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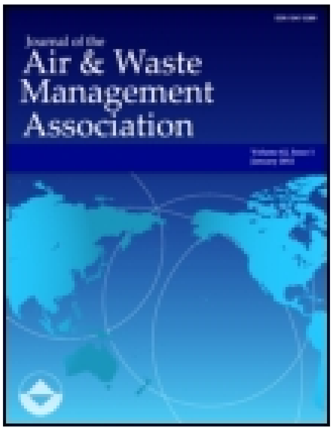

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Analysis of Gaseous Hydrogen Peroxide Concentrations in Raleigh, North Carolina

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Gas-phase total peroxides and hydrogen peroxide (H_2O_2) were monitored in the ambient air in downtown Raleigh, North Carolina as part of the Southern Oxidant Study-Southern Oxidants Research Programs on Ozone Non-Attainment (SOS-SORP/ONA). These measurements were made during September 8-16, 1991, using the continuous dual-channel fluorometric analyzer based on the horseradish peroxidase method. Measurements were also made of other photochemical oxidants and trace gases (O_3, NO, NO_2, NO_x, SO_2, CO, HCHO) and meteorological parameters. Concentrations of H_2O_2 showed a diurnal variation with maximum concentrations in the afternoon (1400-1800) EST. The mean of all observations was 0.2 ppbv and the range measured was below the level of detection (~0.05 ppbv) to about 1 ppbv. An observational-based statistical analysis utilizing Multivariate Principal Component Analysis (PCA) was applied to the data to determine the underlying processes. Four physicochemical components were found to account for ~86 percent of the variability of all the parameters. Application of Kaiser's Varimax orthogonal rotation on the four retained principal components allowed in the physical interpretation of the first four Principal Components as being: photochemical processes, primary pollutant concentrations, emission and transport of SO_2, and air mass type. A multiple linear regression analysis was carried out by regressing H_2O_2 on all the other physicochemical air quality variables and/or a combination of these. It was found that all the variables put together account for 53 percent of the variability in H_2O_2 concentrations. Ozone alone accounts for 11 percent of the variability, and this value increased to 33 percent when temperature, relative humidity and solar radiation were added to ozone. PCA was applied again to the data set (excluding H_2O_2) and the principal components obtained were used as independent variables for the regression analysis of H_2O_2. It was found that photochemical activity and primary pollutant concentrations were the most significant factors in controlling gaseous H_2O_2 concentrations in Raleigh during the measurement period.

Hydrogen peroxide (H_2O_2) plays an important role in atmospheric chemistry as an oxidant of sulfur dioxide (SO_2) in the aqueous phase when the pH is less than 4.5;[1,2] and a source for the hydroxyl radicals in the gas phase. In addition to providing oxidizing capacity of the environment, hydrogen peroxide is also considered to be a potent plant phototoxin.[3]

The presence of H_2O_2 in the atmosphere is mainly due to the same series of photochemical reactions leading to the formation of ozone in its chain termination step. Thus the principal source of H_2O_2 is the bimolecular self reaction of hydroperoxyl radical (HO_2) (Table I). Hydroperoxyl radical is formed as a result of photo-oxidation of formaldehyde (HCHO) and predominantly due to the reaction of hydroxyl radical (OH) with carbon monoxide (CO) where the OH radicals are produced by the photolysis of ozone (O_3) generating excited O (^1D), followed by its reaction with water vapor (Table I).

Implications

Hydrogen peroxide (H_2O_2) has recently received considerable attention in air quality issues because of its role in odd hydrogen chemistry, oxidation capacity of the atmosphere, and importance in the conversion of sulfur dioxide (SO_2) to sulfuric acid in cloud and rain droplets. Yet its formation, rate, and effects in the atmosphere are still not well understood. Therefore, there is a need to understand the importance of the various factors that control the generation of hydrogen peroxide in the atmosphere.

H_2O_2 plays an important role in the free radical balance of the atmosphere by acting as a sink for the odd hydrogen (H, OH, HO_2 = HO_x) species and as an index of hydroperoxyl radical concentrations. Thompson et al.,[4] on the basis of model calculations, have shown that increasing global emissions of trace gases NO, CH_4 and CO can lead to increased tropospheric H_2O_2 levels. They have also predicted a global loss of OH by conversion to HO_2 and H_2O_2 in the atmosphere. This may result in a significant loss of gaseous oxidizing capacity of the atmosphere, and a significant increase in the rate and extent of aqueous-phase oxidizing capacity.

Photochemical models suggest that H_2O_2 should be present in both polluted and clean air.[5-7] Modeling studies also suggest that the major factors affecting the rate of formation of H_2O_2 are the concentrations of primary pollutants (nitrogen oxides, volatile organic compounds and CO) together with solar radiation, temperature and water vapor content.[7]

Reliable instruments for the measurement of gas-phase H_2O_2 have recently become available,[8-11] and thus data on ambient levels of gas-phase H_2O_2 is slowly increasing.[12-15] Reported concentrations of ground level gas phase hydrogen peroxide range from below the level of detection (~ 0.01 ppbv) to about 4 ppbv. Gunz and Hoffmann[16] have given an extensive summary on the H_2O_2 measurements in air, precipitation and cloud water in the troposphere at various places in Europe and the United States.

In this paper we present an analysis of the ground-level measurements of gas phase H_2O_2 at an urban site, i.e., Raleigh, North Carolina during the period September 8-16, 1991 and compare and contrast it in relation to other atmospheric pollutants and meteorological variables. An observational based analysis utilizing multivariate statistical methods were applied to evaluate the possible factors controlling the behavior and gaseous concentrations of hydrogen peroxide in Raleigh.

Methodology

The site is located in downtown Raleigh (35.9° N, 78.7° W, 126.8 m MSL), where one would expect higher background concentrations of primary pollutants, but it is not directly exposed to any industrial or municipal emission sources.

The atmospheric trace gases used in the analysis were O_3, NO, NO_2, NO_x, HCHO and SO_2 and were obtained using a Differential Optical Absorption Spectrometer (DOAS). The data on carbon monoxide was provided by the North Carolina Department of Environmental Health and Natural Resources (NC DEHNR). The meteorological data from the Raleigh-Durham Airport (which is representative of the overall meteorological conditions in the Raleigh area) was used for the analysis. These data were obtained from the National Climatic Data Centre, Asheville, North Carolina. The data on solar radiation (Photosynthetic Active Radiation) for Raleigh was obtained from the National Acid Deposition Program (NADP). Meteorological data included in the analysis are: hourly averaged values of temperature (Temp), relative humidity (RH), wind speed (WS), wind direction (WD) and solar radiation (SR).

Ambient, gas-phase hydrogen peroxide was measured, at 10 m above ground, using a continuous fluorometric analyzer based on the horseradish peroxidase method.[8] The dual channel fluorometric analyzer measures total peroxides on one channel, and by specific enzymatic destruction of hydrogen peroxide, only organic peroxides on the second channel. The residence time of ambient air in the sampling manifold was <0.5 second, and the manifold was heated above the ambient temperature to prevent any condensation. The measurement and calibration procedures are described elsewhere.[15]

Table I. Gas-phase reactions affecting atmospheric hydrogen peroxide concentrations.

SOURCES

Hydrogen peroxide formation:

$HO_2 \bullet HO_2 \bullet \rightarrow H_2O_2 + O_2$ (1)

$H_2O \bullet HO_2 \bullet HO_2 \bullet \rightarrow H_2O_2\ H_2O + O_2$ (2)

Hydroperoxyl formation:

$HCHO + h\upsilon \rightarrow H \bullet + HCO \bullet$ (3)

$H \bullet O_2\ {}_M\, HO_2 \bullet$ (4)

$HCO \bullet + O_2 \rightarrow HO_2 \bullet + CO$ (5)

$O_3 + h\upsilon \rightarrow O(^1D) + O_2$ (6)

$O(^1D) + H_2O \rightarrow 2\ OH \bullet$ (7)

$OH \bullet + CO \rightarrow H_2O \bullet + CO_2$ (8)

Competing reaction for HO_2 radical:

$HO_2 \bullet + NO \rightarrow OH \bullet + NO_2$ (9)

SINKS

1. Hydrogen peroxide destruction:

$H_2O_2 + OH \bullet \rightarrow H_2O + HO_2 \bullet$ (10)

$H_2O_2 + h\upsilon \rightarrow 2\ OH \bullet$ (11)

2. Dry deposition

3. Wet deposition

Results and Discussion

Diurnal Variation of Gaseous Hydrogen Peroxide

During the summer Southern Oxidant Study (SOS) Raleigh exploratory study of 1991 (September 8-16) 205 hourly averaged hydrogen peroxide measurements were recorded. Gas-phase hydrogen peroxide ranged from below the level of detection (~0.05 ppbv) to about 1 ppbv. Field measurements of atmospheric H_2O_2 at various locations in North America, Europe, Brazil and Japan[17] have shown ranges from 10 ppt to about 5 ppbv. The average H_2O_2 concentration for our entire period of measurement was ~0.2 ppbv. The day time (1000-1900) average was found to be 0.36 ppbv and the night time 0.05 ppbv. The difference is statistically significant ($p < 0.05$).

Figure 1 illustrates the composited diurnal trend in the measured hydrogen peroxide. The daily averaged hourly averages for the entire data period indicates that peak H_2O_2 concentrations occurred between (1400-1800) EST and the minimum was observed between (0500-0800) EST, which was generally below the detection limit. This minimum is most likely due to the deposition of H_2O_2 with dew.

Examination of Figure 2 reveals that H_2O_2 concentration peaks about two to three hours after the peaks in ozone concentration and solar radiation are reached. This can be explained by the competition for HO_2 by NO_x during ozone formation, thus inhibiting H_2O_2 production. H_2O_2 does not peak until NO_x concentrations fall to a significantly low level to allow the self combination reaction of HO_2 to generate H_2O_2.

Relationship Between H_2O_2, and Other Atmospheric Pollutants and Meteorology

The relationship between H_2O_2 and atmospheric trace gas pollutants and meteorological parameters was examined by applying statistical methods to understand the factors affecting atmospheric hydrogen peroxide concentrations. A statistical summary of the data on atmospheric pollutants and meteorological parameters is given in Table II.

From the results of a correlation matrix showing the cross correlations between the various environmental parameters used in our study, the relationship between H_2O_2 and other parameters

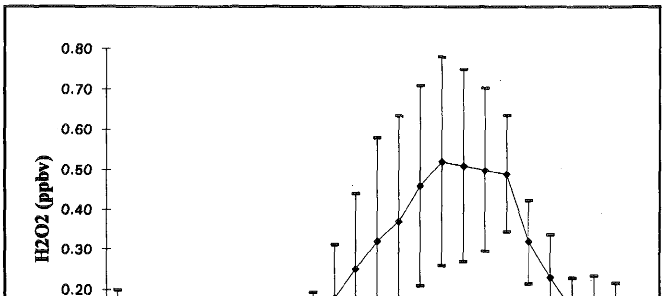

Figure 1. Composite diurnal profile of H_2O_2 for the measurement period.

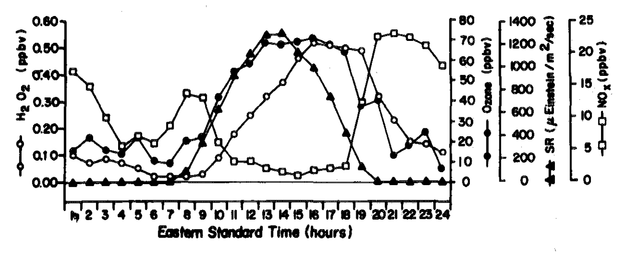

Figure 2. Hourly averaged composited diurnal profiles of H_2O_2, ozone, NO_x, and solar radiation.

were studied. The results indicate that H_2O_2 is most highly correlated with ozone (r = 0.55). A positive correlation has also been observed in recent field experiments by other investigators.[12,13,15] This could be due to the fact that both ozone and hydrogen peroxide share the same diurnal trend and are photochemical products in the atmosphere. H_2O_2 was also found to be significantly correlated with temperature (r = 0.50) and solar radiation (r = 0.40). This is consistent with the modeling studies of Dodge,[18] which indicate an increase in hydrogen peroxide concentration with increasing temperature. Sakugawa et al.[13] and Olszyna et al.[12] have also observed a high H_2O_2 concentration associated with a high solar radiation and high temperature in their field studies.

A negative correlation between H_2O_2 and relative humidity (r = -0.58) was observed. Increase in humidity resulting from the cooling of the air in the presence of a clear nocturnal boundary layer produces aqueous aerosols which scavenge the hydrogen peroxide resulting in decrease of surface level gas-phase H_2O_2 as it is highly soluble in water (Henry's Law constant = 7 x 10^4 mol-L^{-1}-atm^{-1} at 25°C).[19]

H_2O_2 was also found to be negatively correlated with the primary pollutants CO (r = -0.33) and NO_x (r = -0.30). Stockwell[20] showed that H_2O_2 is extremely sensitive to the rate of the reaction of NO_2 with hydroxyl radical (OH) because this reaction removes both NO_x and OH radicals from the pool of photochemical reactants. Thus, consistent with other field studies,[13] we also observe a high concentration of H_2O_2 when all the primary pollutants (NO_x, CO) are relatively low.

Table II. Statistical summary of pollutant concentration and meteorological variables during September 8-15, 1991 in Raleigh, NC.

Variable	N	Mean	Std Dev	Minimum	Maximum
H_2O_2 (ppbv)	188	0.21	0.22	<LOD*	0.97
Ozone (ppbv)	162	37.8	25.0	0.9	81.2
NO_2 (ppbv)	160	10.02	9.73	<LOD*	40.64
NO_x (ppbv)	155	11.43	9.99	0.51	43.00
HCHO (ppbv)	179	4.52	1.79	<LOD*	8.88
SO_2 (ppbv)	161	1.74	1.31	0.06	6.11
CO (ppmv)	188	0.617	0.477	.094	2.73
Temperature (°F)	191	24.6	4.6	16.4	35.00
Relative Humidity (%)	191	58.6	25.4	7	95.00
Wind Speed (m/s)	191	2.6	1.2	0	5.1
Wind direction	191	148.8	94.8	0	360°
Solar radiation (μEinstein/m^2/sec)	191	384	497	0	1441.0

*Level of detection (LOD) ~ 50 pptv

H_2O_2 is positively correlated with formaldehyde (HCHO) (r = 0.33) which is also consistent with modeling studies. Calvert and Stockwell[21] demonstrated that in polluted air, the production of free radicals from the photolysis of formaldehyde is the most important source reaction of free radicals and thus the source reaction of HO_2 radicals.

H_2O_2 was, however, weakly correlated with SO_2 (r = 0.04). This is to be expected as these two compounds do not interact in the gaseous phase and the climatological data for the period of measurement shows mostly clear skies eliminating the heterogeneous reaction of H_2O_2 and SO_2.

Multivariate Principal Component Analysis

Principal component analysis (PCA) was performed to seek the underlying processes accounting for the variance in the data set. Henry and Hidy[22] have compared atmospheric quality with meteorological parameters utilizing multivariate PCA.

PCA is used to identify characteristic, recurring and independent modes of variation among a large data set. The analysis sorts initially correlated data into a hierarchy of statistically independent modes of variation which explain less and less of total variation. The patterns are expressed as mutually orthogonal linear combinations of the original data set. The first pattern is chosen so that it explains the maximum amount of variance, while the next pattern explains the maximum amount of residual variation and so on. PCA can be performed either on the covariance or the correlation matrix. A more detailed description of the principal component analysis is given by Cooley and Lohnes[23] Anderson,[24] and Johnson and Wichern.[25]

Thus, the quantitative description of a system is simplified by reducing the original data matrix to a factor pattern matrix consisting of fewer numbers of variables/components which account for a high percentage of the total variance in the data. This permits the identification of the nature of the components/factors by computing the correlation coefficient or 'loading' between the original variables and the factors. The square of the component loading gives the fraction of a variable's total variance which is accounted for by that factor/component. Usually a variable belongs to that component if its loading is ≥ 0.5.

From the PCA performed on the correlation matrix, four components encompassing various physico-chemical parameters were found to account for 86 percent of the total variance of the original data set. The first, second, third and the fourth principal components (PCs) explained 47, 21, 11 and 8 percent respectively of the total sample variance.

Kaiser's Varimax-rotation was applied on the four retained components to aid in the interpretation of the factors. Kaiser's Varimax method of rotation was chosen because it maximizes the variance of the component loadings between each component. An orthogonal method of rotation rotates the predetermined principal components to better define a distinct grouping of intercorrelated data, while retaining the constraint that the individual components remain orthogonal or uncorrelated to each other. From a comparison of the results of both rotated and unrotated versions, it was evident that the loadings are more clearly reflected in the rotated version.

The results of the analysis are presented in Table III. The analysis is limited to those data-sets (n = 88) for which data on all 12 variables (Ozone, H_2O_2, NO_2, NO_x, HNO_2, HCHO, SO_2, CO, temperature, relative humidity, wind speed, and solar radiation) are available. Loadings for variables considered to be a member of a component (mostly loadings ≥ 0.5) are underlined. The communality (h^2 in the last column of the table) is the sum of the squares of the component loadings for a variable. Communality is the amount of a variable's total variance that may be attributed to the extracted components. One minus h^2 ($1-h^2$) gives the amount of variance for a variable which remains unaccounted for by the factors. The percent total variance is the amount of total variance in the system accounted for by each factor. Summing these percentages gives the amount of the total variance in the system which is explained by the multivariate statistical model. Percent common is the percentage contribution of each factor to the percent total variance accounted for by the model.

From an examination of the component loadings, the ozone, temperature, solar radiation, relative humidity, and H_2O_2 variables are highly loaded on PC_1, whereas NO_2, NO_x and CO are loaded on PC_2. SO_2 and WS were identified with the third factor, whereas HCHO and HNO_2 belonged to the fourth. It seems fairly clear that the first factor/component represents a general condition for photochemical processes as all the variables in PC_1 are identified with photochemical activity. Thus the first component may be termed as 'photochemical processes.' The second component with high loadings of NO_2, NO_x and CO can be seen as the 'primary pollutant concentration' in the atmosphere whereas the third component, consisting of SO_2 and WS, can be attributed to emission and transport' of SO_2. The interpretation of the fourth component, consisting of HCHO and HNO_2, is thought to be the 'air mass type' as they are indicators of polluted air. Thus, 86 percent of the variability of the data used for our analysis can be associated with the combined effects of photochemical processes, primary pollutant concentrations, emission and transport of SO_2, and the air mass type. Table III summarizes the findings.

Multiple Linear Regression Analysis of H_2O_2

A multiple linear regression analysis was conducted on the gas-phase H_2O_2 data set. The independent physico-chemical variables used consisted of O_3, NO_x, HCHO, HNO_2, SO_2, CO, temperature, relative humidity, wind speed and solar radiation. From an examination of the results, it is found that: (1) O_3 accounts for 0.11 of R^2 for H_2O_2. The R^2 is improved by adding SR, Temperature and RH to Ozone ($R^2 = 0.33$). This number is to be viewed with caution as all these variables are intercorrelated and not really independent; (2) NO_x and CO account for 0.07 of R^2; and (3) when all the variables mentioned were used, the R^2 for H_2O_2 was found to be 0.53. Thus all these variables together account for 53 percent of the variability observed in H_2O_2 concentrations in Raleigh for the measurement period.

Table III. Principal component loadings (varimax rotated) of the air quality variables.

	Principle Component Loadings				
	1	2	3	4	h^2
Ozone	0.819	-0.383	-0.132	0.253	0.898
NO_2	-0.252	0.912	0.198	-0.140	0.955
NO_x	-0.274	0.913	0.183	-0.123	0.957
HNO_2	0.443	-0.353	-0115	0.573	0.664
HCHO	0.143	-0.277	-0159	0.914	0.904
H_2O_2	0.621	-0.150	0.070	-0.304	0.985
SO_2	0.055	0.072	0.980	-0.117	0.985
CO	-0.228	0.810	-0.270	-0.189	0.816
Temp	0.805	-0.300	0.220	0.279	0.862
RH	-0.935	0.100	-0.205	0.016	0.926
WS	0.086	0.053	0.984	-0.089	0.987
SR	0.860	-0.365	-0.118	0.004	0.887
Eigen Value	3.735	2.861	2.244	1.491	10.331
% Common Variance	36.16%	27.69%	21.72%	14.43%	

Table IV. Interpretation of principal component analysis.

Principle Component	Group	Physical Interpretation	Variance	Cumulative
PC1	03,H202, Temp., SR, RH	photochemical processes	47.4%	47.4%
PC2	NO_x, CO Sol	primary pollutant concentration	20.6%	68%
PC3	SO_2, WS	emission & transport of SO_2	10.6%	78.6%
PC4	HCHO, HONO		7.5%	86.1%

Table V. Regression analysis of H_2O_2 on the principal components.

Principle Component	Variables associates with the PC's	Variance	R^2 for H202	Significance ($p<0.05$)
PC1	03, temp, SR	49.4%	0.27	significant
PC2	SO_2, WS	22%	0.01	insignificant
PC3	NO_x, CO	12.8%	0.04	significant

Many of the variables used in the multiple regression analysis are highly intercorrelated and this can make the results uncertain. Henry and Hidy,[23] have attempted to remove the multicollinearity effect in the regression analysis and make it more reliable by the application of Principal Component Analysis on the data set (not including the dependent variable) which produces statistically independent linear combinations of the original variables. A regression analysis was then carried out using only these independent parameters which are in fact the principal components. We used the same technique and the results are presented in Table IV.

Ten physico-chemical variables — O_3, NO_x, HCHO, HNO_2, SO_2, CO, Temp, RH, WS and SR — were chosen for the analysis. The data sets consisting of these variables and H_2O_2, which have one or more than one missing parameter were omitted from the analysis. From an examination of the results presented in Table V, we observe that the PC_1, which can be interpreted as 'photochemical activity' accounts for 0.25 of R^2 for H_2O_2 whereas PC_2 'the emission and transport of SO_2' accounts for 0.01 of R^2, which is found to be statistically insignificant at $p = 0.05$. The 'primary pollutant concentration,' which is PC_3, accounts for 0.04 of R^2 for H_2O_2 is found to be statistically significant at $p = 0.05$. These results indicate that the effects of photochemical processes together with primary pollutant concentration are significant in controlling the gaseous H_2O_2 concentrations in Raleigh for the measurement period. Sakugawa and Kaplan[13] measured gaseous H_2O_2 concentrations along with other environmental parameters in Los Angeles from August '85 to September '88 and found that the significant factors controlling the gaseous H_2O_2 concentrations in Los Angeles air are the effects of primary pollutants and solar radiation, i.e., similar to our findings for gaseous H_2O_2 in Raleigh.

Summary

H_2O_2 concentrations exhibited a diurnal variation with the maxima occurring during 1400-1800 EST. The ozone concentration and solar radiation peaks occurred ~2 hours earlier, indicating the role of NO_x chemistry and that H_2O_2 is photochemically generated in the atmosphere.

The mean concentration of H_2O_2 was found to be 0.2 ppb with a range of below the level of detection (~0.05 ppbv) to about 1 ppbv in Raleigh. The mean day time (1000-1900) concentration was found to be 0.36 ppbv.

The results indicate that ozone concentrations, temperature and solar radiation are the most important factors in controlling the concentration of gaseous H_2O_2. Under these conditions of higher solar radiation, temperature and O_3 concentration there is a higher generation rate of radical species like hydroxyl and hydroperoxyl radicals leading to the increased formation rate of H_2O_2.

The concentrations of primary pollutants is also an important factor for controlling gaseous H_2O_2 concentration. Higher H_2O_2 concentrations are favored by lower concentrations of primary pollutants (NO_2, NO_x and CO). We did not have access to the amounts of non-methane hydrocarbons in air which, as shown by modeling studies[21] may also be important for the generation of gaseous H_2O_2 in an urban polluted environment. However the data on formaldehyde showed a positive correlation to H_2O_2 formation.

The effect of relative humidity on the formation of H_2O_2 was found to be inversely correlated. This is explained due to the reverse diurnal variation of relative humidity in relation to H_2O_2. Under this condition gaseous H_2O_2 is removed from the atmosphere by aqueous scavenging and wet deposition. No evidence of heterogeneous H_2O_2 decomposition by SO_2 was found as the skies were clear and no cloud events occurred during the period of measurement.

Admittedly this is a limited data set, but the results justify further study. Additional data and longer periods of field observations encompassing the four seasons on measurements of gaseous H_2O_2, primary pollutants and meteorological parameters are required to improve our understanding of these processes.

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Response

Ronald H. White, Deputy Director, National Programs

American Lung Association

I am writing to respond to an article in the June 1993 issue under the AAMA Newsletter banner (pg. 926). The author utilizes a probabilistic exposure model to argue that only a small percentage of the public is actually exposed to ozone concentrations that will result in adverse health effects. Unfortunately, several of the assumptions used to generate this conclusion are flawed.

One major assumption used in the AAMA analysis is that indoor concentrations of ozone are “a small fraction” of outdoor levels. Studies by Weschler et. al.(1,2) indicate that indoor ozone concentrations closely track outdoor levels and, depending on ventilation rate, are 20-90 percent of the outdoor level. While the percentage of indoor environments with air conditioning is high in Houston, used as the basis for the model’s national ozone conditions, very different results would be found if Los Angeles conditions, where only 45 percent of homes have air conditioning, had been used. Conservatively assuming an indoor ozone concentration that is 70 percent of outdoor ozone levels in structures with open windows rather than air conditioning, outdoor concentrations would need to be only 0.172 parts per million (ppm) for residents to be exposed to ozone levels indoors that would violate the current 1-hour 0.12 ppm federal ozone standard. In 1992, a relatively “mild” ozone pollution year, Los Angeles experienced over 35 days with air quality above this ozone level. Other cities that had one or more days above 0.172 ppm in 1991-92 include: New York City; New Haven, Connecticut; Sacramento and San Diego, California; and Atlantic City, New Jersey.

In contrast to the Houston model, a recent EPA analysis(3) estimates that in 1991 31 percent of all Los Angeles residents experienced a one hour ozone exposure of greater than 0.12 ppm on more than one day while exercising at a high ventilation rate (60 liters per minute or higher). The EPA analysis estimates that 42 percent of children in Los Angeles received the same type of exposure.

The recent literature on ozone health effects indicates that adverse pulmonary function effects are found at ozone levels of 0.08 ppm when exposure occurs for 8 hours at a moderate (40 liters per minute) ventilation rate. The EPA exposure analysis estimates that 45 percent of the total Los Angeles population (excluding outdoor workers) and 51 percent of children were exposed to these conditions in 1991. The AAMA analysis also completely ignores all 1-hour ozone exposures less than 0.125 ppm at exercise levels less than 60 liters per minute. A significant body of clinical and epidemiological studies have found adverse respiratory effects at ozone concentrations below the current standard at this level of exercise.

AAMA presents data from modeling exercises that used outdated EPA breathing rate information. More recent EPA information(4) indicates that more people than previously thought exercise at levels high enough to cause adverse effects, despite a declining trend for public participation in exercise.

In addition, AAMA calculates percentage of population exposed utilizing “people-occurrences,” based on the total population’s possible ozone exposure over 24 hours. Were the exposure percentage calculated with a denominator of people who are outdoors during the day and exercise, the percentage of population exposed is likely to have been two orders of magnitude higher.

Finally, the AAMA analysis excludes the exposure of construction workers and others who are likely to experience long durations of outdoor ozone exposure while working at a high breathing rate.

It would be informative for AAMA to revise the assumptions used in its analysis to provide a more accurate picture of public exposure to ambient ozone levels of concern to public health.

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From the Author

Gerald Esper, Director
American Automobile Manufacturers Association

I write this letter in response to the American Lung Association (ALA) critique and questions regarding the American Automobile Manufacturers Association (AAMA) Newsletter published in the June 1993 issue of the *Journal of the Air & Waste Management Association (A&WMA)*. The title of the subject Newsletter is “Probabilistic Exposure Models Suggest Lower Health Risk From Ambient Ozone.”

AAMA appreciates the interest shown by Mr. White to make sure that the new techniques are technically valid. The concepts referred to in the Newsletter were presented in detail at A&WMA conferences on ozone held in 1991 and 1992 and published in existing or upcoming proceedings,[1] but have not yet had wide distribution. AAMA regrets that space limitations of its Newsletter did not permit a more detailed discussion of these new approaches or permit comparison with the U.S. EPA’s similar draft exploratory analyses.[2] As the full texts of the new methodologies become more widely available, a better understanding of those techniques should result and may help to clear up much of the confusion surrounding the new approaches.

All exposure analyses, including ALA’s own past estimates, are based on a collection of assumptions. The new probabilistic concept also uses a series of assumptions that ALA suggests are “flawed.” However, AAMA believes that the authors of the new concept have introduced innovative techniques that incorporate very realistic assumptions, using state-of-the-art information. Since 1986, the EPA has been developing a number of computer-based exposure distribution models (including newer versions of NEM and pNEM) which incorporate important stochastic elements. Although similar assumptions and the same monitoring data are also used in the new probabilistic approach (EPM), there are at least two significant differences from stochastic approaches.

First, while the stochastic models estimate the random possibility of urban residents encountering different levels of ozone and tabulate the cumulative distributions predicted of one- or eight-hour exposures over the population (most recently, adjusted to equivalent ventilation rates), the probabilistic methodology concentrates on the probability that a randomly-selected person will experience a particular exposure that could predetermine the occurrence of an adverse health effect. In addition, the probabilistic approach estimates the probability that such exposure coincides with other events such as being outdoors, high physical activity, etc., required for the manifestation of a measurable change, or response, to ozone. In this respect, Mr. White’s comments questioning the use of “people-occurrences” based on the total population’s possible exposure are, therefore, more applicable to the EPA stochastic models. In fact, the proper use of “the denominator of people who are outdoors during the day and exercise” at the time of ozone exceedances by the probabilistic methods resulted in estimates that were three orders of magnitude lower, not higher, than previous estimates.

Second, in sharp contrast with the stochastic methods, the probability analysis tabulates only exposures that, under the current state-of-understanding, are considered as the threshold-exceeding conditions that result in measurable changes such as decrements in pulmonary function test performance [i.e., "adverse exposures" with Equivalent Ventilation Rate (EVR) exceeding 36 1/min.m^2 (more than 60 1/min) in two- to three-hour exposures at >0.18 ppm, or EVR >25 1/min.m^2 at >0.24 ppm, etc., according to biological endpoints described in EPA's 1989 Staff Paper]. With these parameters, the probabilistic analysis provides a more realistic estimate of the potential public health impact of ozone than using a cumulative distribution of population exposures.

A direct comparison with the stochastic distribution of all exposures that include no-effect events (such as isolated one-hour contacts with 0.12 ppm ozone in Los Angeles proposed in the ALA comments) is, therefore, not appropriate. In order to verify the methodology, the authors also restricted the analysis to data from 1982 Houston ozone conditions that have been validated by comparison with personal monitors.[3] For the same reasons, the authors specifically excluded the site-specific, exceptional conditions in the California South Coast Air Basin from the analysis and approximated the situation in the entire nation under the assumptions that the 1982 Houston conditions were "at least approximately representative of the urban ozone levels in most American cities (with the exception of Southern California) and that U.S. urban exercising conditions were similar to those of the Houston population."[1] Although we concur with ALA about the continuing unacceptability - in spite of recent air quality improvements - of the ozone pollution in Los Angeles, we feel that unusual meteorological conditions characterize the area as a non-representative site for overall national conditions. AAMA also feels compelled to correct the confusion introduced by several misquotes of EPA's unpublished memo in the ALA comments.

First of all, the ALA seriously misrepresents the EPA analysis in the July 21, 1993, EPA memo.[2] The ALA states:

"...in 1991 31 percent of all Los Angeles residents experienced a one-hour ozone exposure greater than 0.12 ppm on more than one day while exercising at a high ventilation rate (60 liters per minute or higher)."

The correct estimate is:

"...out of 9.1 percent of all Los Angeles residents who have seen one or more one-hour exposures to 0.12 ppm ozone in 1991, only 31 percent of the people were involved in physical activity with pulmonary ventilation exceeding EVR level of 30 L/min.m2 (>60 1/min)."

This represents only 2.8 percent of all Los Angeles residents and not the full third of Los Angeles population that ALA claims.

A similar error exists in the quoted evaluation of <18 year-old children. Again, the ALA states:

"...42 percent of all children in Los Angeles received the same type of exposure."

The correct estimate from the EPA analysis should be:

"...only 42 percent of the 27.1 percent of the Los Angeles children population who experienced more than one-hour exposure to 0.12 ppm in 1991, have exercised at the level of EVR equal or higher than 30 L/min.m2."

Again, this shows that even in Los Angeles only 11.4 percent rather than nearly a half of all exercising children below 18 years had one or more one-hour contact with 0.12 ppm ozone per year in 1991. More importantly, the analysis indicates that the average number of such children exposure occurrences is only 1.8 days, (i.e. less than two days per year). Identical corrections also apply to the misquoted analysis of eight-hour exposures.[4]

These ALA misquotes seriously distort the ozone exposure situation in an area of the nation that is far from being representative of U.S. urban sites. (We note that the highest ozone concentrations in the South Coast Air Basin in 1991, were over 0.30 ppm, i.e., over 2.5 times the current federal standard, and the federal standard was exceeded on more than 90 days in the Basin). Since the quoted EPA memo has not yet been released and the reader cannot easily obtain these data, it is important that these quotes be corrected.

Apart from these errors, the majority of the remaining ALA comments refer to the existing uncertainty in the interpretation of the public health significance of clinical experiments. It should be noted here that the authors of the probabilistic exposure estimates restricted themselves to biological endpoints described in the 1989 EPA Staff Paper. We are looking forward to a discussion of public health significance that will be provided in EPA's new criteria document and staff paper that are scheduled for 1994. Hopefully, the new EPA assessment will provide more reliable information on the variability of the breathing rates in the U.S. population, resolve the clinical significance of transient decrements in pulmonary function testing, and conclude whether or not the evidence for a longer averaging time for the ozone standard is justified. Until that time, we feel that the probability analysis using biological endpoints described in the EPA 1989 Staff Paper provides an improved approach for assessing not only the real public health impact of ozone pollution but also for evaluating the efficiency of regulations aimed at reducing ozone risks in the U.S. population.

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Response

Joel S. Hirschhorn, President
Alan J. Gagnet, Vice President
Hirschhorn & Associates

The Open Forum (August 1993) on "What is Pollution Prevention?" sadly illustrates the ingrained fears of too many environmental professionals. Just as the medical establishment has stubbornly resisted fully supporting and implementing preventive health care, environmental professionals have resisted supporting and implementing a preventive approach because they have too many self-interests, personally and organizationally, in protecting end-of-pipe pollution control and waste management businesses and jobs. Industries which generate waste and pollution fear that government will legally force them to practice real and fundamental pollution prevention which they believe is not economically viable.

While recognizing the legitimacy of both fears, the environmental community must also accept the historic inevitability that true pollution prevention minimizes the need for environmental professionals. This "harm" to one industry is more than offset by making all economic sectors more efficient, profitable and environmentally benign, as well as safer for workers. But just as advocates of preventive health care do not want to altogether eliminate physicians, hospitals, medicines, surgery and medical devices, neither do true pollution prevention advocates believe in eliminating all pollution control, waste management and remediation professionals and all of their technologies. The fundamental issue is whether environmental professionals accept the essential proposition that prevention is better and that preventive measures should be implemented prior to all forms of reaction, control and remediation.

James W. Satterfield and Gwen Eklund want to include pollution control in the definition of pollution prevention, indicating that they do not understand the fundamental tenants of pollution prevention. Such people should read "Clean Production Strategies: Developing Preventive Environmental Management in the Industrial Economy," (Lewis, 1993) or "Prosperity Without Pollution: The Prevention Strategy for Industry and Consumers" (Van Nostrand Reinhold, 1989). Pollution prevention training for scientists, engineers and managers is critically needed.

Thomas Zosel is not content with the inclusion of in-process recycling in the statutory definition of source reduction and EPA's definition of pollution prevention. He wants to include actions which involve the handling, transportation and disposition of non-product outputs for offsite recycling, reuse and reclamation, which the original generator cannot fully control, however. Pollution prevention advocates do not oppose offsite recycling, reuse and reclamation, but we know that many places performing these functions are not Superfund cleanup sites. Why confuse the entire hierarchy of preferred environmental solutions with pollution prevention at the top of the list?

With a combination of over two decades of working to promote pollution prevention, we find it remarkable that so many fearful professionals delude themselves about the proper meaning of pollution prevention, and that so many of them are advocating or practicing sham pollution prevention in their companies or as consultants. It is straightforward to understand the technical and economic boundaries between pollution prevention and everything else. Joseph Padgett did a commendable job of explaining pollution prevention. We add an economic principle: true pollution prevention actions have the inherent capacity to promote the economic self-interests of the enterprise practicing them, by increasing various efficiencies, or by promoting technological innovations which improve products and markets, or by avoiding costly end-of-pipe investments.

In contrast, end-of-pipe actions increase the costs of the entity producing waste and pollution and shift the risk from one medium to another, even though society obtains economic benefits for solving environmental problems. This explains why society has had to legally force private and public entities to do pollution control and cleanup, and why so many companies have voluntarily practiced pollution prevention. Economic benefits are maximized when environmental problems are not created in the first place. Yes, that's what pollution prevention is all about. Not making money from solving environmental problems, but avoiding the costs of solving environmental problems. As members of A&WMA, we hope that many other environmental professionals put pollution prevention for the good of a sustainable global society ahead of narrow, immediate economic interests.

It is disheartening to see so much backsliding among environmental professionals who are undermining, trivializing and perverting true pollution prevention. But, as often is the case, ordinary people are ahead of professionals. Environmentally concerned citizens really do understand source reduction and pollution prevention. Professionals who think that they can sell pollution control and waste management as pollution prevention are out of touch with reality, the law, and the global sustainability movement, no matter how many environmentally correct words they use. Such professionals undermine the integrity and credibility of the environmental profession and industry. It's one thing to make money from cleaning up the errors of the past, it's quite another to keep perpetuating environmental mistakes when there is a better, preventive choice.

Response

Charles Hosler
Environmental Protection Agency (Retired, 1988)

Mr. Babst's discussion of Stratospheric Ozone Protection in the August 1993 JA&WMA is based on the same politically correct conclusions espoused by our scientifically illiterate politicians and environmentalists. It is disingenuous not to point out many of the world's atmospheric scientists' opposing views of the stratospheric ozone depletion issue.

An appraisal of the scientific literature will reveal the following reasons why many respected atmospheric scientists are calling for a further investigation of the proposed phaseout of chlorofluorocarbons (CFCs), as well as an overturning of the Montreal Protocol: stratospheric ozone depletion over the Antarctic region is a natural and seasonal phenomenon, largely due to meteorological dynamics; there is no evidence of a long-term decrease in stratospheric ozone, or, that ozone levels are caused by CFCs in particular (George C. Marshall Institute, December 1991 Report to the World Affairs Council); ultraviolet radiation has decreased at ground level in the United States during the 1970s and 1980s (*Science* 239, p 763, 1988; *Nature* 3431, p 283, Sept. 28, 1989); the ozone "hole" is not a hole but a decrease in concentration, which was measured in the 1950s by French and British scientists, before CFCs were in widespread use; the amount of industrial produced CFCs, as a source of the chlorine that allegedly breaks down ozone in the stratosphere, is about one-tenth of 1 percent of the amount of chlorine from natural sources that may enter the stratosphere (*Nature* 334, p 415-418, Aug. 4, 1988; *The Holes In the Ozone Scare* by R.A. Maduro and R. Schauerhammer, 1992) through stratospheric-tropospheric exchange processes and volcanic eruptions; the recent evidence that heavier-than-air molecules of CFCs are destroyed by soil bacteria and taken up by vegetation, are factors that further limit the amount of CFCs reaching the stratosphere; the danger to humans represented by an increase in ultraviolet radiation has been greatly overestimated, as the alleged increase in ultraviolet is equivalent to moving about 150 miles towards the equator.

The economic and social implications of the proposed phase out of CFCs called for by the Montreal Protocol will cause a disruption in refrigeration that is projected to cost billions of dollars and millions of lives in Third World countries. Unfortunately, the haste to speed up the phase out of CFCs from the year 2000 to 1995, was motivated essentially by political reasons during the presidential campaign of 1992; the decision was not based on scientific facts.

We will be much better off, economically and politically, when solid, peer-reviewed science is used by politicians to make legislation and regulations; also, we will be better off when the media base their reporting on solid, peer-reviewed science, rather than on misdirected, distorted and selective use of data of advocacy and activism, driven by emotion, ignorance and political ideology, rather than by scientific truth.