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The Statistical Identification of Airmass Characteristics during the Mauna Loa Observatory Photochemistry Experiment

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Abstract

Hierarchical cluster and factor analyses were used to identify various influences on free tropospheric air samples at Mauna Loa Observatory in Hawaii during MLOPEX. The cluster analysis separated thirteen chemical and meteorological variables into three characteristic groups (1)clean air, (2)anthropogenically influenced air, (3)marine and volcanic influenced air. The cluster analysis results compared well with those of factor analysis. Six independent components were identified in factor analysis. We have related these components to (1)volcano influenced air, (2)stratosphere-like air, (3)boundary-layer air with recent anthropogenic influence, (4)photochemical haze, (5)marine boundary-layer air, and (6)modified marine tropospheric air. Excluding local influences, we could calculate the nighttime free tropospheric values for O_3(41±10 ppbv), HNO_3(94±45 pptv), NO_3^-(16±10 pptv), $SO_4^=$(60±0 pptv), NH_4^+(71±6 pptv), Na^+(5±1 pptv), PAN (13±9 pptv), $MeNO_3$(3.5±1.5 pptv), 2-butyl NO_3(0.6±0.1 pptv), H_2O_2(1015±44 pptv), C_2Cl_4(3.3±0.1 pptv), condensation nuclei(249±13 cm^{-3}), and dew point(-8.5±5.3 ℃) during this experiment.

1. INTRODUCTION

Over forty chemical species were measured during MLOPEX(the Mauna Loa Observatory Photochemistry Experiment) in May and June of 1988 to investigate variations and "background" mixing ratios in the remote free troposphere(Ridley and Robinson, 1992). The representative background mixing ratios are very useful for evaluating and constraining photochemical models. However, the wide ranges of the observed mixing ratios during MLOPEX make it clear that a simple mean cannot adequately represent the chemistry of remote free tropospheric air for certain species. The variations in mixing ratio for these species have been explained in terms of different sources, photochemistry, and meteorological processes(Atlas et al., 1992; Hahn et al., 1992; Norton et al., 1992; Walega et al., 1992).

In aerosol studies multivariate statistical analysis has been used to identify sources of particulate elements(Hopke et al., 1976; Alpert and Hopke 1980; Thurston and Spengler 1985). To determine the quantitative contribution of each source to samples with factor analysis, the measured compounds or elements must be conserved during any transport and mixing processes. Several factor analysis techniques(Currie et al., 1984; Hopke 1988) were developed to resolve source concentration profiles using the assumption that the observed concentrations were linearly correlated with a number of independent sources. In contrast to the aerosol species, photochemical species in the troposphere are not generally conservative, but are actively produced, removed or changed to other species. It may not, therefore, be possible to positively identify orig-

inal sources for photochemical species by statistical analysis. However, Hopke et al.(1976) and Gaarenstroom et al.(1977) showed that multivariate analysis was particularly useful in interpreting the variance of data in large sets of elements and samples, grouping them into meaningful components. The MLOPEX data set may be explained in terms of a few well defined combinations of concentrations. We postulate that a few typical sets of chemical components may represent the actual behavior of photochemical species at MLO (Mauna Loa Observatory) more realistically than do the individual average mixing ratios. In this paper, the observed mixing ratios of some photochemical compounds and meteorological parameters during MLOPEX were analyzed by the methods of cluster and factor analyses to interpret the composition of each sample.

2. EXPERIMENT

Several criteria were applied to select species for statistical analyses out of forty species during MLOPEX. First of all, we selected variables which could represent the entire MLOPEX experimental period without frequent or long periods of missing data. Priority was given to variables which were measured rather continuously and had few gaps in sampling. Furthermore, the uncertainties(or errors) in mixing ratio measurements had to be smaller than the observed atmospheric variations. In other words, we excluded chemical compounds which were(within analytical uncertainties) unchanging during MLOPEX. Finally, the unique variation of "marker species", which can represent a distinct source or influence, were essential to identify specific sources or events. If similar compounds or meteorological variables exhibited the same pattern, only the one with the largest range of variances and the smallest measurement error was selected and used. O_3, HNO_3, NO_3^-, $SO_4^=$, NH_4^+, Na^+, PAN, $MeNO_3$, 2-butyl NO_3, H_2O_2, C_2Cl_4, condensation nuclei and dew point were chosen according to these criteria and used for our statistical analysis. The details of sampling and analytical strategies for each species are found in the MLOPEX studies (Atlas et al.,1992; .Greenberg et al., 1992; Heikes 1992; Norton et al., 1992; Ridley and Robinson, 1992; Walega et al., 1992).

MLO is located at 3400 m above the sea level. The local meteorology at MLO has a distinct diurnal variation with daytime upslope and nighttime downslope winds induced by rapid solar heating and radiative cooling on the mountain slope (Mendonca, 1969). As it is located well above the mean marine boundary height (1-2km), its air is known to represent the clean free tropospheric one. However, the daytime upslope winds usually contain marine boundary layer air modified by the island. The diurnal variations for various chemical species due to local wind changes at MLO during MLOPEX have been described elsewhere (Hahn et al., 1992). Because the main purpose of this statistical analysis was to investigate the variations of free tropospheric mixing ratios, all daytime data were excluded. We defined nighttime for our purposes as 2100 to 0700 HST(Hawaii standard time). Walega et al.(1992) determined that free tropospheric air was generally present at MLO between 2200 to 1000 HST. Since the first three-hour aerosol and nitric acid vapor sampling period started at 2100 HST each night, our definition is not exactly coincident with theirs. The species we used were measured according to several different sampling time schemes, so we averaged each chemical and meteorological parameter over the same 3-hour periods as the nitric acid vapor and aerosol sampling intervals (Norton et al., 1992). Normally each night was divided into three time periods 2100-2400, 0100-0400 and 0400-0700 HST.

2.1 FACTOR ANALYSIS

The first step in the factor analysis is to transform the variables into dimensionless, standardized forms. Most of the variables during MLOPEX have either normal or log-normal distributions. The mixing ratios of variables with log-normal distributions were logarithmically transformed, so that all variables had normal distributions in the statistical analysis. To be useful in these statistical analyses, each variable must be transformed into a dimensionless standard form, which ensures unit variance on each variable.

The calculation of factor analysis was done with

the common statistical package SYSTAT(Systat, Inc) and the factors were rotated by the VARIMAX method. The VARIMAX rotation has been used because it produces reasonably unique source compositions that have a maximum amount of inter-element variability, i.e. a few major elements and many minor ones(Henry, 1987). After rotating, the factors were much easier to interpret, with high loadings of "marker species" on a particular factor.

2.2 CLUSTER ANALYSIS

The basic distinction of cluster analysis is the ability to extract a number of common factors (Harman, 1967). We used cluster analysis to find the relationship between the variables. Each variable begins with its own domain which is called a cluster. The distance(degree of difference in behavior) of the initial independent variables in the data set are calculated by the correlation matrix. The closest two variables(or clusters) keep joining together to make a new cluster according to the distances among variables(or clusters) until every variable combines to one cluster. The result of clustering is displayed by a tree-type dendrogram whose horizontal distance is proportionally related to distance between clusters. The hierarchical clustering was calculated by the VARCLUS method, using the SAS program (Sarle, 1985).

3. RESULTS AND DISCUSSION

Table 1 shows the minimum, maximum, median, mean and standard deviation of the 13 selected variables used in our statistical analysis. The detailed photochemical significance and variation for each of these variables during MLOPEX are described elsewhere(Carroll et al., 1992; Liu et al., 1992; Ridley et al., 1992).

3.1 CLUSTER ANALYSIS

The results of the cluster analysis are shown in Fig. 1. One group(C) including O_3, dew point, $MeNO_3$ and HNO_3 is first separated from a group whose sources may be largely anthropogenic(B) and another which resembles the marine boundary layer(A). It is satisfying to note that these statistically-derived relationships agree very nicely with our intuitive understanding of chemical sources and air mass types. The characteristics of group A were the strong positive correlation between O_3 and HNO_3, and negative correlation between O_3(or HNO_3) and either $MeNO_3$ or dew point. The very low dew point and high mixing ratio of O_3 and HNO_3 strongly indicate stratospheric influences (Danielson et al., 1987). On the other hand, the stratospheric or upper tropospheric influences can not explain the negative $MeNO_3$ correlation with O_3 and HNO_3. $MeNO_3$ is thermally very stable and has a very slow rate of photolysis and reaction even with the OH radical(Senum et al., 1986). It may, thus, have a longer lifetime than other chemical species in the atmosphere. The combination of high mixing ratio of $MeNO_3$, low mixing ratios of O_3 and HNO_3, and high dew points may represent lower tropospheric air. As the thermal degradation of tropospheric organic nitrate species, such as PAN, is a major source of MeNO3, Walega et al.(1992) postulated that a high dew point with $MeNO_3$ may indicate well-aged warm marine tropospheric air.

Table 1. Statistical summary of the variables used in MLOPEX data analysis.

Variable	Minimum	Maximum	Mean	Median	Std. Dev.
O_3*	16	65	43	41	12
HNO_3	7	313	107	88	65
NO_3	bdl	365	37	13	54
SO_4	7	1126	101	53	154
NH_4	bdl	904	126	70	210
Na	bdl	250	21	3	40
PAN	bdl	54	17	14	14
$MeNO_3$	1.3	10.9	3.7	3.0	1.9
2-Butyl NO_3	0.19	2.89	0.82	0.66	0.56
H_2O_2	40	2344	1045	1036	389
C_2Cl_4	2.0	7.0	3.6	3.3	1.1
CN**	39	2146	297	232	275
DPT***	-24.6	1.2	-9.6	-7.6	6.4

all units are pptv except*; ppbv,
; number/cc, *; ℃
pptv; part per trillion by volume
ppbv; part per billion by volume
the number of observational periods used in the analysis is 74, each period was 3 hours in length.
bdl; below detection limit

This cluster may represent either relatively clean and well-aged marine tropospheric air(low O_3 and HNO_3, and high $MeNO_3$ and dew point), or recent stratospheric influence(high O_3 and HNO_3, and low $MeNO_3$ and dew point). We may assume that the combination of these variables in this cluster represents clean remote tropospheric air.

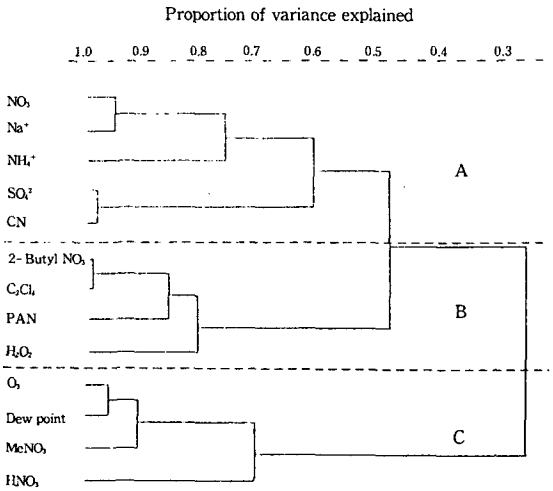

Fig. 1. Dendrogram for the cluster analysis. Horizontal distance among cluster is proportional to the degree of separations between behaviors of two clusters.

Group B is composed of 2-butyl nitrate, C_2Cl_4, PAN and H_2O_2, which are all positively correlated with each other. These variables are mainly products and byproducts of anthropogenic activity. H_2O_2 and PAN are separated at an early stage in group B. 2-butyl nitrate and C_2Cl_4 have the strongest correlation among these variables. This indicates at either the behavior or source of 2-butyl nitrate and C_2Cl_4 differs from that of PAN and H_2O_2. 2-butyl nitrate and C_2Cl_4 may indicate direct anthropogenic influence from local and remote sources with little modification(Atlas et al., 1992). The lifetime of PAN is more sensitive to temperature than those of C_2Cl_4 and 2-butyl nitrate(Cox and Roffey,1977). In addition, H_2O_2 and PAN are secondary products of anthropogenic sources, via photochemical reactions. Although variables in this cluster are closely linked to human activities, different source and sink reactions make their behaviors different.

The most distinct characteristic of group A is that it contains only aerosol species. Each variable was positively correlated with the others. The $SO_4^=$ and condensation nuclei in group A, among the greatest correlation pairs, are indicators of the local volcanic plume. Usually, air from the volcano was first detected by a rapid increase of the CN (Condensation Nuclei) count and elevated mixing ratios of $SO_4^=$ aerosol. The aggregation of the NO_3^-, NH_4^+, and Na^+ aerosol has the characteristics of the marine boundary layer. Because NH_4^+ aerosol usually accompanies either NO_3^- or $SO_4^=$ aerosol and has a boundary layer source, it lies in between the marine and volcanic air types. This group may represent relatively clean marine boundary layer air, containing volcanic influences but little anthropogenic material.

3.2 FACTOR ANALYSIS

The most subjective and critical procedure in factor analysis is the determination of the number of factors. Even though there are some criteria for this decision, none of them can be rigorously supported by an objective argument(Henry, 1987). Since the main purpose of factor analysis is to find useful arrangements of information from a large data set, we chose the number of factors based on our ability to understand and interpret them. In this study, six factors were computed, as shown in Table 2. The eigenvalue in each column represents the fraction of variance of that substance's mixing ratio explained by that factor. Theoretically, if this analysis explains all of the variance in the original data with these six factors, the sum of the eigenvalues(shown as the final value in the communality column in Table 2) should be thirteen because thirteen variables(total variances) were used. However, the amount of explained variance is 11.75, which tells us that this six-factor analysis can explain only 90 % of the total variance. As the factor loadings for each factor are related to the source compositions(Henry et al., 1984), we can understand the nature of each factor from its characteristic composition.

Table 2. Factor pattern after VARIMAX rotation for the data of MLOPEX

Variable	Factor loading						Final communality
	1*	2	3	4	5	6	
O_3	-0.083	0.926	0.221	-0.026	0.110	0.165	0.953
HNO_3	0207	0.701	-0.538	0.288	-0.064	0.068	0.915
NO_3	0.035	0.036	0.557	0.614	0.076	-0.403	0.697
SO_4	0.616	-0.108	0.305	0.470	0.436	0.101	0.905
NH_4	0.295	0.019	0.096	0.816	0.312	0.103	0.870
Na	0.231	0.072	0.222	0.124	0.894	-0.043	0.924
PAN	0.362	0.481	0.663	0.039	-0.059	-0.219	0.854
$MeNO_3$	-0.003	-0.427	-0.232	0.087	-0.029	0.840	0.950
2-Butyl NO_3	0.057	-0.087	0.924	0.129	0.109	-0.112	0.906
H_2O_2	-0.002	-0.042	-0.573	0.676	-0.297	0.121	0.890
C_2Cl_4	-0.086	-0.016	0.882	-0.018	0.233	-0.054	0.843
CN	0.948	-0.085	-0.081	0.122	0.155	-0.026	0.952
DPT	0.164	-0.916	0.120	0.090	0.008	0.223	0.938
Eigenvalues	1.637	2.637	3.275	1.869	1.291	1.050	11.750

1* : Volcanic, 2 : Upper tropospheric, 3 : Direct anthropogenic
4 : Photochemical haze, 5 : Marine aerosol, 6 : Warmed PAN

The distinct features of factor 1 are high $SO_4^=$ and condensation nuclei loading. This suggests that this factor is a sulfate aerosol component from active(boundary layer) volcanoes nearby. Although nighttime downslope winds should generally be free tropospheric air, it is not surprising that residues of volcanic plumes have been measured at night at MLO. Our decision to include samples which started at 2100 HST may have increased the potential for us to encounter residual volcanic aerosols from the daytime upslope flow.

High positive loadings of O_3 and HNO_3 with a strong negative dew point loadings are the distinct features of the second factor, which also appeared in cluster analysis. The very weak loadings of other pollution-derived variables in this factor support the role of either stratospheric injection or clean upper tropospheric air. It is interesting that this factor also has a relatively large loading(0.481) for PAN. For years there has been speculation that PAN(which is stable at the low temperature of the upper free troposphere), might be transmitting fixed nitrogen over long distances(Lee et al., 1994). This factor confirms that it is at least associated with the high ozone and nitric acid characteristic of air near the tropopause.

The third factor has loadings of 2-butyl nitrate and C_2Cl_4, with some other anthropogenic chemical species like PAN and NO_3^-, which are indicators of anthropogenic influences. This factor is apparently the direct result of human activity, either on the islands or in more distinct regions.

The fourth factor, with high loadings of NH_4^+, NO_3^-, and H_2O_2, is interesting because it is a well-described feature of this experiment, which occurred only once. During this event, high mixing ratios of many photochemical and aerosol species were observed(Atlas et al., 1992; Norton et al., 1992; Walega et al., 1992; Heikes, 1992). This factor represents a photochemical haze event, which was apparently the result of biomass fires on Maui. This is in contrast to the relatively direct urban influences which constitute factor three.

The fifth factor contains high sodium and aerosol species, which are characteristic of marine boundary layer air. It is striking, however, that this factor included none of the dew point variance, since sodium is strongly associated with moist marine boundary-layer air. Apparently the dramatic dew point differences between the extremely dry upper-tropospheric air and all other air masses(which shows up in factor 2) dominates the variance from other

sources. If we had chosen to use absolute humidity as the water vapor variable, the marine boundary layer/free troposphere humidity difference might have been more evident than it is with dew point.

The high loading of methyl nitrate in factor 6 separated from factor 3(anthropogenic influence) in a very early stage of factor analysis, as was the case with cluster analysis. This unique single-variable factor emphasizes the distinct behavior of $MeNO_3$, which is unlikely other anthropogenic chemical species. As we discussed before, it seems that factor 6 may be related to factor 2 and 3, both of which contain PAN. Factor 6 may be result of warming and aging air which had contained anthropogenic PAN.

Fig. 2 shows variations of factor scores for each sample. The vertical axis in Fig. 2 indicates how closely each sample resembles the composition of that factor. These factor scores are related to source contributions(Henry et al., 1984). Periods of different meteorological and chemical behavior(listed as A, B, C, D, E, F, G, H, I and J in Fig. 2), which were identified and defined in Table 3(from Hahn et al., 1992), are separated by dotted lines. The first factor(volcanic influences) appears sporadically but strongly in some cases(Fig. 2-a). The influence of the volcano is largely dependent upon the complex island air flow pattern and intermittent volcanic activity. Most of these volcanic influences in Fig. 2-a appear strongly in the evening sampling hours(from 9 PM to 12 AM, the first of three connected points) and then decrease after 2400 HST. This indicates that the northward, down slope winds often contains residues of the volcanic plume which had not yet been totally swept away during the evening hours.

Factor 2 in Fig. 2-b shows the stratospheric influences during MLOPEX. Compared with the broad O_3 and HNO3 peaks during MLOPEX, this factor appears rather scattered during most periods. Periods A and F are the most obvious times of upper tropospheric influence. Very dry air was descending from high altitude with high O_3 and HNO_3 during these two periods(Table 3). There was a negative correlation between O_3 and HNO_3 during most of period B and C, which is why factor 2 does not appear during most of these two periods.

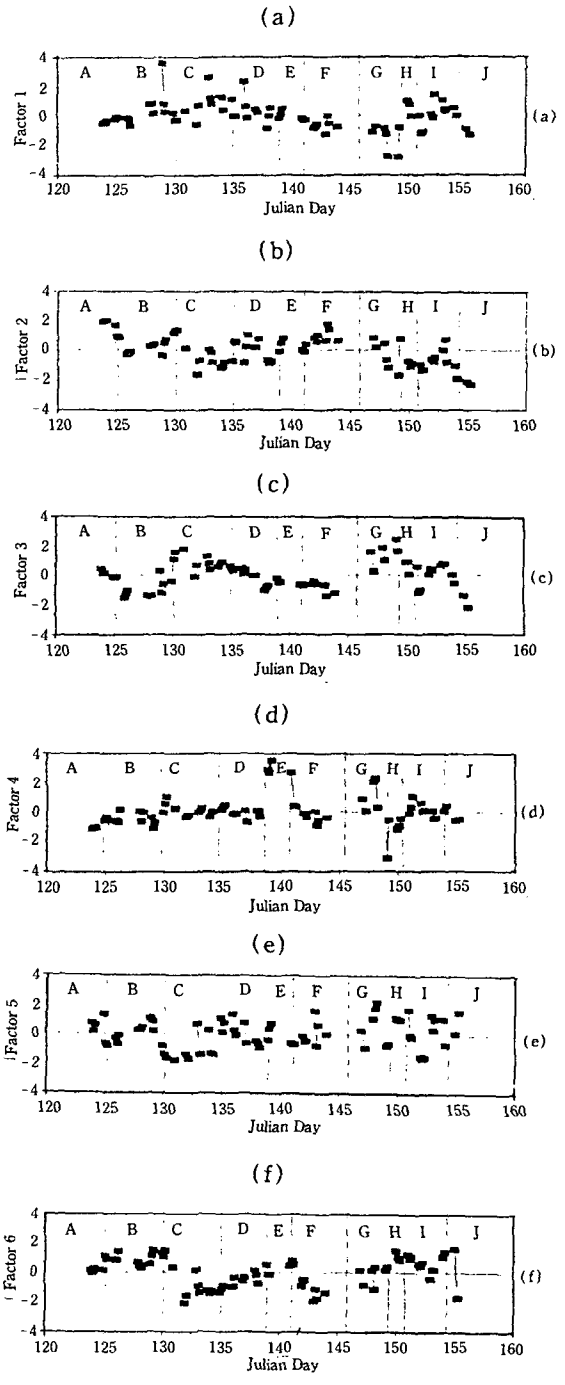

Fig. 2. Variations of factor scores during MLOPEX. Numbers on x-axis show the Julian days and letters inside of figures indicate periods defined in Table 3. Continuous samples were connected by lines.

Table 3. Classificaton of Sampling Periods During MLOPEX

Period	Julian day	Air Mass Origin	Local Influences.
May 1-3	122-124 A*	Northern latitude, Upper tropospheric.	Minimum marine boundary layer. (MBL) influence at night.
4-8	125-129 B	Local/ambiguous.	MBL influence day and night.
9-13	130-134 C	Northern latitude, Upper tropospheric. Asia	Local influences variable.
(10-11)	(131-132)		Passage through storm tracks.
14-16	135-137 D	Local/ambiguous.	Little local influence at night.
17-19	138-140 E	Southeast	Visible haze and strong island and MBL influence.
20-24	141-145 F	Descending marine air from northeast/western Pacific.	Little local influence day or night.
25-27	146-148 G	Suggestion of air from northeast/Asia but ambiguous.	Increasing influence of MBL.
28-29	149-150 H	Southeast	Strong MBL influence.
May 30-June 2	151-153 I	Ascending air from southeast.	Variable island influence.
June 3-4	154-155 J	Descending marine air from northeast/western Pacific.	Little local influence.

From Hahn et al., 1992

*; Letter for each classified period appeared in Figure 2, 3.

Factor 3(Fig. 2-c) appears during the period from May 28 to 29(G and H). It is evident that this factor is related to boundary layer air with direct anthropogenic influences. A smaller but continuous influence of this factor also appears during period C(May 9 to 15). However, during these intervals(C and G), it is thought that Asian continental influence was also present(Hahn et al., 1992; Walega et al., 1992). To the extent that this factor indicates local anthropogenic influences, it should be closely related with marine boundary layer air (factor 1 and 5), because human activities are mostly confined to the marine boundary layer. But the period of large score values for this factor is well separated from the marine boundary layer influence factors except during period H. Interestingly, cluster analysis also clearly separated these anthropogenically-produced chemical species from marine boundary layer species. Given these aspects, it is likely that this factor represents remote (Asian) anthropogenic influences, at least during periods C and G.

Fig. 2-d shows the influence of factor 4 on the distinct photochemical haze event during period E. In fact, this haze event, which was both visually and chemically documented, is a good check on how closely calculated factor scores can reproduce this unique period in the MLOPEX data set. Small influences of factor 4 also appear during period G when the influence of marine boundary layer air increases, implying that there was some photochemically-processed urban material in the marine boundary layer air of period G.

Factor 5's marine aerosol influences are scattered over each of the lettered intervals in Fig. 2-e. However, the most positive factor scores occur during periods G and H, when local and marine boundary layer influences increased(Table 3). As with the volcanic factor, this marine factor was often strongest during the evening sample. This is supported by the observation that the average sodium mixing ratio early in the night was, on average, slightly higher than those later at night. This suggests, as factor 1 does, that we occasionally sampled return flow of the boundary layer upslope winds during the early downslope winds in the eve-

ning.

The influences of factor 6 in Fig. 2-f were especially strong during periods B, H and J. These were identified as periods of marine boundary layer influence. The absence of other anthropogenic species in this factor indicates relatively clean marine air, whose only anthropogenic influence is long-range transport.

The best way to evaluate the results of factor analysis is to see how well the calculated factor scores and factor loadings reproduce the original data set. We calculated each standardized variable for each sample from the factor scores(Fig. 2) and factor loadings(Table 2). Then the calculated standardized values were transformed to their original scales. Log-transformed variables were converted to their original scales as well. The calculated values for each variable are usually close to measured ones with some exceptions, especially in very high mixing ratio samples. For example, even though our factor analysis explains only 69 %(final communality in Table 2) of the entire variation of aerosol NO_3^-, the calculated values and their patterns were well matched with measured data. The comparisons of measurement data and calculated data for aerosol NO_3^-, are shown in Fig. 3.

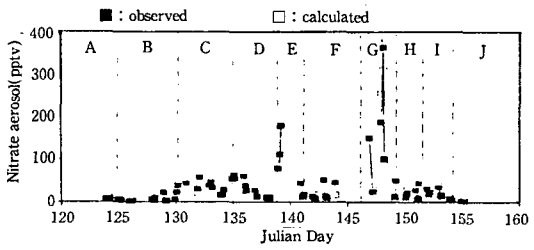

Fig. 3. Comparisons between measured nitrate aerosol during MLOPEX and estimated values of nitrate aerosol by factor scores and factor loadings obtained from the factor analysis. The filled squares and empty squares indicate the observed values and the calculated values, respectively. Numbers on x-amis show the Julian days and letters inside of figures indicate periods defined in Table 3.

One way to identify "background" free tropospheric mixing-ratios is to remove the effects of all identifiable local sources. To this end, we excluded the influences of volcanic air, anthropogenic air, marine boundary layer air, and the photochemical haze events from the factor scores matrix. Thus, we effectively defined a combination of upper tropospheric air(high altitude) and clean marine tropospheric air(low altitude) as "background" free tropospheric air. The cluster analysis had also separated the variables with specific sources from the "background", which emphasized HNO_3, O_3, and $MeNO_3$. Thus, we can safely use factor 2 and 6 to sort out the influence of nearby natural sources and human activities and leave a background composition. For most of the aerosol species, the free tropospheric background mixing ratios defined in this way did not vary much throughout the experiment. These results were expected, since we had excluded all immediate marine boundary layer and anthropogenic influences. However, some gaseous species ,such as O3, HNO3 and PAN, showed still larger variations than other aerosol or anthropogenic species.

Table 4. Statistically Estimated Free Tropospheric Values for Variables during MLOPEX.

Variable	Mean of estimated "background" free tropospheric values	Median	Std. Dev.
O_3*	41	42	10
HNO_3	94	85	45
NO_3	16	13	10
SO_4	60	59	9
NH_4	71	73	6
Na	5	5	1
PAN	13	11	9
$MeNO_3$	3.5	3.1	1.5
2-Butyl NO_3	0.60	0.65	0.10
H_2O_2	1015	1020	44
C_2Cl_4	3.3	3.3	0.1
CN**	249	249	13
DPT***	-8.5	-8.0	5.3

all units are pptv except*; ppbv,
; number/cc, *; ℃
pptv; part per trillion by volume
ppbv; part per billion by volume
the number of observational periods used in the analysis is 74, Each period was 3 hours in length.

The statistically estimated "background" free tropospheric means(Table 4) for most species are only slightly different from the overall means of Table 1. However, there are large difference between background and overall means for the aerosol species. These differences between the two sets of aerosol means is due to the significant increase of aerosols during the photochemical haze period and times of marine boundary layer air influence. By contrast, the differences between over medians and background medians are smaller than those between the means. The overall medians are also closer to background means than the overall means, emphasizing the impact of events(and local sources) on the overall mean statistic.

4. CONCLUSION

Multivariate statistical analyses were found to be very useful for identifying the influences of photochemistry and local and distance sources on the free troposphere during MLOPEX. Using cluster analysis and factor analysis, various influences on the composition of air at MLO were successfully separated and classified using 13 variables in nighttime data. Both methods pointed to similar combinations of species as indicators of certain air-mass histories.

"Background" free tropospheric mixing-ratios were derived from the identified sources and their contributions to each sample. Most of the factors and clusters were relatively well understood and clearly defined, thus minimizing ambiguities in their interpretation. The subjectivity inherent in that assignment of an interpretation is clearly the main limitation of statistical analysis for identifying airmass sources and influences. Nevertheless, the statistical methods provide an objective basis upon which to relate the composition of an airmass to its history.

This study shows that statistical methods, which are not often employed with non-conservative species, can be useful under some circumstances for understanding the behavior of photochemical compounds.

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Mauna Loa (Hawaii)에서 관측된 대기질 특성의 통계적 분석

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초 록

40가지 이상의 대기중 화학성분과 기상조건이 1988년 5월과 6월 사이의 MLOPEX기간 동안 동시 측정되었다. MLOPEX의 기본 목표는 인간의 직접적 오염을 받지 않는 청정 대류권(free troposphere)에 위치한 Mauna Loa(Hawaii) 관측소에서 대기중 여러 화학 물질들의 배경 농도들을 파악하고 그들의 상관관계를 규명하며, 그 결과를 광화학적 모델에 적용하여 모델의 적합성과 보완점을 이해하는 것이었다. 예상과는 달리 청정 대류권내에서도 상당히 복잡하고 다양한 농도의 변화를 보여 모델에 적용시킬 배경농도를 단순히 평균값으로 결정하기에는 어려움이 있었다. 이 연구에서는 cluster와 factor 분석의 통계적 방법을 이용하여 MLOPEX 기간동안 관측소에 나타난 기단(airmass)의 특성을 분류하고, 그 중 청정대기를 대표할 수 있는 농도를 결정하는 것이다. cluster 분석방법은 13가지 분석변수(variable)들을 크게 3가지의 그룹; (1)상대적으로 깨끗하고 오래된 공기를 대표하는 변수들 (2)인위적인 오염을 지시하는 변수들 (3)주위 해양과 화산의 영향을 나타내는 변수들로 분리하였다. 또 factor 분석에 의해서는 (1)화산 영향 대기 (2)성층권 대기 (3)오염된 대기경계층 공기(boundary-layer air) (4)광화학적 연무(haze) (5)해양성 대기경계층 공기 (6)해양성 청정공기들로 분류되었다. 이 결과를 가지고 계산한 Mauna Loa 관측소의 청정공기 배경농도와 조건값들은 다음과 같다.: O_3(41±10ppbv), HNO_3(94±45pptv), NO_3^-(16±10pptv), $SO_4^=$(60±0pptv), NH_4^+(71±6pptv), Na^+(5±1pptv), PAN(13±9pptv), $MeNO_3$(methyl nitrate, 3.5±1.5pptv), 2-butyl NO_3(0.6±0.1pptv), H_2O_2(1015±44pptv), C_2Cl_4(3.3±0.1pptv), 응결핵(249±13cm^{-3}), 이슬점온도(-8.5±5.3℃).