characterization of Pollutant Concentrations by a Relative Measure of Variability

INTRODUCTION

The peak to mean, or mean to peak concentrations of a given pollutant in air, where the peak or maximum concentration is for a short sampling period, and the mean or average concentration is for a longer sampling time, has been widely reported in the literature as a means of describing pollutant plume behavior or characteristics (1,2,3,4). In practice, the ratio is not routinely reported in analyzing air quality data. The reasons for this are complex, but the chief difficulty is that the time-averaging periods for determining the peak and mean concentrations have to be determined by experiment and these times may vary widely under different conditions. At most air monitoring stations, pollutant concentrations are reported as 5-minute, 1-hour, 24-hour averages, etc. Therefore, if one is to use a peak to mean ratio in analyzing air quality data on a routine basis, it must be within the constraints of time-averaging periods normally used in reporting air quality data.

Gibson and Peters have used the 24-hr maximum concentration to the annual mean concentration ratio to obtain R for SO_2 data obtained at Louisville, Kentucky, as a relative measure of the variability of this pollutant (5). Montgomery and Coleman have reported on peak to mean ratios for various averaging times of SO_2 concentrations for air quality data monitored near the TVA coal-fired power plants (6). These authors have relied on time-averaging periods as normally used in reporting air quality data.

The purpose of this report is to develop a general equation which can be used to determine the relative measure of variability of pollutant concentrations in air for any set of time-averaging periods such as the 5-minute maximum/1-hour average, 5-minute maximum/24-hour average, 1-hour maximum/24-hour average, etc. The concept is straightforward but, as pointed out by Montgomery and Coleman in their version, a rapid scan of large amounts of data can easily be made without recourse to more sophisticated methods and equipment (6). Furthermore, the relative

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measure of variability could serve as an air monitoring site characterization parameter and be used for comparison with other air monitoring sites. In addition, the relative measure of variability can be used to obtain a better handle on pollutant plume behavior as it intercepts the air monitoring sampling probe.

THEORY

Visual observation of pollutant plumes is seen, at times, as a continuous cloud or as fragmented sections of a plume in which various pollutants are mixed. This suggests that plumes are composed of puffs of pollutant; a contiguous series of puffs is seen as a continuous plume, and a fragmented plume as a series of separate puffs. Consequently, pollutant puffs, intercepting an air sampling probe, will vary in duration and concentration over a long sampling period. Therefore, determining the number of such puffs could serve as a parameter in characterizing pollutant plumes.

Consider, for example, a long sampling time of T minutes broken down into N segments of t minutes, T > t, for a given pollutant, and, where N - n segments have zero concentration, and each n segment has a concentration, C, (all n segments have the same concentration).

The average concentration at time T is;

$$\frac{nC_1}{N} = (C_{avg})_T \quad , \qquad (1)$$

and the peak, or maximum concentration at time t is;

$$C_1 = (C_{max})_t \quad . \qquad (2)$$

Substituting equation (2) into equation (1) and rearranging lead to;

$$n = \frac{N \cdot (C_{avg})_T}{(C_{max})_t} \quad . \qquad (3)$$

For a given set of time-averaging periods, T and t, n can be redefined as:

$$n = (P_e)_{t/T} , \qquad (4)$$

where $(P_e)_{t/T}$ is now the relative measure of variability at a fixed set of averaging times.

Substituting equation (4) into equation (3) leads to the general equation:

$$(P_e)_{t/T} \frac{N \cdot (C_{avg})_T}{(C_{max})_t} \qquad . \qquad (5)$$

Since N is defined as:

$$N = \frac{T}{t} , \qquad (6)$$

a whole series of specific equations can be derived from the general equation. For example, the 5-min/1-hr system can be defined by:

$$(P_e)_{\frac{5\text{-min}}{1\text{-hr}}} = \frac{12 \cdot (C_{avg})_{1\text{-hr}}}{(C_{max})_{5\text{-min}}} , \qquad (7)$$

and, for the 5-min/24-hr system:

$$(P_e)_{\frac{5\text{-min}}{24\text{-hr}}} = \frac{288 \cdot (C_{avg})_{24\text{-hr}}}{(C_{max})_{5\text{-min}}} , \qquad (8)$$

or, for the 1-hr/24-hr system:

$$(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}} = \frac{24 \cdot (C_{avg})_{24\text{-hr}}}{(C_{max})_{1\text{-hr}}} \quad . \qquad (9)$$

According to general equation (5), values of $(P_e)_{t/T}$ fall within the limits of one and N. Low values of $(P_e)_{t/T}$ indicate puff-like characteristics of a pollutant plume and high values of $(P_e)_{t/T}$ suggest a semi-contiguous series of puffs. Furthermore, a $(P_e)_{t/T}$ value of one indicates a single burst of emissions from an air pollution source, and a $(P_e)_{t/T}$ value equal to N indicates a continuous plume. It might also be argued that sections of a meandering plume, intercepted by the air sampling probe, may be considered as puffs.

An example of calculating the realtive measure of variability is shown in Table 1. In actual practice, a scan of a continuous array of sequential air quality data for a given pollutant will be to determine the maximum and arithmetic mean concentrations for a given set of time-averaging periods, choose the appropriate equation, and solve for $(P_e)_{t/T}$.

The answer to the example in Table 1 is equivalent to six of the 5-minute periods having zero concentration and the other six periods having each a concentration of 12 ppm (v/v). In both cases, the 5-minute maximum concentration is the same, and so is the hourly average. In fact, there are other possible arrays of air quality data that will give the same result as the example in Table 1. The unifying parameters are the unique values for the maximum and average concentrations as shown in the example. Therefore, to apply any of the equations for calculating the relative measure of variability, only the maximum and average concentrations for the appropriate time-averaging periods are necessary. This is the procedure that will be used for analyzing the NRL air quality data.

Table 1

Example for Calculating $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$

number of continuous 5-minute intervals	$C_{5\text{-minute average}}$ [ppm (v/v)]
1	12*
2	11
3	7
4	10
5	5
6	1
7	1
8	8
9	5
10	3
11	3
12	6

$$C_{1\text{-hr avg}} = \frac{\Sigma C_{5\text{-min avg}}}{N} = 6 \text{ ppm (v/v)}$$

$$* \; C_{5\text{-min max}} = 12 \text{ ppm (v/v)}$$

$$(P_e)_{\frac{5\text{-min}}{1\text{-hr}}} = \frac{12 \cdot C_{1\text{-hr avg}}}{C_{5\text{-min max}}} = \frac{12 \times 6}{12} = 6$$

EXPERIMENTAL DATA AND RESULTS

The continuous air monitoring program at NRL includes data for ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), total hydrocarbons (THC), methane (CH_4), non-methane hydrocarbons (RHC), and carbon monoxide (CO) (7). The analyzers for these pollutants and gases are interfaced to a data acquisition system with input on a magnetic tape. After a month's run, the magnetic tape is submitted to the Laboratory's Research Computer Center for analysis and a printout (8). Subsequently, air quality data from the monthly computer printout can be used for calculating the relative measure of variability. Some examples are shown in the following tables.

Table 2 lists the relative measure of variability of pollutant concentrations in air for the 5-minute maximum/1-hour average system from data obtained on March 16, 1977. For ease of presentation, THC and CH_4 are included as pollutants.

Table 2

Relative Measure, $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$, of Variability of Pollutants at the NRL Air Monitoring Station on March 16, 1977

Hour Beginning At	$(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$						
	O_3	SO_2	NO_2	THC	CH_4	RHC	CO
00 (Midnight)	8.0	10.1	10.8	11.9	9.9	7.1	9.9
01	8.0	9.8	11.2	9.4	9.2	7.0	9.4
02	5.2	10.5	11.4	9.9	8.6	7.8	8.8
03	9.0	9.6	10.5	10.7	10.6	9.3	10.7
04	8.0	10.3	11.1	9.4	4.9	5.9	5.8
05	8.5	8.9	11.2	10.4	9.9	4.0	8.8
06	12.0	8.6	11.6	9.1	6.7	4.1	7.6
07	5.5	8.3	11.2	7.7	5.0	4.5	6.0
08	8.9	9.2	10.5	11.7	11.9	10.7	11.8
09	11.4	10.9	11.4	11.8	11.9	10.1	11.9
10	11.4	10.9	11.7	11.6	11.6	10.6	11.8
11	12.0	10.8	10.3	11.9	11.9	10.3	11.8
12 (Noon)	11.4	12.0	11.5	11.9	11.8	11.2	11.8
13	11.4	9.8	11.7	11.7	11.8	9.9	11.8
14	11.4	10.2	11.7	11.8	10.8	10.9	10.5
15	11.4	8.8	11.4	11.9	11.8	10.8	11.9
16	11.4	9.7	11.7	11.8	11.8	10.6	11.9
17	10.8	9.6	11.5	11.9	11.8	11.3	11.9
18	10.5	10.3	11.6	11.9	11.8	11.3	11.8
19	10.3	11.4	11.7	11.9	11.8	11.0	11.8
20	11.2	11.2	11.5	11.9	11.8	11.3	11.8
21	11.3	11.3	11.2	11.7	11.7	11.6	11.8
22	11.3	11.1	11.9	11.8	11.8	10.8	11.8
23 (11 p.m.)	10.7	4.4	10.8	11.7	11.8	9.2	11.7
$(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ Avg	10.9	9.9	11.3	11.1	10.5	9.2	10.6

From the data in Table 2, it can be seen that most of the $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ are high and near the maximum value of 12. This indicates that, for most of the time on this particular day, pollutant plumes of at least an hour's duration were fairly constant in concentration, i.e., nearly contiguous plumes. Plumes of longer duration than an hour could overlap into the next hour's analysis. Over the course of the day, most of the pollutants show a wide range of $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values with some pollutants having a wider range than others. These ranges in values are due to variations in meteorological conditions, type, kind, and number of emission sources, and distance from source to air sampling probe. Meteorological conditions can break up a plume into puffs, or cause it to meander, resulting in low values for the relative measure. Nearby single point emission sources can be characterized by low values of the relative measure. For example, emissions from a nearby coal-fired electric power plant are probably the reason why some of the $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values for SO_2, listed in Table 2 are not all about the same value. On the other hand, it seems reasonable to suspect that, meteorological conditions being equal, area and line emission sources would be characterized by high $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values because of the better chances of mixing in the atmosphere before intercepting the air sampling probe. This is probably why NO_2 shows the least variations in $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$. In fact, analysis of other NO_2 data, not shown here, suggests that this is a characteristic of NO_2, i.e., a narrow range and high values of $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$.

It will be further noted from the data listed in Table 2, that RHC has the widest range of $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values. This is indicated by the average $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ value listed at the bottom of the table. This also suggests that some RHC emissions, like SO_2, are from a nearby source.

It is interesting to conjecture that O_3 has, at times, puff-like characteristics, as indicated by the low $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values, for that pollutant, in Table 2. It might have been supposed that O_3, as a secondary pollutant, i.e., one formed in the atmosphere by a series of photochemical reactions and not emitted from a primary emission source, would be well mixed in the atmosphere and behave as a plume. The low O_3 $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values in the early morning hours suggest otherwise. Furthermore, since O_3 concentrations normally peak in the midafternoon hours, it might have been more reasonable to suspect that the lower $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ would also have occurred in this same time period of the day. It remains to be seen if O_3 has the behavior indicated by the $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values listed in Table 2.

It is interesting to note, from the data listed in Table 2, that for most of the pollutants the low $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values occurred in the early morning hours. If this turns out to be a characteristic trend, it may turn out to be of interest in understanding pollutant behavior in the atmosphere.

The THC, CH_4, and CO $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values listed in Table 2, appear, in most cases, to be comparable. Differences in the $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ values among these three pollutants at the same time of day suggest different sources (including both combustion and non-combustion sources).

Table 3 lists the $(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}$ values for the pollutants of interest and include data for April 1977. The $(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}$ data were calculated from equation (9) and with limits from one to 24. Because of the greater range of $(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}$

Table 3

Relative Measure, $(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}$ of Variability of Pollutant Concentrations Measured at the NRL Air Monitoring Station during April 1977

Day	$(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}$						
	O_3	SO_2	NO_2	THC	CH_4	RHC	CO
2	13.4	13.8	16.3	--	--	--	--
3	11.1	9.6	8.4	--	--	--	--
4	13.0	7.7	16.8	--	--	--	--
5	12.0	--	18.7	--	--	--	--
6	15.5	7.2	16.8	22.6	21.4	19.2	16.3
7	16.0	8.4	--	13.4	13.0	12.4	18.3
8	16.8	12.0	15.8	8.8	9.4	5.2	20.1
9	14.6	13.8	11.9	13.8	14.6	8.4	8.5
10	11.0	9.8	15.6	15.6	15.6	10.8	9.1
11	10.4	17.4	15.3	12.5	10.7	10.0	8.5
12	10.3	--	13.6	13.2	13.2	7.8	9.6
13	9.7	8.2	16.6	11.9	11.5	10.2	12.2
14	13.2	7.0	15.5	11.9	12.9	7.6	14.9
15	12.0	6.6	14.9	--	--	--	--
16	13.1	14.2	15.6	12.7	12.5	12.8	9.4
17	12.0	9.8	16.4	11.9	10.8	11.8	10.8
18	11.7	10.2	14.2	17.1	16.0	19.4	10.3
19	10.8	7.7	15.1	11.3	17.5	8.0	10.2
20	14.6	8.3	15.0	21.8	20.4	19.9	12.9
21	13.0	9.4	16.2	19.1	19.9	16.8	10.7
22	12.0	--	15.4	14.1	12.4	14.4	17.8
23	17.3	13.4	21.6	14.1	13.2	7.4	24.0
24	14.9	5.5	16.2	13.8	12.3	16.3	23.0
25	10.6	7.2	18.2	21.0	19.2	20.3	21.6
26	14.9	9.2	18.0	18.7	19.0	18.0	9.1
27	12.6	9.4	14.6	12.5	11.4	15.0	22.2
28	11.5	5.2	18.6	12.8	11.7	16.6	10.3
$(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}$ Average	13.3	12.9	17.2	14.8	14.5	13.1	14.1

values, most of the pollutants have a wide range of values, i.e., a semi-contiguous pattern. Again, some pollutants like RHC and SO_2 have the widest range of $(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}$ values indicating a more puff-like character. In addition, NO_2 shows the same characteristic as described for the NO_2 $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ system.

For the other pollutants, i.e., O_3, THC, CH_4, and CO, it is difficult to come to any conclusion with respect to their $(P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}$ values other than the remarks pertaining to the $(P_e)_{\frac{5\text{-min}}{1\text{-hr}}}$ system. The main point is that, on a given day, some pollutants are more well-mixed $\left[\text{high } (P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}\right]$ than others $\left[\text{low } (P_e)_{\frac{1\text{-hr}}{24\text{-hr}}}\right]$.

Table 4 lists the $(P_e)_{\frac{5\text{-min}}{24\text{-hr}}}$ values for O_3, SO_2, NO_2, THC, CH_4, RHC, and CO. The $(P_e)_{\frac{5\text{-min}}{24\text{-hr}}}$ values were calculated for these pollutants by use of equation (8). The values of $(P_e)_{\frac{5\text{-min}}{24\text{-hr}}}$ can range from one to 288 for this time-averaging set. Consequently, this system will have the widest range of values of the relative measure of variability.

Table 4

Relative Measure, $(P_e)_{\frac{5\text{-min}}{24\text{-hr}}}$, of Variability of Pollutant Concentrations Measured at the NRL Air Monitoring Station on March 16, 1977

Pollutant	$(P_e)_{\frac{5\text{-min}}{24\text{-hr}}}$
O_3	183.2
SO_2	89.3
NO_2	195.8
THC	124.4
CH_4	71.1
RHC	66.5
CO	88.4

According to the data listed in Table 4, RHC has the most puff-like characteristic (lowest $(P_e)_{\frac{5\text{-min}}{24\text{-hr}}}$ value) and NO_2 has the plume-like behavior (highest $(P_e)_{\frac{5\text{-min}}{24\text{-hr}}}$ value). This appears to be a characteristic pattern for these two pollutants as further indicated for the other time-averaging systems. The other pollutants listed in Table 4 fall between RHC and NO_2 in their plume behavior. For example, O_3 and THC plumes (or clouds) are less fragmented than the SO_2, CH_4, and CO plumes.

SUMMARY

A general equation has been developed for measuring the relative measuring of variability of pollutant concentrations in air for any set of time-averaging periods. In this report relative measures of variability were calculated for ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), total hydrocarbons (THC), methane (CH_4), non-methane hydrocarbons (RHC), and carbon monoxide (CO). The time-averaging periods used were the 5-min/1-hr, 1-hr/24-hr, and the 5-min/24-hr systems. High values of the relative measure of variability for any time-averaging set indicate a semi-contiguous series of pollutant puffs while low values of the relative measure of variability indicate pollutant puffs (fragmented plumes). According to the data in this report, NO_2 has the most continuous plume-like behavior and RHC has the most puff-like behavior based on their relative measure of variability. The other pollutants reveal intermediate behavior between NO_2 and RHC. Factors which affect the relative measure of variability include variations in meteorological conditions and in the kind, type, number and location of pollution emission sources. It is further suggested that, for corresponding periods of time, some pollutants are more well-mixed in the atmosphere than others. A well-mixed atmosphere results in high values of the relative measure of variability and a poorly mixed atmosphere results in low values of the relative measure of variability. It is recommended that the relative measure of variability be routinely reported in any analysis of air quality data so as to establish pollutant behavior characteristic of an air monitoring system.

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