Tellus (1997), 49B, 327–342
Printed in UK – all rights reserved

TELLUS
ISSN 0280–6509

Application of vector autoregressive time series analysis to aerosol studies

By KUANG-JUNG HSU, *Department of Atmospheric Sciences, National Taiwan University, Taipei, Taiwan*

(Manuscript received 12 March 1996; in final form 26 February 1997)

ABSTRACT

Interpretation of aerosol processes, such as those related to acid deposition, based on linking laboratory experimental results with atmospheric observations can be difficult, often involving complicated models. In this study, statistical relationships in a time series of aerosol chemical composition measurements are examined to identify different aerosol groups and to estimate their atmospheric lifetimes. Vector autoregressive model (VAR) and vector moving average representations were applied to quantitatively study the relationships among chemical species in aerosols, with emphasis on sulfur oxidation. Data used were collected in Barrow, Alaska from 17 March to 21 April 1986. Results from the statistical analyses indicate: (1) chemical species can roughly be separated into 2 subgroups for either fine or coarse aerosols; and generally, there is no correlation between chemical species in these two subgroups; (2) durations and magnitudes of chemical influences in fine and coarse aerosols are different; (3) the principal species for controlling S variations is Cl or K in coarse particulates and Fe in fine particulates; the reverse relationships are less important; (4) sulfur variations in coarse particles were most likely controlled by the mass transfer process; (5) variations of S-compounds in fine aerosols, dominated by chemical reactions, have estimated lifetimes of 9 to 29 h. Further laboratory and field studies based on these hypotheses are, however, necessary to investigate causality.

1. Introduction

Acid deposition is a very serious pollution problem, leading to acidification of lakes and damage to forests and architecture. Vast efforts have been devoted to field monitoring, laboratory studies, and modeling of this problem. Due to the size and complexity of real situations, there are difficulties in studying these processes in laboratory conditions. The importance of each variable must be evaluated by sensitivity tests under similar conditions (Pandis and Seinfeld, 1989).

In this study, a statistical time series analysis was applied to an aerosol system in order to quantitatively examine the importance of various chemical species in sulfur oxidation without using complicated models. It is well-known that species involved in a chemical reaction system evolve with time. Acid deposition and photochemical smog usually take hours to several days to develop, and their effects far from sources can be substantial. During the development of a typical photochemical smog, concentrations of reactants vary, and their maxima do not appear at the same time (Finlayson-Pitts and Pitts, 1986). Similarly, the composition of chemical species in particulates, especially those involved in acid formation, may change between the sources and receptors.

For particulate data collected in time series at one location, past receptor-modeling studies have used the principal components analysis technique to elucidate possible origins of components in aerosol mixtures. Such a model usually assumes a purely physical mixing of different aerosol components throughout the time series of measurements, often several weeks long. For certain

chemical species, transformations definitely occur after leaving the sources, so that during the travel time between sources and receptors, the chemical composition of a particulate component may change. In this situation, a statistical time series analysis is a useful alternative to investigate relationships among various chemical species in particulate matter.

Several earlier studies applied the time series analysis technique to pollution problems: Merz et al. (1972), Tiao et al. (1975), Bojkov et. al. (1990), to name but a few. These were limited to investigating the time-dependent variations of individual chemical species, thus not considering chemical relationships among pollutants. Other authors have examined several species, for example Zinsmeister and Redman (1980) applied Box and Jenkins (1976) time series analysis methods to sequential aerosol composition measurements and examined elemental associations for comparison with principal components. Hsu (1992) used multivariate time series analysis to study the interdependence among NO, NO_2, and O_3 at 2 locations. The time-dependent response of one chemical species to perturbations by another species was derived, so that evidence for the importance of photochemistry and transport processes could be studied, although laboratory and field studies would be necessary to investigate causality.

In this paper, similar technique to those used in the Hsu(1992) gas phase study are adopted to investigate the relationships among chemical species in particulates. Particulate data were those of Li and Winchester (1990), who used principal component analysis. Samples were collected from 17 March to 21 April 1986 at Barrow, Alaska using a two-stage circular streaker sampler, a slowly rotating device which separated aerosols into coarse (>2.5 μm) and fine (<2.5 μm) particulate fractions as time-dependent streaks on a thin-film impaction surface and a nuclepore filter, respectively. Elemental concentrations were determined by particle induced X-ray emission analysis, PIXE, using a collimated proton beam and energy-dispersive X-ray detection (Johansson and Campbell, 1988). A total of 14 elements in each fraction were analyzed: Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Fe, Ni, Cu, Zn, and Br. During the sampling period, winds generally came from the north, bringing in Arctic air, although actual air flow directions varied as indicated by isobaric back trajectory calculations. The AGASP-II aircraft observed a major haze event from 25 March to 2 April 1986. During this period, air trajectories originated mainly over Russia or northern Europe, and some came from the North Pacific (Barrie, 1986; Herbert et al., 1989). The relative humidity was about 80% (Bridgman et al., 1989), and temperatures ranged from between -40°C to -20°C. Under such conditions, there were relatively few water molecules available in the air. According to analyses by Li and Winchester (1990), there was more mass in the fine fraction than in the coarse for all elements. For example, for S, the ratio was about 16 to 1. Although it is difficult to totally exclude the possibility of aerosol growth by water condensation, if such a phenomenon did exist, their effect would be small.

Oxidation of sulfur to sulfate in aerosols is our major interest in the present study. According to Parungo et al. (1990), sulfate is the dominant S-containing species in the aerosol samples. For simplicity, we therefore assume all S-containing aerosol species to be sulfate. Model development for relating sulfate with other chemical species is presented in Section 2. Since many chemical species are expected to be auto- and cross-correlated through time, vector time series analyses were performed to determine relationships among various elements. Vector autoregressive representations were applied to characterize the dynamic behavior of each chemical species, and the appropriate time lag lengths were determined. The model was then transferred to vector-moving average representations to evaluate the direct time-dependent relationship among chemical species. The time-dependent response functions of sulfur-related species to unit perturbations were derived. The fractional contributions to one chemical species by all related chemical species were examined by variance decomposition. Chemical lifetimes in fine aerosols were estimated. Finally, implications resulting from this study and further applications are discussed.

2. Model

As an illustrative example, suppose that a system is composed of the following elementary

reactions:

$$A_1 + A_2 \rightarrow A_3 + A_4 \quad (1)$$

$$A_3 \rightarrow A_1 + A_5 \quad (2)$$

$$A_4 + A_5 \rightarrow A_2 . \quad (3)$$

At time t, concentrations of these species are $Z_{1,t}$, $Z_{2,t}$, $Z_{3,t}$, $Z_{4,t}$, and $Z_{5,t}$, respectively. If no other processes except these reactions exist, the time-dependent concentration changes can be expressed as follows:

$$\frac{d[A_1]}{dt} = -k_1[A_1][A_2] + k_2[A_3]$$

$$= -k_1 Z_{1,t} Z_{2,t} + k_2 Z_{3,t} \approx \frac{\Delta Z_{1,t}}{\Delta t}, \quad (4)$$

$$\frac{d[A_2]}{dt} = -k_1[A_1][A_2] + k_3[A_4][A_5]$$

$$= -k_1 Z_{1,t} Z_{2,t} + k_3 Z_{4,t} Z_{5,t} \approx \frac{\Delta Z_{2,t}}{\Delta t}, \quad (5)$$

and we have:

$$Z_{1,t+1} = \Delta Z_{1,t} + Z_{1,t}$$

$$= (-k_1 Z_{1,t} Z_{2,t} + k_2 Z_{3,t})\Delta t + Z_{1,t}, \quad (6)$$

$$Z_{2,t+1} = \Delta Z_{2,t} + Z_{2,t}$$

$$= (-k_1 Z_{1,t} Z_{2,t} + k_3 Z_{4,t} Z_{5,t})\Delta t + Z_{2,t} . \quad (7)$$

We now consider a system with n variables, and allow a non-zero mean and random fluctuations for each variable; such a system can be well approximated by a vector autoregression (VAR) model of order p (VAR(p)):

$$Z_t = A(L)Z_{t-1} + M + U_t, \qquad t = 0, 1, 2, \ldots, \quad (8)$$

where Z_t is an $n \times 1$ vector $[Z_{1,t}, Z_{2,t}, \ldots, Z_{n,t}]$, $M = [M_1, M_2, \ldots, M_n]$ is a vector containing the mean (possibly non-zero) for each of the variables, and U_t is an $n \times 1$ vector of serially uncorrelated population residuals. $A(L)$ is the matrix polynomial of order p-1 in the lag operator L, with $A(L) = A_1 + A_2 L^1 + A_3 L^2 + \ldots + A_p L^{p-1}$. The parameters, M and $A(L)$, in this VAR model can be estimated using the least squares approach, once the order p was determined (Priestley, 1981, p.310). In the following discussion, M was removed for the sake of simplicity.

As described by Tiao and Box (1981) and Lütkepohl (1991, p.125), a χ^2 test was applied in the identification procedure for autoregression (AR) processes to determine the appropriate lag lengths. The χ^2 statistic is defined as:

$$\chi^2 = (T-K)\,[\ln|\Sigma_p| - \ln|\Sigma_{p+1}|]. \quad (9)$$

Here, T is the sample size, $K = (p+1) \times n$ and Σ_p is the estimated variance-covariance matrix of residuals when the order of $A(L)$ is set to p. If the number of equations equals the number of variables in the χ^2 test, the test degrees of freedom are the number of restrictions between 2 models, n^2. For example, if a system consists of 5 equations, each containing 5 variables, the number of restrictions is 25. The null hypothesis states that 2 models are essentially the same. We do not reject the null hypothesis if the χ^2 value is less than the critical value at a desired significance level. We used 0.05 in this study. Otherwise, we reject the null hypothesis (Lütkepohl, 1991, p.125). Using the χ^2 test, we can also divide these 14 chemical species into sulfur-related and non-related groups for both fine and coarse particles, as will be described further in Section 3. Besides the null hypothesis, a number of technical procedures can be used in determining the order(s) of the time series models (Priestley, 1981, p.370; Lütkepohl, 1991, p.128).

Results estimated from VAR may include both direct and indirect chemical interactions. For example, an increase in A_5 may lead to a decrease in A_4 due to reaction (3). With more A_2 produced, there will be some increase in A_4 due to reaction (1). Using VAR, we probably find Z_4 influenced by all 5 species, including indirect effects from A_3 through reaction (2). In order to evaluate the direct response functions to perturbations (or impulse) on certain chemical species, the unrestricted VAR model given previously was changed to the vector-moving average representation

$$Z_t = \sum_{j=0}^{\infty} C_j U_{t-j} = C(L) \cdot U_t, \quad (10)$$

where the C_js are $n \times n$ matrices. Normalization of Z_t has to be performed before computing impulse response functions, since all these parameters may be correlated. A lower triangular matrix W was chosen such that $WU_t = S_t$ has a diagonal covariance matrix. There are an infinite number of ways of normalization. Choosing a lower triangular matrix implies that the kth equation, $Z_{k,t}$ may contain influence from $Z_{1,t}, \ldots, Z_{(k-1),t}$, and not $Z_{k,t}$, $Z_{(k+1),t}, \ldots,$

(Lütkepohl, 1991, p.51–52). Changing order means the the influences of variables were altered. Therefore, the conclusion may be different. More explanation will be given in Subsection 3.1. The impulse response function, D_j can be written as

$$Z_t = \sum_{j=0}^{\infty} D_j S_{t-j} = D(L) S_t , \qquad (11)$$

where $D_j = C_j W^{-1}$, and the variance of S_t is given by $\Sigma_s = \mathbf{E}[S_t, S_t^{\mathrm{T}}] = W \Sigma_p W^T$. The D_j's represent the response of a dynamic system to the orthogonal inputs S_t. More specifically, the ilth element of D_s, D_{ils}, represents a response of Z_{it} to the fundamental variation in Z_{lt} after s periods, isolated from effects due to changes in other parameters.

Another use of the moving-average representations in the previous equation is that we can examine what proportion of the variance of one variable is accounted for by a given pulsed input in different variables. First, the variance of the m-step ahead forecasting errors in Z_t is (Lütkepohl, 1991, p. 56)

$$\mathrm{Var}_m(Z_t) = \sum_{j=0}^{m=1} D_j \Sigma_s D_j^T . \qquad (12)$$

Here as m approaches infinity, $\mathrm{Var}_m(Z_t)$ converges to the unconditional variance of Z_t. As a result, the unconditional variance of a typical variable Z_{it} that is attributable to the pulsed inputs in Z_{jt}, is well approximated by calculating (12) for large values of m. When there is substantial correlation among fundamental changes in Z_t, the ordering of Z_t could affect the result obtained in the variance decomposition.

3. Results and discussion

Flights and other measurements observed a haze period from 25 March to 2 April 1986 during the AGASP-II experiment. Isobaric air trajectories calculated for the 2 periods indicated transport of air parcels from different source areas. Tests were performed using several chemicals of interest on the whole period (A), 25 March to 21 April (B), 25 March to 2 April (I) and 3 April to 21 April (II). The null hypothesis was tested with A against B, B against I, and B against II for every element of interest. The procedure used was the log-likelihood ratio statistic which has a χ^2 distribution. The log-likelihood ratio was larger than the critical number at 0.05 significance level. Result indicated that the maximum possible probabilities (mean values) to observations, period I, II, and B, differ a lot (Priestley, 1981, p.304). Accordingly, data were separated into 4 groups for analyses: Coarse-I and Fine-I from 25 March to 2 April haze period, and Coarse-II and Fine-II from 3 April to 21 April. Later in this study, information from 17 March to 24 March were not included.

In Coarse-I during the haze period, species containing S, as well as Si (but not Al), K, Ca, Fe, Br, and possibly Cl, were more abundant, while in Coarse-II during the 2nd period, Na and Mg were generally more abundant; concentrations of Al, Ti, Ni, Cu, and Zn were similar in the 2 periods. Fine-I and -II do not have such distinct differences in average elemental mass concentrations. Taking the average sea salt weight ratio for $SO_4^{2-}/\mathrm{Na} = 0.252$ (Mason, 1966, p.194), sea salt contributions were about 9% and 40% in S for Coarse-I and Coarse-II, estimated using the sea salt ratio $\mathrm{S} = 0.084\mathrm{Na}$. It was less than 2% for fine particulates in both periods. Non-sea salt S were used in the following section by correcting the sea salt contributions.

The main interest of this study is to use the statistical technique to investigate relationships among various chemical species in aerosols, with particular emphasis on sulfur. In the following discussion, all the S-containing species were assumed to be sulfate. Chemical species coming from crustal origins should not change significantly during transport over several days to weeks. On the other hand, oxidation of S-containing gaseous species and uptake by aerosols is known to be important for acid formation, and the content of S relative to other elemental constituents in aerosols may change with time.

In order for sulfur oxidation to occur in the atmosphere, chemical reactions and physical transfer processes must take place. These processes include the gas phase and aqueous phase diffusion, mass transfer across the interface, ionization, and chemical reactions (Seinfeld, 1986, p.251). The controlling process can be identified by comparing the characteristic time of these processes. Consider as average condition $T = 253$ K, $P_{SO_2} = 1$ ppb, $P_{O_3} = 20$ ppb, and the liquid water content of 2×10^{-8} L of H_2O per m^3. The ionization processes are rapid enough, $\sim 10^{-7}$ s, to be neglected here. For 2.5 μm diameter particles, the characteristic times for gas phase and aqueous phase

diffusion are about 10^{-7} s and 10^{-3} s, respectively. Both chemical reactions and the modified Henry Law coefficients are pH-dependent. Assuming all metals are at their highest oxidation states, and S as SO_4^{2-}, analyses by Li and Winchester (1990) gave 2 major coarse components having close to acid-base neutral states by the measured elements. The 3rd component has cation/anion ratio around 20. Therefore, the pH values of coarse particulates were assumed to be 7. The estimated characteristic time for reaction with ozone is 1–2 s and that for mass transfer across the interface is 6×10^5 s with a sticking coefficient of 0.1. The rate for chemical reactions is much faster than that for SO_2 across the interface. Therefore, the rate of sulfur oxidation within the atmospheric aerosol phase is most likely controlled by the mass transfer process.

Values of pH $\leqslant 5$ are expected in fine particles, since these are formed mainly by coagulation of gas-phase molecules. In this case, the apparent Henry Law coefficients are much smaller than those at higher pH. At pH = 5, the characteristic time for crossing the interface is ≈ 10 s. As the total dissolved S(IV) decreases with decreasing pH, reaction of S(IV) with O_3 takes a much longer time, 3×10^3 s as estimated using room temperature rate constants. Even the faster oxidation reaction with H_2O_2 has a longer characteristic time at pH < 5 than that of crossing the interface. Therefore, chemical reaction is the rate-determining process. Numerous studies also report the catalytic effects of Fe^{3+} on sulfate formation in aqueous phase. However, its importance is not clear in real situations. Based on the available data, reaction rates as well as the importance of mass transfer and the iron catalytic effects in sulfur oxidation will be carefully examined.

3.1. *Coarse-I*

This data set contains observations of 14 chemical species, not all of which necessarily having any direct correlation with sulfur. In order to reduce the size of our model, univariate analyses were carried out for each of the 14 elements. For example, with S being the only variable, tests were performed to determine the AR order by reducing lag length till one of the null hypotheses is rejected, as described in Lütkepohl (1991, p.125). Then, each of the 13 other elements with lag length, e.g. 15, combining with above S system were tested against the system with sulfur only. In this case, the test degree of freedom is 15. The chemical is said to belong to S-related species if the null hypotheses was rejected. Several different lag lengths were used in the test. Results with lag length of 10 are listed in Table 1. At signigicance level of 0.05, the particular variable is significant if its result from the χ^2 test, $\chi^2(p)$, is 18.3 or greater at $p = 10$. Results, listed in Table 1, indicate that only S, and Cl are significant in determining the concentration changes of sulfur, the next element being Si in significance. As a whole, variations in S, Cl, K, and Cu mainly depend on these 4 elements, which account for about 31% of the total mass. Fe was added to the system for later comparison. Similar tests were also applied to test the significance of each element with zero lag, the test degree of freedom is 1. Elements with significant $\chi^2(1)$ values are Na(16.8) and Cl(13.3) for S; Na(12.6), S(17.6), K(26.7), Ca(9.36), Fe(19.6) for Cl; and Cl(17.4) for Fe. Such a strong correlation at the exact hour suggests that these elements came from nearby sources.

For fear of underestimation of the type I error, VAR were set with 5 chemical elements each with lag 10 in the system. Other elements were tested one by one against the newly-formed model to double check their significances. The most appropriate order of the VAR model was obtained by applying the χ^2 tests to each element separately. Estimated at 95% confidence level, the most

Table 1. *Results from the χ^2 tests with lags of 10 for: S, Cl, Fe, K, and Cu in Coarse-I*

Element	S	Cl	Fe	K	Cu
Na	9.46	22.2	3.44	19.1	20.4
Mg	5.96	2.78	3.11	10.8	5.15
Al	4.52	4.40	7.06	7.48	2.46
Si	12.1	28.6	18.6	13.3	13.9
S	19.9	8.53	3.74	5.82	6.91
Cl	18.9	29.3	13.4	12.7	23.5
K	8.35	27.2	22.8	24.6	27.4
Ca	5.68	10.4	19.7	6.37	13.7
Ti	6.67	14.9	17.7	11.9	7.88
Fe	5.40	9.51	7.67	4.31	3.11
Ni	3.09	6.56	12.0	3.99	4.49
Cu	7.89	24.7	39.7	13.5	19.0
Zn	3.97	13.3	17.2	7.94	8.21
Br	9.26	5.27	7.04	5.21	2.76

Note: $\chi^2_{0.95}(10) = 18.3$; one lag equals 3 h.

Table 2. *Estimated lag ranges with involved elements derived by VAR for (a) Coarse-I, (b) Coarse-II, (c) Fine-I, and (d) Fine-II at 95% confidence level*

	Element	Element (the most appropriate lag ranges)	r^2
(a)	S	S(1,3) Cl(1,1)	0.3252
	Cl	Cl(1,1) Na(1,3) K(1,3) Si(1,1) Cu(1,2)	0.6498
	K	Na(1,1) K(1,1)	0.3029
	Cu	Cl(1,1) Na(1,3) Cu(1,1) K(1,1)	0.3912
	Fe	Si(1,2) K(1,1) Cu(1,2) Ca(1,3)	0.5350
(b)	S	S(1,1) Fe(1,2) K(1,2) Ni(1,1)	0.1950
	Cl	S(1,1) Cl(1,1) K(1,4) Mg(1,4) Ni(1,1)	0.1782
	K	Mg(1,1) K(1,1) Ni(1,3)	0.1309
	Ni	S(1,3) Si(1,3) Ni(1,1)	0.0670
	Fe	S(1,1) Al(1,4) Fe(1,6) Ni(1,3)	0.2572
(c)	S	S(1,1) Fe(1,2) Cl(1,1) Zn(1,4)	0.8473
	Cl	S(1,5) Cl(1,1) Fe(1,1) Ni(1,2)	0.6370
	Fe	S(1,6) Fe(1,1)	0.6206
	Zn	Fe(1,3) Zn(1,6)	0.7699
	K	K(1,1) Fe(1,5)	0.3536
(d)	S	S(1,1) Fe(1,1) Zn(1,1) Si(1,1) Al(1,3)	0.8572
	Cl	Cl(1,3) Mg(1,3) K(1,1)	0.4331
	Fe	S(1,5) Si(1,1) Fe(1,1)	0.6332
	Zn	S(1,1) Zn(1,3)	0.2451
	Si	Si(1,5) S(1,1) Cl(1,1) Fe(1,1)	0.7944

Note: $A(x, y)$ stands for elements indicated in label were influenced by species A from lag x to lag y. One lag equals 3 h.

appropriate lag lengths are listed in Table 2a. Percentages of the variance explained, r^2, for the elements are: $r^2(S)=0.3252$, $r^2(Cl)=0.6498$, $r^2(K)=0.3029$, $r^2(Cu)=0.3912$, and $r^2(Fe)=0.5350$. Fig. 1 gives the residual autocorrelation plots of S, Cl, and Fe, with 2 dotted lines defining the 95% confidence intervals. All points fall within the range, indicating that these estimations are reasonable (Box and Jenkins, 1976, p.289).

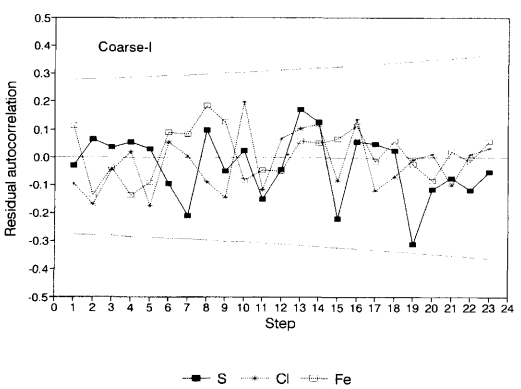

Fig. 1. Residual autocorrelation plots for S, Cl, and Na in Coarse-I period. Dotted lines indicate the 95% confidence interval estimated according to Box and Jenkins (1976).

In this case, elemental correlations were short-lived. It is possible that fast chemical interactions are involved and their influences die down within 3 h (1st step). However, as discussed already, coarse particles were mainly formed by mechanical force, and mass transfer across the interface may be the rate-controlling step. The strong correlation between S, Cl, and Na at the exact hour also indicates little chemical interactions among these elements, which then must have come together from nearby sources. It was suggested by Li and Winchester (1989) that the strong association of non-sea salt SO_4^{2-} with K may be contributed to by combustion and could be carried to the Arctic on sea salt particles, although certain meteorological conditions may induce strong correlation between elements, even though their origin may be far away from each other. The probability of such conicidence will be reduced as the sample number increases. However, there is no way for us to entirely rule out such possibility.

These derived correlations may include both direct and indirect influences among chemical elements. In order to evaluate the direct responses to sudden variations, the model was changed to the moving-average (MA) representations. Changing the representation order means the influences among variables were altered. Therefore, the conclusion may be different. In the coarse particulates, changing ordering did not produce significant change. It is known that the only possible reaction is due to sulfate replacement of chloride ion. Analyses by Li and Winchester (1990) on the same set of data indicate such possibility are very small, since 2 major coarse components have near acid-base balances. In fine aerosols, equations were arranged in the following order: Cl first, S last and Fe in between. How these observed chemicals affect the sulfur oxidation process is the major focus of this study. That is the reason for setting up the above sequence. Changing equation orders in fine aerosol estimations did produce some change. The major change comes from alternating Fe and S order. In this study, concentrations of chemical species of interest are not of the same magnitudes. One standard deviation of each chemical element was taken to be an impulse. The derived impulse response functions for 3 days are shown in Fig. 2 for S, Cl, and Fe, respectively.

Given an impulse of sulfur, only sulfur has a significant response, as indicated in Fig. 2a. The response functions of the 3 elements, S, Cl, Fe, to a Cl impulse are given in Fig. 2b. Both S and Cl show similar strong response and Fe has little variation. Given an impulse of Fe, behavior of S and Cl were small and almost identical. In general, all the responses were on short time scales, which was consistent with the results from VAR analyses.

Variance decompositions were performed to quantitatively examine the relations among these chemical elements. As shown in Table 3, results for the 5 elements are consistent with results from impulse response calculations. For sulfur, the major contribution came from Cl, at 30–34%, and sulfur itself, at 50–64%. Cu, K, and Fe have less than 15% influence on S and about 65% on Cl. For Fe, as expected, the influence from Cl is about 0 to 1.41% and the major contribution came from Fe, 50–96% and Cu, up to 38%.

3.2. *Coarse-II*

Results were similar to those obtained in Coarse-I with small differences. The χ^2 tests indicated that S, Cl, K, Fe, and Ni are S-related species. The total variances explained were smaller than those obtained in Coarse-I. The appropriate lag lengths for these species are listed in Table 2b with the r^2 values: 0.1950 (S), 0.1782 (Cl), 0.1309 (K), 0.0670 (Ni), and 0.2572 (Fe). Similar to Coarse-I, strong correlations among some elements at the exact hour were obtained. Cl is important for S(90.9) and Fe(11.2) variation. The calculated impulse response functions for S, Cl, and Fe are shown in Fig. 3, and were quite similar to those in Coarse-I. Decomposition of variances were not listed due to very low r^2s.

For coarse particulates obtained in both periods, the above analyses indicate that correlations among chemical elements were short-lived. Such phenomenum cannot be explained by known chemical mechanisms, and the good correlation between sulfur and Cl at zero lag indicates the importance of marine sources. The ineffectiveness of iron on sulfur variation means that catalytic oxidation of S(IV) is not an important process in coarse particulate. Li and Winchester (1990) using the same set of data drew similar conclusion. If aging of coarse aerosols is a function of serosol coagulation and the degree of H_2SO_4-base reaction, then the ratios S/cation may be used as indicators of aerosol residence time. For coarse particulates, the ratios S/cation $=0.80\pm0.39$ and 0.44 ± 0.09 of major components indicate that those aerosols were semi-aged. The extent of direct oxidation of S(IV) in the aerosol was small.

3.3. *Fine-I*

Similar procedures used in analyzing coarse aerosols were applied. Using the χ^2 tests, it is found that S, Cl, Fe, and Zn are important in determining S content. Cl, S, Fe, and Ni are important for Cl variations. Fe was influenced by Fe and S. Therefore, S-related species include S, Cl, Fe, Zn, and Ni, with an average of 70.5% of the total mass. The best estimated lag lengths from the χ^2 tests are listed in Table 2c. Much better correlations were obtained for fine aerosols than those for coarse particles. Squares of the correlation coefficients from VAR for S, Cl, Fe, Ni, and Zn are 0.8473, 0.6370, 0.6206, 0.3536, and 0.7699, respectively. Results from examining the significance at the zero lag are: 19.6 for Fe influen-

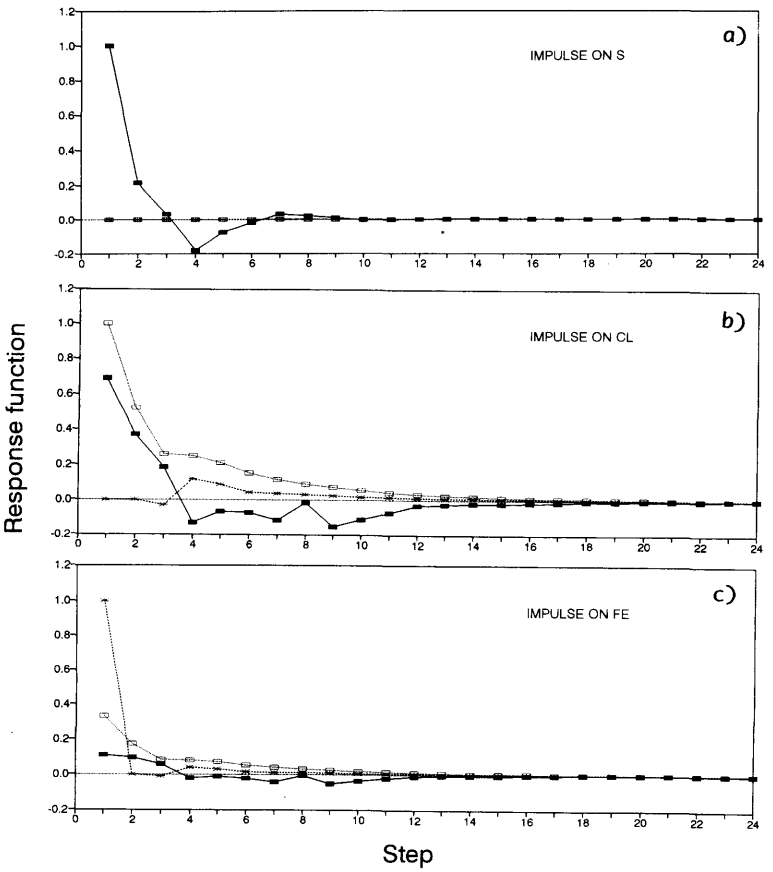

Fig. 2. The 3-days response functions of S, Cl, and Fe to impulses of (a) S, (b) Cl, and (c) Fe in Coarse-I.

cing S and 9.23 for S affecting Fe; their influences on Cl were negligible, 0.889 and 0.030.

The derived impulse response functions of 24 steps (i.e., 3 days) are shown in Fig. 4 for S, Cl, and Fe. As unit perturbation of sulfur was imposed on the system, equilibrium between H^+ and sulfate was broken. More S(IV) dissolved with increasing pH value; the rate of S(IV) oxidation increases and more sulfate was produced. The rate of this process will become slower as the pH value gradually decreases. Fe varies slightly and there is no clear pattern on the Cl response. These chemical correlations were quantitatively examined by the variance decompositions; see Table 4. Influences from S account for less than 1% Fe variance, while the influences on Cl increased from almost zero to 12%. Fig. 4b plots the impulse response functions of these 3 species after an impulse of Cl was given. Response of S and Fe are small compared to that of Cl. The contributions from Cl were about 3% each, see Table 4. Given a shock on Fe, response functions are shown in Fig. 4c. Strong variations of S were derived while Cl varies only slightly. Influences from Fe to S increase from 16% to 64%. Less than 10% of the Cl variance was contributed by Fe perturbation. For these 3 chemical elements, the influence from either Zn or Ni is small, $\leqslant 10\%$.

3.4. *Fine-II*

5 chemical elements, S, Cl, Fe, Si, and Zn, were included in the system for estimation. Mass percentages of the sulfate-related species were, about 73.6%, slightly more than that in Fine-I. The optimal lag lengths are listed in Table 2d. Values

Table 3. *Results from the variance decomposition for (a) S, (b) Cl, and (c) Fe in Coarse-I.*

	Step*	Std. error**	S***	Cl	Fe	K	Cu
(a)	1	0.0297	63.7	30.1	0.76	2.53	2.70
	2	0.0321	57.4	33.4	1.17	4.42	3.49
	3	0.0325	55.7	34.2	1.31	5.03	3.60
	4	0.0331	55.6	34.0	1.29	4.92	4.06
	5	0.0333	55.2	33.8	1.28	4.92	4.76
	7	0.0336	54.4	34.2	1.37	4.98	4.86
	10	0.0345	51.6	34.2	1.50	6.03	6.49
	15	0.0352	49.6	33.3	1.48	7.29	8.18
	20	0.0352	49.5	33.2	1.48	7.49	8.24
(b)	1	0.0199	0.00	54.4	5.93	28.1	11.4
	2	0.0222	0.00	55.6	6.05	28.0	10.2
	3	0.0257	0.00	44.0	4.79	22.8	28.3
	4	0.0281	0.00	38.3	4.17	24.2	33.1
	5	0.0296	0.00	35.8	3.90	27.0	33.1
	7	0.0310	0.00	33.4	3.64	29.8	33.0
	10	0.0317	0.00	32.2	3.51	31.3	32.8
	15	0.0319	0.00	31.9	3.48	31.7	32.7
	20	0.0320	0.00	31.9	3.47	31.8	32.7
(c)	1	0.0337	0.00	0.00	96.2	3.72	0.01
	2	0.0343	0.00	0.00	93.3	3.66	3.00
	3	0.0431	0.00	0.054	59.0	2.35	38.5
	4	0.0453	0.00	0.822	53.5	8.70	36.9
	5	0.0462	0.00	1.18	51.5	11.5	35.6
	7	0.0468	0.00	1.31	50.1	12.9	35.5
	10	0.0471	0.00	1.39	49.4	13.7	35.3
	15	0.0472	0.00	1.41	49.2	13.9	35.3
	20	0.0472	0.00	1.41	49.2	13.9	35.3

*One step = 3 h.

**Total standard error for elements (a) S, (b) Cl, and (c) Fe at different steps.

***Percentage contribution from S to (a) S, (b) Cl, and (c) Fe. For example, at step 1, S contributes 63.7%, 0.0%, and 0.0% to the total standard deviations of (a) S, (b) Cl, and (c) Fe, respectively. At step 2, contributions from S, Cl, Fe, K, and Cu to S are 57.4%, 33.4%, 1.17%, 4.42%, and 3.49%, respectively.

of r^2 for S, Cl, Fe, Si, and Zn are 0.8572, 0.4331, 0.6332, 0.7944, and 0.2451, respectively.

Response functions to unit perturbations of S, Cl, and Fe are plotted in Fig. 5. Quantitative results from variance decomposition are listed in Table 5. There was no influence on Cl by either S or Fe in this case. Fig. 5a shows that a sudden increase in S causes no change in Cl. Sulfate influence on Fe started near zero and increased with time to ~21% at the 20th step. The contribution from Cl to S is no more than 5%, and 2.3% to Fe variances. Cl perturbation induces small variations on Fe and S, as shown in Fig. 5b. The variance of S decrease from 45% to about 10%, were contributed to by Fe. Contributions from Zn to S are up to ~30% and less than 13% to Fe. Contributions from Si are less than 7% to S and less than 15% to Fe.

The response functions to a sudden impulse of certain chemical elements represent the chemical variations under the preset condition. Li and Winchester (1990) found little Cl displacement in the coarse aerosol sampled, while the first fine component had a Cl deficit. Due to large uncertainty in the ratio S/cation, it is not certain whether Cl was displaced by S. Of the 4 Cl response functions derived in this study, only one, in Fine-I, indicates the possibility of Cl displacement by S, see Fig. 4a. Since the process of sulfur oxidation would not be altered by Cl displacement, response functions of S to impulses of Cl were not considered in the following estimations. As indicated in

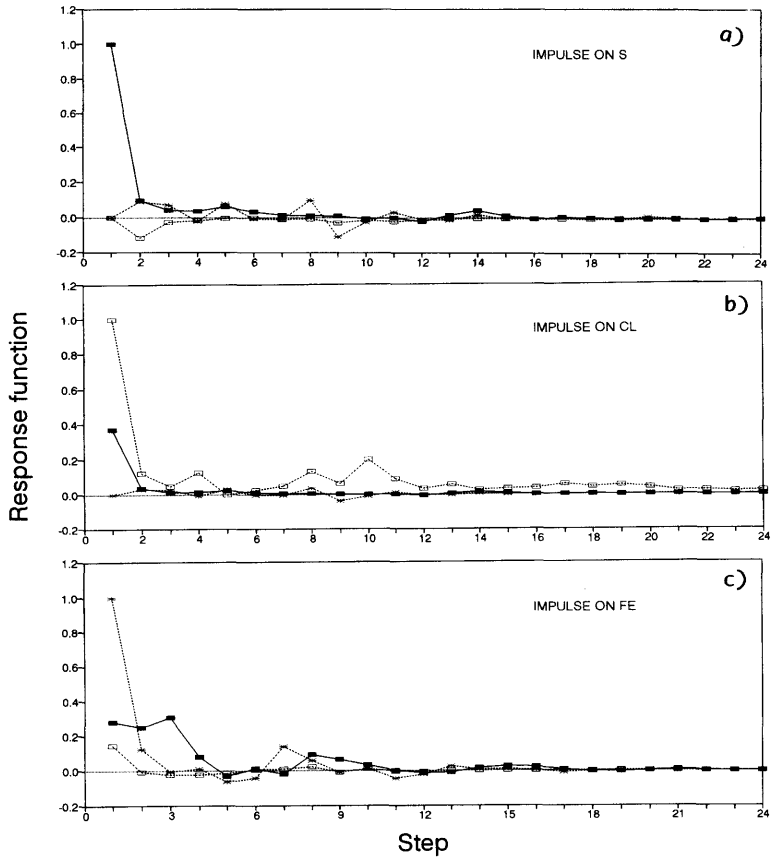

Fig. 3. The 3-days response functions of S, Cl, and Fe to impulses of (a) S, (b) Cl, and (c) Fe in Coarse-II.

the response functions, chemistry is not important in the coarse particulates; therefore only the fine particles are discussed in the following. It is known that sulfates were formed by the oxidation of S(IV) reacting with O_3, H_2O_2, Fe^{3+}, and Mn^{2+} (Brandt and van Eldik, 1995). Relative importances of these reactions were mainly controlled by pH value, temperature, and concentrations of reactants in the system. In this study, only the abundances of S and Fe were available. The oxidation processes were simplified to two reactions: (1) reaction of S(IV) and (2) Fe(III) catalytic reaction. According to Hoffmann and Calvert (1985) and Martin (1984), the rate of catalytic reaction also depends on S(IV). Since the decrease in S(IV) corresponds to the increase of sulfate, *S*, the sulfate variation can be derived as $-\mathrm{d}[S]/\mathrm{d}t \approx k_1[S] + k_2[Fe]$ with $k_2 = k^{\mathrm{I}}[S]$. Variation of S in fine particulates can therefore be expressed as $-\mathrm{dln}[S]/\mathrm{d}t \approx k_1 + \mathrm{k}^{\mathrm{I}}[Fe] = k_1 + k_2[Fe]/[S]$. Let slope *S* represent the slope derived from the log response functions of *S* to an impulse of itself, and slope *Fe* for that derived from response of *S* to *Fe* impulse. The time-dependent response function of *S* becomes $-\Delta\ln[S]/\Delta t = \text{slope}\ \ S + \text{slope}\ \ Fe \times ([Fe]/[S])$, where $([Fe]/[S])$ represents the ratio of their standard deviations.

Figs. 6, 7 are the logarithmic plots of the response functions for Fine-I and Fine-II particulates, respectively. Values of slope *S* derived from Figs. 6, 7 are 0.108 h^{-1} and 0.0300 h^{-1}; values of slope *Fe* are 0.076 h^{-1} and 0.137 h^{-1} for Fine-I and Fine-II, respectively. For Fine-I and Fine-II, $([Fe]/[S])$s are 0.0235 and 0.0297, respectively. The overall oxidation rates are (0.108+

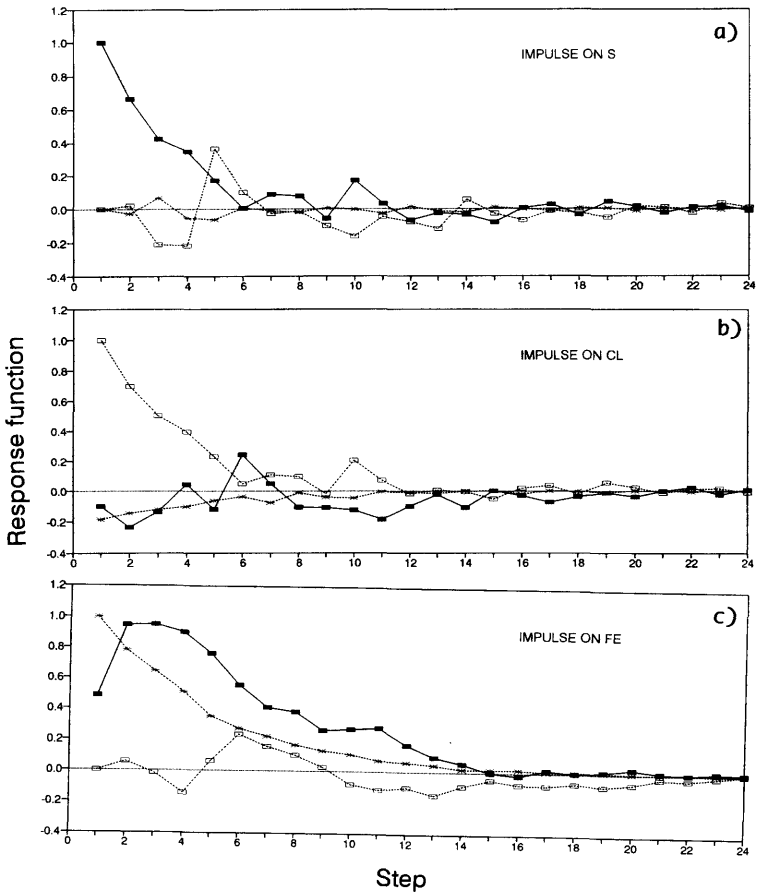

Fig. 4. The 3-days response functions of S, Cl, and Fe to impulses of (a) S, (b) Cl, and (c) Fe in Fine-I.

$0.0235 \times 0.076) = 11\%$ for Fine-I and $(0.030 + 0.0279 \times 0.137) = 3.4\%$ per hour for Fine-II. These correspond to lifetimes of ~9 h for Fine-I, and about 29 h for Fine-II. Based on the observed ratios of SO_4^{2-} to V and to SO_2, Barrie et al. (1989) estimated the average oxidation rate of 0.25 to 0.4% per hour at Alert, Canada. Using similar methodology, they gave a slower oxidation rate of 0.07% per hour in Barrow, Alaska, even though the air contained extremely high concentrations of anthropogenic pollutants. Results from this study may have large uncertainties due to several simple assumptions. However, calculations by Herbert et al. (1989) indicated that such rapid oxidation rates are possible. Besides, those values agree well with oxidation rates, 1.2–13% per hour, obtained in relatively polluted area (Roberts and Friedlander, 1975; Alkezweeny and Powell, 1977; and Chang, 1979). Contributions of iron catalytic reaction to the overall oxidation rate are less than 2% for Fine-I, and about 11% for Fine-II. This is in good agreement with earlier discussion that particulates received in the 1st period contain relatively fresher pollutants. pH values of fresher particulates are expected to be higher than those of aged ones. With less Fe(III) dissolved, the catalytic effects are smaller in particulates received in the earlier period.

It is also very interesting to closely examine the decomposed variance in fine aerosols. For Fine-I, the influence of Fe on sulfate increases with increasing time steps, while the influence of sulfate

Table 4. *Results from the variance decomposition for (a) S, (b) Cl, and (c) Fe in Fine-I.*

	Step	Std. error	S	Cl	Fe	K	Zn
(a)	1	0.099	68.5	0.643	15.9	3.86	11.0
	2	0.141	49.4	2.23	38.7	2.75	6.84
	3	0.166	39.9	2.04	50.2	2.22	5.48
	4	0.184	34.8	1.69	57.0	1.93	4.52
	5	0.196	31.4	1.75	60.9	1.74	4.05
	7	0.205	28.7	2.61	63.2	1.59	3.77
	10	0.211	27.6	3.03	64.0	1.53	3.65
	15	0.215	27.0	3.77	64.0	1.50	3.58
	20	0.215	27.0	3.88	63.9	1.50	3.58
(b)	1	0.0133	0.00	100.0	0.00	0.00	0.00
	2	0.0162	0.022	99.7	0.243	0.001	0.003
	3	0.0178	2.48	96.7	0.210	0.140	0.411
	4	0.0189	4.55	93.3	1.20	0.253	0.624
	5	0.0199	9.99	86.5	1.25	0.564	1.61
	7	0.0204	9.98	83.2	4.63	0.561	1.56
	10	0.0209	11.0	81.3	5.18	0.621	1.82
	15	0.0213	11.6	78.7	7.14	0.653	1.85
	20	0.0215	11.7	77.6	8.04	0.659	1.87
(c)	1	0.00549	0.00	3.26	96.7	0.00	0.00
	2	0.00697	0.047	3.25	96.6	0.002	0.007
	3	0.00784	0.249	3.23	96.4	0.014	0.045
	4	0.00834	0.342	3.28	96.2	0.019	0.070
	5	0.00857	0.487	3.25	96.1	0.027	0.080
	7	0.00880	0.468	3.34	96.0	0.026	0.076
	10	0.00891	0.472	3.39	96.0	0.026	0.078
	15	0.00893	0.530	3.38	95.9	0.029	0.088
	20	0.00893	0.539	3.40	95.9	0.030	0.090

Note: same representations used as those in Table 3.

on itself decreases. Such relationships in Fine-II are the opposite: the influence of Fe decreases as that of sulfate increases slightly. According to Hoffmann and Calvert (1985), catalytic oxidation of S(IV) in aqueous solution depends on $[Fe(III)_{(aq)}]$ and $[HSO_{3(aq)}^{-}]$ at pH $\leqslant 4$. At higher pH, catalytic oxidation is 1st-order in $[Fe(III)_{(aq)}]$ and $[S(IV)_{(aq)}]$ (Martin, 1984). Most of the time, pH values in fresh pollutants were relatively high. There is much total dissolved S(IV) to be oxidized and only a small amount of dissolved Fe(III). The quantity of the latter becomes rate determining. As the oxidation continues, more sulfate is formed, and pH values decrease. More Fe(III) is dissolved and its importance increases. As a consequence, the total dissolved S(IV) is reduced, and so is its influence. As pH decreases, more and more Fe(III) is in solution, while [S(IV)] and $[HSO_3^-]$ decrease. The oxidation rate depends more and more on the availability of HSO_3^-. As indicated in Table 5 for Fine-II, influence of Fe on S decreases with time, while S influence on itself is increasing.

From the above analyses, coarse and fine particulates show distinctively different characteristics. For coarse particulates, close correlations between *S* and *Cl* at zero lag suggest the importance of marine sources. Chemical interactions in either Coarse-I or Coarse-II are of little importance. It is the mass transfer across the gas-liquid interface that controls the oxidation processes. For both Fine-I and Fine-II, strong correlations between Fe and S were derived. The response time of S in Fine-I is about 3 times faster than that in Fine-II. The time-dependent variance decomposition in Fe and S for both Fine-I and Fine-II also indicates that the former type is fresher than the latter type.

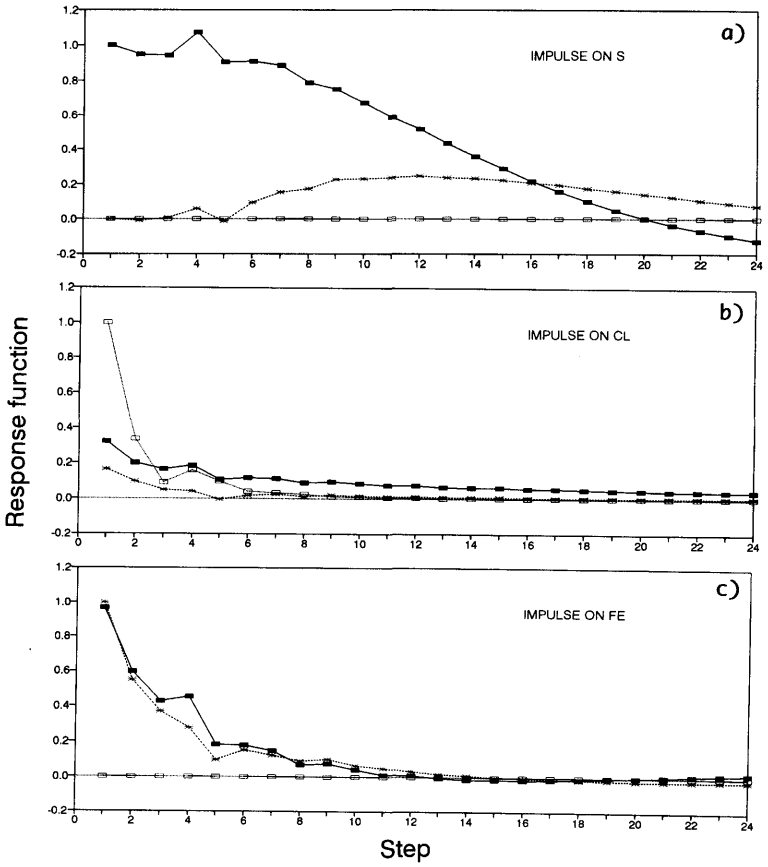

Fig. 5. The 3-days response functions of S, Cl, and Fe to impulses of (a) S, (b) Cl, and (c) Fe in Fine-II.

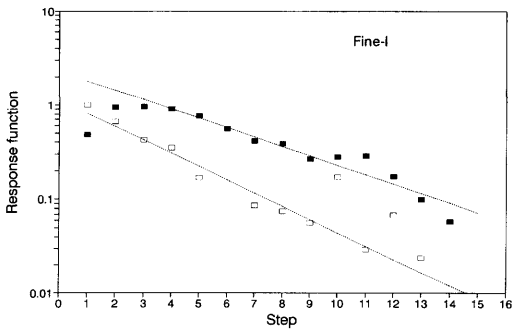

Fig. 6. Logarithmic plot of the S response functions to impulses of S in particulates received in Fine-I.

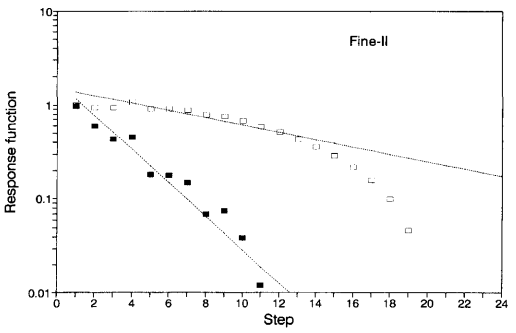

Fig. 7. Logarithmic plot of the S response functions to impulses of S and Fe in particulates received in Fine-II.

4. Conclusions

Interpretation of aerosol processes, such as those related to acid deposition, based on linking laboratory experimental results with atmospheric observations can be difficult, often involving complicated models. This study applied multivariate time series analyses to study relationships among

Table 5. *Results from the variance decomposition for (a) S, (b) Cl, and (c) Fe in Fine-II.*

	Step	Std. error	S	Cl	Fe	Zn	Si
(a)	1	0.101	48.5	5.00	45.4	0.213	0.775
	2	0.134	52.2	3.94	35.4	7.94	0.475
	3	0.159	54.7	3.35	28.9	12.5	0.387
	4	0.185	56.8	2.96	24.2	15.5	0.391
	5	0.204	56.5	2.58	20.3	19.8	0.636
	7	0.236	56.6	2.16	15.7	24.2	1.25
	10	0.268	55.1	1.84	12.2	28.3	2.44
	15	0.291	52.6	1.69	10.4	30.6	4.59
	20	0.296	51.3	1.71	10.0	30.6	6.24
(b)	1	0.130	0.00	100.0	0.00	0.00	0.00
	2	0.138	0.00	100.0	0.00	0.00	0.00
	3	0.138	0.00	100.0	0.00	0.00	0.00
	4	0.140	0.00	100.0	0.00	0.00	0.00
	5	0.140	0.00	100.0	0.00	0.00	0.00
	7	0.140	0.00	100.0	0.00	0.00	0.00
	10	0.140	0.00	100.0	0.00	0.00	0.00
	15	0.140	0.00	100.0	0.00	0.00	0.00
	20	0.140	0.00	100.0	0.00	0.00	0.00
(c)							
	1	0.00415	0.000	2.32	87.9	1.44	8.31
	2	0.00483	0.008	2.32	84.5	1.52	11.6
	3	0.00511	0.009	2.21	83.4	1.56	12.7
	4	0.00528	0.192	2.16	82.4	1.52	13.6
	5	0.00532	0.202	2.12	81.7	1.50	14.4
	7	0.00546	1.87	2.06	79.5	1.54	14.9
	10	0.00575	7.85	1.90	72.7	3.31	14.1
	15	0.00631	17.0	1.59	60.5	8.97	11.8
	20	0.00666	20.7	1.43	54.3	12.6	10.7

Note: same representations used as those in Table 3.

chemical species in particulates based on available observations. Results from these statistical analyses can be directly compared with the laboratory results, and statistical studies can lead to hypotheses for further laboratory study.

Generally, chemical relationships are different in different types of particles. Chemical behaviors were similar for the same type of particulates even when collected under different meterological conditions. The major species influencing S in coarse particulates are either Cl or K. In fine aerosols, Fe is the dominant chemical element influencing sulfate content, more than 40% in both cases. It was estimated that mass transfer is the rate-controlling process of sulfur oxidation in coarse particulates. Chemical relationships derived for fine aerosols indicate that particulates received in the earlier period contain fresher pollutants. Over 70% of the total variance of sulfate in fine aerosols was explained by chemical relationships using the available data. Lifetimes derived for sulfur oxidation in fine particulates are about 9 h during the haze period and about 29 h in normal Arctic atmosphere. Variables not monitored, such as H_2O_2 mixing ratio and $[Mn(II)_{(aq)}]$, may also be important. Their contributions could be tested if observations of these variables were available.

In an earlier study (Hsu, 1992), similar techniques were applied to O_3, NO, NO_2 data collected at 2 locations in Taipei, Taiwan. Comparison of derived information indicates that pollutant formation in one location is more chemically dominated than that in the other location. Therefore, meteorological parameters may be more important in the latter location. In these analyses, vector autoregressive approaches have provided results that are usually only obtained from more complex geophysical models. These

analyses cannot replace these complex models, but are useful in their own right (in addition to geophysical models) due to the relative simplicity of the statistical models. Not all variables, such as temperature, wind speed, wind directions, detailed chemical inventories, etc., are necessary for such a statistical model. The time scale of these pollutants may vary from hours to weeks; to study their interactions needs data sampled at higher frequency. Observations on photochemical pollutants often meet such requirements. In many aerosol studies, samples have only been collected once every 1 or 2 weeks. This does not allow information on shorter time scales to be retrieved. If more suitable observations become available, future studies can cover topics such as spatial correlations, influences of atmospheric variables, and the responses to control measures.

Multivariate time-series modelling provides a means to investigate relationships among observed variables, and somtimes predict their changes in response to changes in other variables. Direct comparisons between this technique and the complicated models would be very interesting. Finally, it should be emphasized that results derived in this study are based only on the variables for which data were collected. Interactions with, and responses to, other variables cannot be estimated. As Lütkepohl (1991, p.55) discusses, if important variables were indeed missing, conclusions may change with their inclusion.

5. Acknowledgements

The author would like to thank Professor John W. Winchester for providing the data set and many thorough comments on this manuscript. The authors wish to acknowledge Professor Kenneth S. Lin for his suggestions and technical support in time series analysis. Thanks are also due to Drs. Xufeng Niu, Shaw C. Liu, William B. DeMore, and C. P. Chen for their valuable comments. Suggestions from referees improved this manuscript extensively both in its readability and scientific content.

REFERENCES

Alkezweeny, A. J. and Powel, D. C. 1977. Estimation of transformation rate of SO_2 to SO_4 from atmospheric concentration data. *Atmos. Environ.* **11**, 179–182.

Barrie, L. A. 1986. Arctic air pollution: An overview of current knowledge. *Atmos. Environ.* **20**, 643–663.

Barrie, L. A., den Harlog, G., and Bottenheim, J. W. 1989. Anthropogenic aerosols and gases in the lower troposphere at Alert, Canada in April 1986 *J. Atmos. Chem.* **9**, 101–127.

Bojkov, R., Bishop, L., Hill, W. J., Reinsel, G. C., and Tiao, G. C. 1990. A statistical trend analysis of revised Dobson total ozone data over Northern Hemisphere. *J. Geophys. Res.* **95**, 9785–9807.

Box, G. E. P. and Jenkins, G. M. 1976. *Time series analysis forecasting and control*, 2nd edition. Holden-Day, San Francisco.

Brandt, C. and R. van Eldik, 1995. Transition metal-catalyzed oxidation of sulfur (IV) oxides. Atmospheric relevance and mechanisms. *Chem. Rev.* **95**, 119–190.

Bridgman, H. A., Schnell, R. C., Herbert, G. A., Bodhaine, B. A. and Oltmans, S. J. 1989. Meteorology and haze structure during AGASP-II, part 2: Canadian Arctic flights, 13–16 April 1986. *J. Atmos. Chem.* **9** 49–70.

Chang, T. Y. 1979. Estimate of the conversion rate of SO_2 to SO_4 from the DaVinci Flight Data. *Atmos. Environ.* **13**, 1663–1664.

Finlayson-Pitts, B. J. and Pitts, Jr., J. N. 1986. *Atmospheric chemistry: fundamentals and experimental techniques.* John Wiley & Sons, Inc. New York, p. 393.

Herbert, G. A., Schnell, R. C., Bridgman, H. A., Bodhaine, B. A., Oltmans, S. J. and Shaw, G. E. 1989. Meteorology and haze structure during AGASP-II, Part 1: Alaskan Arctic flights, 2–10 April, 1986. *J. Atmospheric Chemistry* **9**, 17–48.

Hoffmann, M. R. and Calvert, J. G. 1985. *Chemical transformation modules for Eulerian acid deposition models*, volume II. *The aqueous-phase chemistry.* National Center for Atmospheric Research, Boulder, Colorado.

Hsu, K. J. 1992. Time series analysis of the interdependence among air pollutants. *Atmos. Environ.* **26B**, 491–503.

Johansson, S. A. E. and Campbell, J. L., 1988. *PIXE: A novel technique for elemental analysis.* Wiley, Chichester, 1988.

Li, S. M. and Winchester, J. W. 1989. Resolution of ionic components of late winter Arctic aerosols. *Atmos. Environ.* **23**, 2387–2399.

Li, S. M. and Winchester, J. W. 1990. Haze and other aerosol components in late winter Arctic Alaska, 1986. *J. Geophys. Res.* **95**, 1797–1810.

Lütkepohl, H. 1991. *Introduction to multiple time series analysis.* Springer-Verlag, New York.

Martin, L. R. 1984. Kinetic studies of sulfite oxidation in aqueous solution. *SO_2, NO, NO_2 oxidation mechanisms: atmospheric considerations*, J. G. Calvert (ed). Butterworth, Boston, pp. 63–100.

Mason, B. 1966. *Principles of geochemistry*, 3rd edition. John Wiley, New York.

Merz, P. H., Painter, L. J. and Ryason, P. R. 1972. Aerometric data analysis — Time series analysis and forecast and an atmospheric smog diagram. *Atmos. Environ.* **6**, 319–342.

Pandis, S. N. and Seinfeld, J. H. 1989. Sensitivity analysis of a chemical mechanism for aqueous-phase atmospheric chemistry. *J. Geophys. Res.* **94**, 1105–1126.

Parungo, F. P., Nagamoto, C. T., Sheridan, P. S. and Schnell, R. C. 1990. Aerosol characteristics of Arctic haze sampled during AGASP-II. *Atmos. Environ.* **24A**, 937–949.

Priestley, M. B. 1981. *Spectral analysis and time series.* Academic Press, London.

Roberts, P. T. and Friedlander, S. K. 1975. Conversion of SO_2 to sulfur particulate in the Los Angeles atmosphere. *Environ. Health Persp.* **10**, 103–108.

Seinfeld, J. H. 1986. *Atmospheric chemistry and physics of air pollution.* Wiley Interscience, New York.

Seigneur, C. and Saxena, P. 1984. A study of atmospheric acid formation in different environments. *Atmos. Environ.* **18**, 2109–2124.

Tiao, G. C., Box, G. E. P. and Hamming, W. J. 1975. Analysis of Los Angeles photochemical smog data: A statistical overview. *J. Air Pollution Control Association* **25**, 260–268.

Tiao, G. C. and Box, G. E. P. 1981. Modeling multiple time series with applications. *J. American Statistical Association* **76**, 802–816.

Zinsmeister, A. R. and Redman, T. C. 1980. A time series analysis of aerosol composition measurements. *Atmos. Environ.* **14**, 201–215.