Uncertainty and Sensitivity Analyses of OH-Initiated Dimethyl Sulphide (DMS) Oxidation Kinetics

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Abstract. A numerical experiment has been conducted on the OH-initiated tropospheric oxidation of DMS. This involved the selection of a set of reactions describing the OH-initiated oxidation kinetics and the conversion of the present level of uncertainty of the system into uncertainty ranges and distributions for the relevant system parameters (kinetic constants and initial concentrations). Uncertainties have been propagated through the model onto the output variables of interest. This has allowed (a) the uncertainty in model prediction to be quantified and compared with observations (uncertainty analysis) and (b) the relative importance of each input parameter in determining the output uncertainty to be quantified (sensitivity analysis). Output considered were the ratio of $MSA/(SO_2 + H_2SO_4)$ concentration at a given time, the ratio SO_2/H_2SO_4, the total peroxynitrate species concentrations and the relative fraction of SO_2 and H_2SO_4 formed through the various pathways. Conditional upon the model and data assumptions underlying the experiment, the following main conclusions were drawn:

(1) The possibility of direct formation of SO_3 without SO_2 as intermediate as suggested by Bandy *et al.* (1992) and Yin *et al.* (1990), involving direct thermal decomposition of $CH_3SO_3 \cdot$ does not seem to play a major role in the overall generation of sulphate. This is relevant to the issue of gas to particle conversion over remote areas.
(2) Reaction of $CH_3SOO \cdot$ intermediate may be the most important pathway to the formation of SO_2.
(3) The dominating peroxynitrate is $CH_3S(O)_2O_2NO_2$.

Through sensitivity analysis the kinetic constants have been identified which – because of their uncertainty and of their impact on the output – mostly contribute to the output uncertainty.

Key words: Dimethyl sulphide, sulphur dioxide, methane sulphonic acid, non sea-salt sulphate, air, chemical kinetics, uncertainty analysis, sensitivity analysis.

1. Introduction

In recent years a copious literature has addressed aspects of the sulphur cycle because of its hypothesised climatic role. Biogenic plus anthropogenic sulphur components of this cycle could in fact counteract the anthropogenic forcing due to the greenhouse gases (Shaw, 1983; Charlson *et al.*, 1987; Bates *et al.*, 1987; Schwartz, 1988; Wigley, 1989). Recent assessment of the strength of the effect can be found in Foley *et al.* (1991), Charlson *et al.* (1991, 1992), Kiehl and Briegleb (1993), Langner *et al.* (1992), Lelieveld and Heintzenberg (1992).

Dimethyl sulphide (DMS; CH_3SCH_3) plays a crucial role in the formation of climatically active aerosols. DMS originates from the ocean biota, and is oxidized by reactions with OH and NO_3 radicals to form a number of sulphur-containing molecules, sulphur dioxide, sulphuric acid and methane sulphonic acid (MSA; CH_3SO_3H; Hatakeyama et al., 1985; Yin et al., 1990; Jensen et al., 1992). The strength of the biogenic sulphur gas flux (ocean plus land) could be comparable in magnitude to the total anthropogenic flux of SO_2 (Andreae, 1983; Spiro et al., 1992). The strong hemispheric asymmetry of the anthropogenic sulphur, makes the biogenic sulphur flux to equate the anthropogenic one in the southern hemisphere. Most of the sulphur dioxide is believed to be oxidized in the aqueous phase, with only a minor fraction of the sulphuric acid being formed through gas-phase oxidation (Lelieveld and Hentzenberg, 1992). Sulphuric acid and – to a lesser extent – MSA are known to be efficient in forming new aerosol particles, which in turn can act as Cloud Condensation Nuclei (CCN). The postulated feed-back mechanism between DMS and climate involves a positive influence of insolation on the DMS production (Foley et al., 1991), and a negative forcing of sulphur on the amount of solar radiation reaching earth due to light scattering by aerosol (direct effect) and by increased cloud-scattering efficiency due to the larger CCN populations (indirect effect). The strength of this negative forcing is presently debated, with recent assessments (Kiehl et al., 1993; Langner et al., 1992; Lelieveld et al., 1992) tending to lower initial estimates by Charlson (1991, 1992). A number of relevant papers can also be found in the proceedings of a workshop on 'DMS: oceans, atmosphere and climate', held in 1993 in Belgirate (I), (Restelli and Angeletti, 1993).

DMS chemistry is an important part of the picture, which is covered by an abundant literature (see reviews by Yin et al., 1990b; Tyndall and Ravishankara, 1991; Turnipseed and Ravishankara, 1993). The present article concentrates on gas-phase DMS kinetics, and investigates the OH-initiated tropospheric oxidation of DMS in the gas phase. Alternative pathways for DMS oxidation such as reactions with NO_3, are not addressed here. Also neglected is the heterogeneous (aqueous phase) SO_2 oxidation kinetics. Special attention is devoted to the possibility of direct formation of SO_3 without SO_2 as intermediate (Yin et al., 1990), an aspect of considerable importance especially after the speculations of Lin and Chameides, (1993) and the field measurements of Bandy et al. (1992). This would involve thermal decomposition of $CH_3SO_3 \bullet$ and has been hypothesised as a possible explanation of the discrepancy between non-sea-salt (nss) sulphate concentrations over remote areas and that computed based on DMS oxidation kinetics involving SO_2 as intermediate.

A kinetic model of the tropospheric oxidation of DMS comprehending 354 reactions was developed and evaluated by Yin et al. (1990), where the values of most rate constants of reactions involving sulphur-species were estimated but not based on direct experimental measurements.

A more recent numerical model study of the oxidation of DMS in the marine troposphere was performed by Koga and Tanaka (1993) where the treatment of the sulphur chemistry is that of Lin *et al.*, apart from the assumed pathways to formation of MSA.

We feel that the studies performed in the latest years in the laboratory as well as in the field have provided so much new information and new focus on certain aspects of DMS chemistry that another modelling exercise should be made. We have chosen a somewhat more simplifying approach to the development of the reaction scheme, including only the reactions that, according to our present knowledge, may be of significant importance and representing only the sulphur chemistry explicitly in the model.

Given the large uncertainties in the parameters governing DMS oxidation kinetics, an uncertainty propagation analysis is performed to investigate the different oxidation pathways. The imprecise knowledge of the various reactions and of their relative weights is reduced to uncertainty ranges for the relevant model input parameters. Finally the model, encoded in a computer programme, is run in a Monte Carlo fashion propagating the uncertainty in the input parameters onto the output variables. This allows:

(1) The uncertainty in model prediction (e.g. ratio of $MSA/(SO_2 + H_2SO_4)$ concentration at a given time) to be quantified and

(2) The relative importance of each input parameter in determining (1) above to be quantified.

In the literature this type of investigtions are described as uncertainty analysis and sensitivity analysis (UA, SA). For a review of current methods and practices in UA/SA see Helton (1993). As far as sensitivity analysis is concerned the techniques available in the literature can be divided into two broad classes: the local sensitivity methods and the global sensitivity ones. For reasons discussed in Section 3 only global sensitivity techniques are used here.

The present study can be seen as a numerical experiment meant to identify crucial areas in the input parameters' space; this could help in focusing experimental research on those reactions pointed out as main contributors to the total uncertainty.

The limitations of the present work are mainly related to the fact that certain mechanistic aspects of the chemistry of DMS are so poorly understood that the error bars associated with the rate constants involved are almost arbitrary. Furthermore the results are conditional on the reaction scheme assumed and on the uncertainty ranges assigned. On the other hand this approach allows the experimental knowledge to be compared with weighted averages of the output quantities, which facilitates the highlighting of possible model and data inadequacies. Finally the model used here considers only part of the complex picture of the DMS oxidation. E.g. the potentially relevant reactions of intermediates with HO_2 or RO_2 radicals have not been addressed because of the complexity and the substantial

lack of knowledge of such reactions, involving sulphur species. The non-inclusion of the heterogeneous chemistry and dry deposition, by far the largest sinks for SO_2 molecules, will also be kept in mind in the discussion of the results.

It may give some confidence in the validity of the model that the calculated ratio between MSA and $SO_2 + H_2SO_4$ (between 5 and 9%) is in reasonable agreement with field observations of MSA to non-sea-salt-sulphate ratios. The analysis gives some hints to which kinetic parameters it would be most relevant to determine more accurately in order to understand the pathways leading to formation of SO_2, H_2SO_4 and MSA under ambient conditions. In the case of SO_2 it is found that the reactions of the $CH_3SOO \bullet$ radical may be the most important source. In the case of the ratio MSA to $SO_2 + H_2SO_4$ and the ratio between the indirect (i.e. via SO_2) and the direct pathway to formation of H_2SO_4, the key uncertainties are found to be on the rate constant of a reaction leading to the $CH_3SO_3 \bullet$ radical and the reactions of this radical to form either SO_3 or MSA. The notion of dissociation of $CH_3SO_3 \bullet$ being a major source of H_2SO_4 in the marine troposphere (Bandy *et al.*, 1992) is not realistic according to the present analysis which predicts a yield of SO_3 of less than 2% of that of SO_2, thus contributing only marginally to the overall formation of sulphate.

2. Reaction Mechanism

2.1. REACTIONS OF CH_3SCH_3 (DMS) AND $CH_3S \bullet (OH)CH_3$

Although the main sulphur containing products of the oxidation of DMS have been identified in laboratory chamber experiments as SO_2 and H_2SO_4 with CH_3SO_3H and apparently also $CH_3S(O)CH_3$ and $CH_3S(O)_2CH_3$ (Barnes *et al.*, 1988) as minor products, there are still very serious gaps in our understanding of the pathways leading to the formation of these products. Thus it is not well understood exactly how MSA is formed and how the yield is influenced by physical and chemical environmental parameters.

A maybe even more important uncertainty regards how much H_2SO_4 is formed via the oxidation of SO_2 and how much may be formed directly from DMS without SO_2 as an intermediate (Bandy *et al.*, 1992).

The reactions that have been included in the present kinetic model simulating the oxidation of DMS initiated by OH radicals in ambient air are given in Figure 1. Table I indicates the selected ranges for the model parameters. In the following the reactions shall be referred to by the subscript number of the kinetic constant involved, i.e. Reaction (23) is (Figure 1)

$$CH_3SO \bullet \xrightarrow{k_{23}} CH_3SO_3H \qquad\qquad (2.1)$$
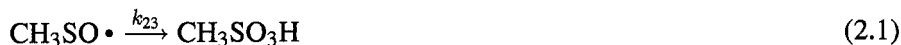
Far from all elementary reactions have been included in this scheme; when possible, reactions involving several steps have been condensed into one equation. As this

(MSA) CH_3SO_3H $CH_3SO_3\bullet$ $+ H_2O, fast$ SO_3 k_{22} H_2SO_4 k_{23}

$CH_3S(O)_2O_2NO_2$ k_{20}, k_{-20} $+ NO_2$ $+NO, k_{26}$ $+NO_2, k_{17}$ $+O_3, k_{18}$

$CH_3S(O)_2O_2\bullet$ k_{19}, k_{-19} $+ O_2$ $CH_3SO_2\bullet$ SO_2 k_{21} $+ OH, k_{25}$

$+NO_2, k_{12}$ $+O_3, k_{10}$ $+NO, k_{16}$

SO_2 k_8 $+NO_2, k_{13}$ $+O_3, k_{11}$ $CH_3SO\bullet$ k_{14}, k_{-14} $+ O_2$ $CH_3S(O)O_2\bullet$ k_{15}, k_{-15} $+ NO_2$ $CH_3S(O)_2O_2NO_2$

$+NO, k_9$ $+O_3, k_{29}$ $+NO_2, k_5$ $+O_3, k_6$ k_3

CH_3SOONO_2 k_{28}, k_{-28} $+ NO_2$ $CH_3SOO\bullet$ $+ O_2, k_{31}$ k_7, k_{-7} $+ O_2$ $CH_3S\bullet$ $CH_3S\bullet(OH)CH_3$ k_4 $CH_3SO_2CH_3$

SO_2 $+ O_2, k_{30}$ CH_3SCH_3 $+ OH, k_1$ $+ OH, k_2$ (DMS)

Reaction scheme and sensitivity analysis. Reactions which contribute most to the output uncertainty are highlighted. Three output are considered:
$MSA/(SO_2 + H_2SO_4)$
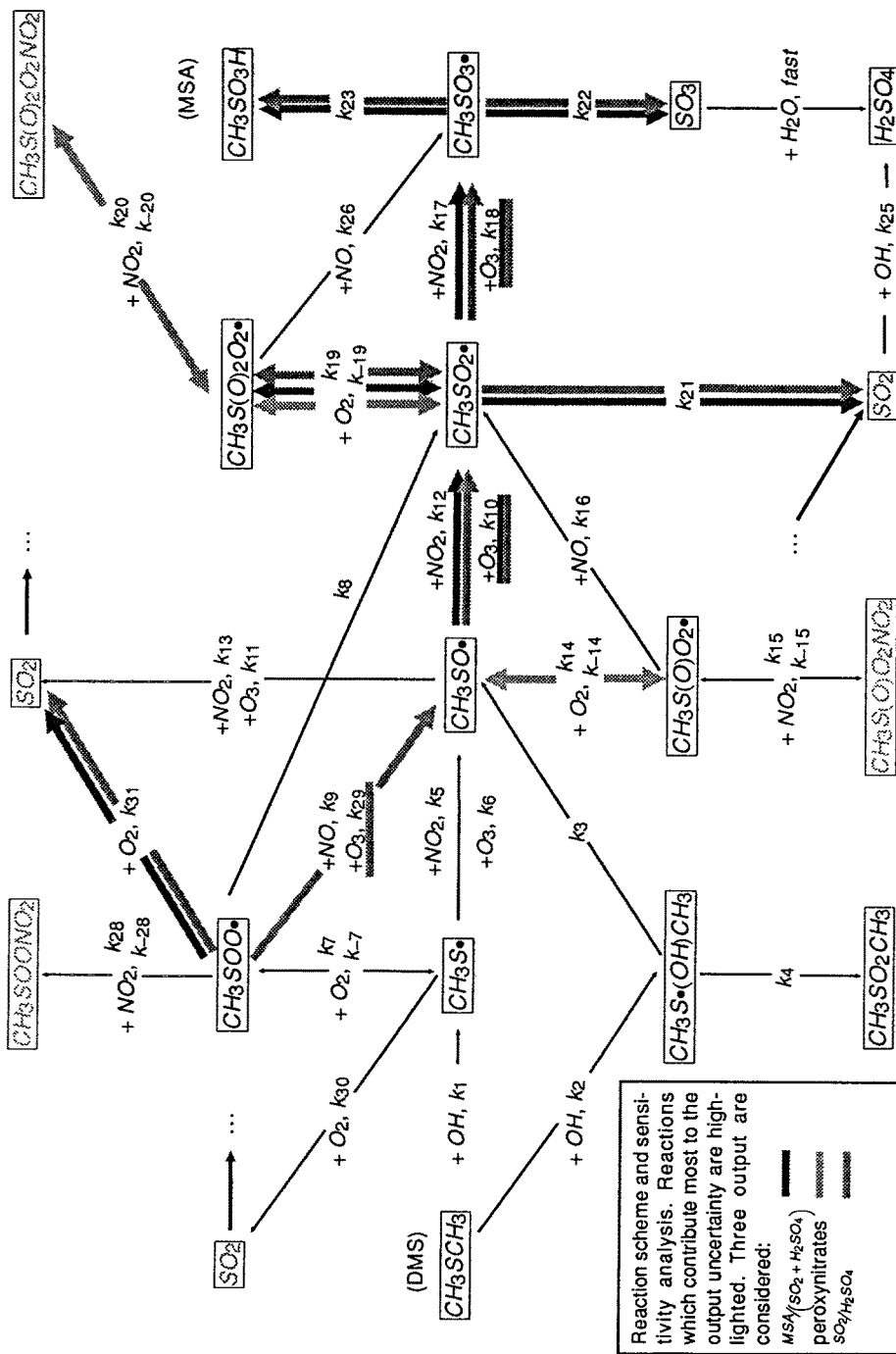peroxynitrates
SO_2/H_2SO_4

Fig. 1.

exercise is focused on the sulphur-containing reaction products, other products are not considered.

While the rate constant of the direct abstraction pathway (1) is well-established, the importance of the addition pathway is more uncertain; the value of k_2 used in this study is based on the work of Hynes *et al.* (1986). We find that the radical formed by the initial H-abstraction ($CH_3SCH_2 \cdot$) is most likely to react further to form $CH_3S \cdot$, e.g. by elimination of CH_2O from $CH_3SCH_2O \cdot$ as suggested by Turnipseed and Ravishankara (1993).

The fate of the DMS-OH adduct is more uncertain. It is believed (Turnipseed and Ravishankara, 1993) to react with O_2 to form products which can be $CH_3S(O)_2CH_3$ (as observed by Barnes *et al.*, 1988), most probably formed by oxidation of initially formed dimethyl sulphoxide:

$$CH_3S \cdot (OH)CH_3 + O_2 \rightarrow CH_3S(O)CH_3, \tag{2.2}$$

or, alternatively, go through cleavage of the C–S-bond, e.g. to form $CH_3SO \cdot$ as assumed here. Dimethyl sulphoxide has in fact been observed at ppt levels in marine atmosphere conditions (Berresheim *et al.*, 1993).

Some pathways, included in the reaction scheme proposed by Koga and Tanaka (1993), which lead from the DMS–OH adduct to MSA through other intermediates than those discussed here, have not been included in the present model because of lack of experimental evidence for their existence.

2.2. REACTIONS OF CH3S •, CH3SOO •, CH3SO • AND CH3SO2 •

The $CH_3S \cdot$ radical is clearly a key intermedite in the oxidation of DMS. Its reaction with O_2 was found to be slow (Tyndall and Ravishankara, 1989), but a more recent study (Turnipseed *et al.*, 1992) has demonstrated that there is a rapid equilibrium between $CH_3S \cdot$ and $CH_3SOO \cdot$ (Reaction (7), (–7)).

At typical atmospheric conditions the concentrations of $CH_3S \cdot$ and $CH_3SOO \cdot$ should be approximately equal (Turnipseed *et al.*, 1993), so reactions of $CH_3SOO \cdot$ are potentially important steps in the oxidation of DMS. In the reaction scheme we have included the reaction with NO (Reaction 9), NO_2 (Reaction 28) and O_3 (Reaction 29). The rate constants found at low temperatures by Turnipseed *et al.* (1993) have been applied. In the case of Reaction (9) and Reaction (28) the temperature dependence was found to be weak so that the use of a value determined at low-temperature can be justified; in the case of the reaction with O_3 there is no indication of the temperature-dependence and the value of k_{29} at 227 K has been selected because no better approximation to the true value at 298 K is available; we have applied the upper limit determined at 227 K assuming that the rate constant is independent of temperature. The products of these reactions in the reaction scheme in the model have not been identified by direct measurements but are those expected by analogies to similar reactions.

TABLE I. Input data for the 'Polluted' environment test case

Symbol	Source:	Units	Distribution	Value 1	Value 2
k_1	De More et al., 1992	cm³/mol/s	NORMAL	9.800E–13	4.900E–12
k_2	Hynes et al., 1986	cm³/mol/s	UNIFORM	6.000E–13	1.800E–12
k_3	Barnes et al., 1988, Hynes et al., 1992 quoted after Turnipseed and Ravishankara, 1993)	1/s	UNIFORM	2.500E–01	7.500E–01
k_5	De More et al., 1992	cm³/mol/s	NORMAL	1.680E–11	5.600E–11
k_6	De More et al., 1992	cm³/mol/s	NORMAL	1.620E–12	5.400E–12
k_7/k_{-7}	Turnipseed et al., 1992	cm³/mol	UNIFORM	2.500E–19	9.700E–19
k_8	Turnipseed and Ravishankara, 1993	1/s	UNIFORM	0.000E+00	1.000E+01
k_9	Turnipseed et al., 1993	cm³/mol/s	NORMAL	4.400E–12	1.110E–11
k_{10}	De More et al., 1992	cm³/mol/s	UNIFORM	0.000E+00	6.000E–13
k_{12}	De More et al., 1992	cm³/mol/s	NORMAL	3.600E–12	1.200E–11
k_{13}	see Chapter 2	cm³/mol/s	UNIFORM	0.000E+00	1.700E–11
k_{14}	Yin et al., 1990b	cm³/mol/s	LOGUNIFORM	7.700E–19	7.700E–17
k_{-14}	Yin et al., 1990b	1/s	LOGUNIFORM	1.700E+01	1.700E+03
k_{15}	De More et al., 1992 (by analogy to PAN)	cm³/mol/s	LOGNORMAL	5.000E–01	–1.123E+01
k_{-15}	Jensen and Hjorth, 1994	1/s	LOGNORMAL	5.000E–01	–1.951E+00
k_{16}	De More et al., 1992 (by analogy to PAN)	cm³/mol/s	LOGNORMAL	5.000E–01	–1.062E+01
k_{17}	De More et al., 1992 (by analogy to k_{12})	cm³/mol/s	LOGNORMAL	5.000E–01	–1.092E+01
k_{18}	(by analogy to k_{10})	cm³/mol/s	LOGNORMAL	5.000E–01	–1.222E+01
k_{19}	Yin et al., 1990b	cm³/mol/s	LOGUNIFORM	2.600E–20	2.600E–16
k_{-19}	Yin et al., 1990b	1/s	LOGUNIFORM	3.300E–02	3.300E+02
k_{20}	De More et al., 1992 (by analogy to PAN)	cm³/mol/s	LOGNORMAL	5.000E–01	–1.123E+01
k_{-20}	Jensen and Hjorth, 1994	1/s	LOGNORMAL	5.000E–01	–1.951E+00
k_{21}	Good and Thynne, 1967 and Mellouki et al., 1988	1/s	UNIFORM	2.700E–03	1.000E+01
k_{22}	(by analogy to k_{21})	1/s	UNIFORM	2.700E–03	1.000E+01
k_{23}	see Chapter 2	1/s	UNIFORM	1.000E–02	1.000E+01
k_{25}	De More et al., 1992	cm³/mol/s	CONSTANT	1.000E–12	
k_{26}	De More et al., 1992 (by analogy to PAN)	cm³/mol/s	LOGNORMAL	5.000E–01	–1.062E+01
k_{28}	De More et al., 1992 (by analogy to PAN)	cm³/mol/s	LOGNORMAL	5.000E–01	–1.130E+01

TABLE I. *(Continued)*

Symbol	Source:	Units	Distribution	Value 1	Value 2
k_{-28}	Jensen and Hjorth, 1994	1/s	LOGNORMAL	5.000E–01	2.553E–01
k_{29}	Turnipseed *et al.*, 1993	cm^3/mol/s	LOGNORMAL	1.000E+00	–1.21E+01
k_{30}	Turnipseed *et al.*, 1993	cm^3/mol/s	UNIFORM	0.000E+00	6.000E–18
k_{31}	Turnipseed *et al.*, 1993	cm^3/mol/s	UNIFORM	0.000E+00	6.000E–18
$[DMS]_0$		mol/cm^3	CONSTANT	2.6E+09	
$[OH]_0$		mol/cm^3	UNIFORM	0.000E+00	4.000E+06
$[NO_2]_0$		mol/cm^3	LOGUNIFORM	2.460E+08	2.460E+11
$[O_3]_0$		mol/cm^3	UNIFORM	2.460E+11	2.460E+12
$[O_2]_0$		mol/cm^3	CONSTANT	5.2E+18	
$[NO]_0$		mol/cm^3	LOGUNIFORM	5.000E+07	5.000E+10
$[H_2O]_0$		mol/cm^3	CONSTANT	2.5E+17	
$[SO_2]_0$		mol/cm^3	CONSTANT	0.0	
k_4	see k_3	1/s	RELATION	$1 \cdot -k_3$	
k_{11}	see Chapter 2	cm^3/mol/s	RELATION	$6.0E-13-k_{10}$	
$[NO_2]_0, [NO]_0$		[0]	CORRELATION	0.8	

This table has been generated from PREP input and retains some characteristics of the input specification syntax.

Distributions. A variable with distribution UNIFORM varies uniformly between Value 1 and Value 2. A variable with distribution LOGUNIFORM varies log-uniformly between Value 1 and Value 2. A variable with distribution NORMAL is normally distributed with standard deviation Value 1 and mean Value 2. The base 10 logarithm of a variable with distribution LOGNORMAL is normally distributed with standard deviation Value 1 and mean Value 2.
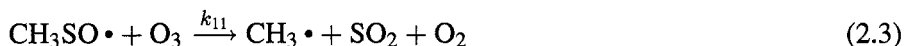
Relations and correlations. 'Relation' variables allow the generation of input variables which are function of other sampled variables, e.g. $k_4 = 1 - k_3$ (penultimate line in the table). 'Correlation' variables allow different input variables to be correlated. The 0.8 entry (last line of the table) means that we wish variables $[NO_2]_0$ and $[NO]_0$ to be correlated while preserving their marginal distributions. The input for the 'unpolluted' environment test case is identical apart for
(1) *Value 2* 100 times lower for both $[NO_2]_0$ and $[NO]_0$.
(2) *Value 2* reduced by one half for $[O_3]_0$.

The rate constants of the reactions of $CH_3S \bullet$ with NO_2 and with O_3 (Reactions 5 and 6) have been accurately determined and in the case of the reaction with NO_2 also the products seem to be well-established. In the case of the reaction with O_3 the products are much more uncertain (Turnipseed and Ravishankara, 1993); the most likely pathway appears to be formation of $CH_3SO \bullet$ (analogous to the reaction between HS and O_3). Dominé *et al.* (1992) found only a 15% yield of this product, but this could well be because of dissociation of excited state $CH_3SO \bullet$ in the low-pressure system, considering the strongly exothermic reaction

($\Delta H = -61$ kcal/mole); no other proposed pathways of the reaction seem to be important (Turnipseed et al., 1993).

The CH$_3$SO • radical can be oxidized (Reactions 10 and 12) to form CH$_3$SO$_2$ • or it may react with O$_2$ to form a peroxyradical (Reaction 14)). Further, we have proposed the reactions

$$CH_3SO \bullet + O_3 \xrightarrow{k_{11}} CH_3 \bullet + SO_2 + O_2 \qquad (2.3)$$

$$CH_3SO \bullet + NO_2 \xrightarrow{k_{13}} CH_3 \bullet + SO_2 + NO \qquad (2.4)$$

where the CH$_3$SO$_2$ •, formed in an excited state, dissociates before it is collisionally deactivated. Some indirect evidence for such a reaction pathway has been reported by Jensen et al. (1992). The limits on k_{11} and k_{13} can only be rather arbitrarily set. A similar kind of pathway is conceivable also in the reactions of the CH$_3$S • radical with O$_3$ and NO$_2$. However, the reactions of O$_3$ and NO$_2$ with CH$_3$S • are less exothermic than those of CH$_3$SO •. ΔH's for Reactions (5) and (6) are −35 and −61 kcal/mole respectively while the values for Reactions (12) and (10) are −71 and −91 kcal/mole, respectively; for this reason the possibility of the dissociation of an excited CH$_3$SO • radical has not been considered in the model.

In the case of the reaction between CH$_3$SO • and O$_3$, the yield of SO$_2$ could be almost unity, as very little is known about the reaction products. The only reaction channel that to our knowledge has been quantitatively evaluated is the one leading to the regeneration of CH$_3$S •, accounting for 13 ± 6% of the total according to Dominé et al. (1992). Also an estimated 10% yield of CH$_2$SO was observed but it was questionable whether this was a primary product of the reaction. Both these reactions have been considered as negligible in the present study.

In the case of the reaction between CH$_3$SO • and NO$_2$ the yield of SO$_2$ could not be unity as the oxidation of DMS in the presence of high concentration levels of NO$_2$ gives relatively low yields of SO$_2$ (Yin et al., 1990b; Jensen et al., 1992). An upper limit of $0.3 \times k_{12}$ for k_{13} was then adopted, deduced from reported yields of SO$_2$ in laboratory experiments applying high levels of NO$_2$.

The rate of the thermal dissociation of CH$_3$SO$_2$ • (Reaction 21) is a key problem in understanding the oxidation mechanism for DMS in the troposphere as this represents the most straightforward pathway to the observed formation of SO$_2$. The data presented in literature show strong discrepancies; in an older study (Good and Thynne, 1967) it was found that k_{21} should be rather slow (2.7×10^{-3} s^{-1}) while a newer study (Mellouki et al., 1988) indicated a much higher value ($\approx 10^{-1}$ s^{-1}); both results were based on kinetic analysis of a complex chemical system. Very recent results obtained by Barnes et al. (1993) appear to demonstrate that Reaction (21) is of negligible importance compared to competing reactions taking place in the system. These last results do not necesarily exclude that Reaction (21) is as fast as the upper limit of the rate constant established by Mellouki et al., but it would be necessary that alternative loss processes for CH$_3$SO$_2$ •, probably initiated

by Reaction (19), should be faster at ambient O_2 concentrations. In the present model we have let k_{21} vary between the extreme limits given by the two values obtained from experimental observations.

2.3. REACTIONS OF $CH_3SO_3 \cdot$

The rate of the thermal decomposition of $CH_3SO_3 \cdot$ is not known at all. The calculated bond dissociation energies for Reaction (21) and Reaction (22) (Yin *et al.*, 1990) are 17.2 and 22 kcal/mole respectively while the dissociation reaction

$$CH_3SO \cdot \xrightarrow{k_{32}} CH_3 \cdot + SO \qquad\qquad (2.5)$$

is much more endothermic ($\Delta H - 50$ kcal/mole). For this reason Yin *et al.* expect Reaction (22) to be relatively fast (as they also expect Reaction (21) to be fast) and Reaction (32) to be slow. However, the very recent results obtained by Barnes (1993) indicate that Reaction (22) is too slow to be of importance compared to H-abstraction reactions leading to the formation of MSA, at least under the conditions applied in these experiments. Also in this case the choice of the uncertainty limits for the rate constant must be somewhat arbitrary; we have applied the same limits to k_{22} as those applied to k_{21} due to the similarity of the two reactions.
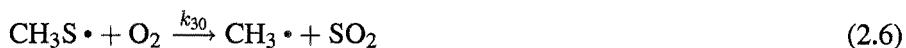

2.4. REACTIONS INVOLVING SO_2 AND H_2SO_4

The notion of Reaction (22) being fast is in agreement with the analysis by Bandy and coworkers (1992) who find that the predominance of this reaction could explain their observations. Although it appears most likely that DMS eventually is oxidized to H_2SO_4 in the marine troposphere, the concentrations of SO_2 measured by Bandy and coworkers in marine air were lower than what was to be expected if SO_2 were the main intermediate in the oxidation of DMS. Thus, according to Bandy and coworkers, DMS is oxidised to H_2SO_4 in the marine troposphere but this process does not involve formation of SO_2. This hypothesis, however, contradicts the results of several smog chamber experiments (see e.g. Yin *et al.*, 1990b) where SO_2 is found to be the main product of the oxidation of DMS in air.
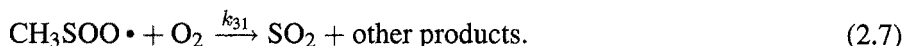
It is evident that the reactions leading to formation of SO_2 and, in turn, to H_2SO_4 as well as a possible direct pathway to H_2SO_4 are very poorly understood and consequently the involved rate constants have been attributed large uncertainties in the model.

Considering that there is evidence (Barnes, 1993) that Reaction (21) is slow compared to the competing reactions leading to $CH_3S(O)_2O_2 \cdot$ and $CH_3SO_3 \cdot$, alternative pathways to formation of SO_2 must be examined. We have proposed the dissociation of $CH_3SO_2 \cdot$ in an excited state (Reactions 11 and 13), but other pathways must exist because SO_2 is formed in high yields by the oxidation of

$CH_3S \bullet$ also in the absence of NO_2, and O_3 (Barnes, 1993). This could be the result of a reaction of O_2 with either $CH_3S \bullet$, leading to other products than $CH_3SOO \bullet$:

$$CH_3S \bullet + O_2 \xrightarrow{k_{30}} CH_3 \bullet + SO_2 \tag{2.6}$$

or with $CH_3SOO \bullet$:

$$CH_3SOO \bullet + O_2 \xrightarrow{k_{31}} SO_2 + \text{other products.} \tag{2.7}$$

The upper limit of k_{30} was estimated by Turnipseed et al. (1993) as 6×10^{-18} cm^3 s^{-1} molecule^{-1}. The analysis by Turnipseed et al. demonstrates that also k_{31} must be below 6×10^{-18} cm^3 s^{-1} molecule^{-1}, however with the constraint imposed that the sum of k_{30} and k_{31} must not exceed 6×10^{-18} cm^3 s^{-1} molecule^{-1}.

Heterogeneous SO_2 oxidation is not considered in the present study which is focused on homogeneous gas-phase chemistry. The consequences of this assumption are discussed in Section 4.

2.5. PEROXYNITRATE INTERMEDIATES

Three peroxynitrate intermediates are formed in the present reaction scheme:

CH_3SOONO_2
$CH_3S(O)O_2NO_2$
$CH_3S(O)_2O_2NO_2$
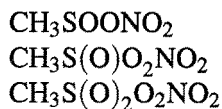
The rate constant of Reaction (28) has been determined experimentally (Turnipseed et al., 1993) while those of Reaction (15) and Reaction (20) have been estimated by assuming them equal to that of the reaction forming peroxyacetylnitrate (PAN):

$$CH_3C(O)OO \bullet + NO_2(+M) \rightarrow CH_3(O)OONO_2(+M) \tag{2.8}$$
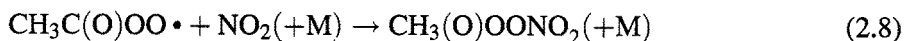
A relatively stable, PAN-like peroxynitrate intermediate has been observed in laboratory experiments on the oxidation of DMS in the presence of NO_2 (Barnes et al., 1987; Jensen et al., 1991; Jensen et al., 1992) and the thermal dissociation rate of this intermediate has been studied over a range of temperatures (Jensen and Hjorth, 1995); however, it was not found possible to verify whether the stable intermediate observed was $CH_3S(O)O_2NO_2$ or $CH_3S(O)_2O_2NO_2$.

In the present model we have assigned the rate constant found by Jensen and Hjorth (1995) to Reaction (−15) as well as Reaction (−20). In the case of the thermal dissociation of CH_3SOONO_2, which can not be resonance-stabilised in a way analogous to that of PAN, we have adopted the rate constant for the thermal dissociation of $CH_3O_2NO_2$ but attributed a large uncertainty to this estimate. We have not considered any further reactions of peroxynitrate species apart from dissociation.
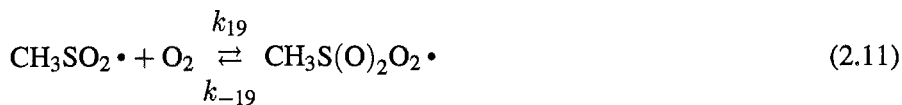
It should be noted that the outcome of the present analysis does not fully reflect the potential importance of peroxynitrate intermediates in the troposphere because

the stability of these species increases strongly with decreasing temperature, while the present study considers only kinetics at 298 K.

2.6. MODEL ASSUMPTIONS

Assumptions made for the analysis include:

(i) The three reactions

$$CH_3S \cdot + O_2 \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} CH_3SOO \cdot \qquad (2.9)$$

$$CH_3SO \cdot + O_2 \underset{k_{-14}}{\overset{k_{14}}{\rightleftarrows}} CH_3S(O)O_2 \cdot \qquad (2.10)$$

$$CH_3SO_2 \cdot + O_2 \underset{k_{-19}}{\overset{k_{19}}{\rightleftarrows}} CH_3S(O)_2O_2 \cdot \qquad (2.11)$$

have been assumed at the equilibrium i.e. they are considered to be fast compared to alternative reaction pathways.

(ii) The formation of SO_3 is not considered explicitly because it is assumed to form H_2SO_4 instantaneously:

$$CH_3SO_3 \cdot \xrightarrow{k_{22}} H_2SO_4 \qquad (2.12)$$

(iii) The concentration of DMS, OH, NO, NO_2, O_2, O_3, H_2O have been assumed constant with time, as if those products were not consumed in the reactions. This choice has been made because the concentrations of these species are presumably controlled by factors not included in the model. Furthermore, the model seems to respond almost linearly to variations in these concentrations, because there are no interactions among intermediates or reaction products (see discussion in Section 4.6).

(iv) In the uncertainty and sensitivity analysis calculations the initial concentrations of NO, NO_2 were correlated; a rank correlation of about 0.6 was obtained using a technique described by Iman and Conover (1982); this corresponds to the 0.8 'requested' correlation in Table I.

(v) As shown in Table I two main 'cases' (set of simulations) have been considered. The first one with the data in Table I and referred to as 'Polluted Environment'. The second one named 'Unpolluted Environment' has been generated by lowering by two orders of magnitude the upper bounds of the concentrations of NO, NO_2, and by reducing to one half the upper bound of the concentrations of O_3. This choice reflects the dramatic difference between NO_x concentrations measured in remote

two orders of magnitude the upper bounds of the concentrations of NO, NO_2, and by reducing to one half the upper bound of the concentrations of O_3. This choice reflects the dramatic difference between NO_x concentrations measured in remote sites and those measured in the vicinity of anthropogenic sources due to the short atmospheric residence times of NO_x.

3. Methods and Tools

3.1. KIM

The scheme implemented in KIM (the chemical KInetics Model of the OH-initiated oxidation of DMS in air), is given in Figure 1. Data on the reactions considered are given in Table I. KIM solves a system of 28 differential equations. Switches in KIM allow the reversible reactions, e.g.

$$CH_3S \cdot + O_2 \; \overset{k_7}{\underset{k_{-7}}{\rightleftarrows}} \; CH_3SOO \cdot \tag{3.1}$$

to be considered either kinetically (the results then depending on both k_7 and k_{-7}) or at the equilibrium (the results only depending on the ratio k_7/k_{-7}). The input data and the relative selected uncertainties are also given in Table I.

The integration of the equations given in Figure 1 is performed using a Runge Kutta 4th order algorithm with adaptive step control.

3.2. STATISTICAL SUBROUTINES

KIM, as part of a larger model of the sulphur cycle described in Saltelli *et al.* (1993b) is embedded into a statistical driver which allows parameters to be input in the form of distribution, whereby the analysis of the uncertainties is to a large extent automated (Homma and Saltelli, 1991; Saltelli and Homma, 1991). PREP (data PRE Processor) generates the input sample for a Monte Carlo simulation. Different sampling schemes (random, hypercube, quasirandom, . . .) are allowed. A pure Monte Carlo sampling scheme was adopted for the present work. Input variables can be correlated after Iman and Conover (1982).

SPOP, (Statistical POst Processor) performs the Uncertainty and Sensitivity Anayses (UA, SA) on the output of the model. UA means here all the statistics used to assess the uncertainty in the model prediction. These would include the computation of the output mean, its standard deviation and the uncertainty bounds on the mean value. SA looks instead at which parameters are mostly responsible for the output's uncertainty. As shown in the next sections SA is performed with correlation-regression based estimators as well as with importance measures. These latter investigate the fraction of the output variance accounted for by each input parameter. Alternative software is available for SA; many references are given in Helton (1993).

3.3. THE ANALYSIS

The numerical experiment conducted on KIM investigate the relative influence of
the uncertainties in input data (kinetic constants, initial concentration of DMS,
OH, NO, ...) on output concentrations and concentration ratios such as for
MSA/(SO_2 + H_2SO_4) ratio. The validity of such an analysis is conditional upon: (1)
The correctness of the reaction schemes included in the model (Fig. 1) and (2) The
likelihood of the uncertainty ranges selected for the input parameters (Table I; an
example of the impact of changing input distributions is given in Section 4.6).

In the literature a variety of methods have been employed for sensitivity analysis,
also in conjunction with chemical kinetics models. A number of *local sensitivity*
methods are reviewed in Pandis and Seinfeld (1989). Those techniques aim at (and
are based on) evaluating the derivative of some output function y_r with respect
to any of the input variables X_i's at some fixed point in the space of the input
parameters. A special case is the work of Vajda *et al.* (1985) where local sensitivities
are coupled with a principal component analysis. This method enables – among
other things – the selection of minimal reaction set in complex chemical kinetics
model, and the investigation of the validity of quasi-steady-state assumptions.

The local sensitivity approach is practicable when the variation around the
midpoint of the input variables X_i's is small; in general this allows the $y = y(\mathbf{x})$
relationship (where $\mathbf{x}$ is the X_i's vector) to be assumed as linear. Furthermore, if
the variation is the same for all the variables, then the relative importance of the
input parameters can be determined (Pandis and Seinfeld, 1989). One shortcoming
of the linear sensitivity approach is that it is unable to assess effectively the impact
of possible differences in the scales of variation of the X_i's (unless the model is
linear). It has been recognised in the literature since a number of years (Cukier *et
al.*, 1973; Iman *et al.*, 1978) that when the model is nonlinear and the various X_i's
are affected by uncertainties of different orders of magnitude a *global sensitivity*
measure should be used. Global SA techniques are discussed by Cukier *et al.*
(1978), Iman and Helton (1988), Sobol' (1990), Helton *et al.* (1991), Saltelli and
Homma (1992).

For an example of global SA in the field of chemical kinetics using the Fourier
Amplitude Sensitivity Test (FAST) see Schaibly and Schuler (1973). An applica-
tion of global Monte Carlo methods of UA/SA to tropospheric photochemistry is
given in Thompson and Stewart (1991). Other interesting applications of global
UA/SA can be found in the review of Helton (1993). Investigations of prediction
uncertainty and parameters sensitivity in models of environmental impact can be
found in Wigley (1989); Alcamo and Bartnicki (1990). For a comparison of UA/SA
techniques see also Iman and Helton (1988), Helton *et al.* (1991), Helton (1993),
Saltelli and Marivoet (1990), Saltelli and Homma (1992), Saltelli *et al.* (1993a).

The SA study presented here is 'global', in the sense that all the parameters
are varied simultaneously and the sensitivity is measured over the entire range of
each input parameter using a Monte Carlo approach. Local sensitivity methods

would be inappropriate for the present investigation mostly because: (i) The range of parameters' variation is large and the model is known to be nonlinear in this range and (ii) the object of the study is the absolute influence of a parameter on the output and not the relative one.

One way of performing global SA is by building a regression model for the output function. A useful regression scheme is that based on the Standardised Regression Coefficients (*SRC*) or the Standardised Rank Regression Coefficients (*SRRC*).

The *SRC* are computed from the least-square regression analysis applied to the output of a Monte Carlo simulation. Let $\mathbf{y}$ be the vector of the output variables, and $\mathbf{X}$ the input data matrix. Let y_m be the value of the selected output for the run number m, and x_{mi} the value of the input variable i selected for the same run. The regression coefficients b_i can be computed by least square (Draper and Smith, 1981), yielding

$$y_m = b_0 + \sum_{i=1}^{K} b_i x_{mi} + \epsilon_m \qquad \text{with } m = 1, 2, \ldots \text{ N} \tag{3.2}$$

where the ϵ_m are the error terms. Once the b_i's are computed a regressin model is available to compute the output associated with a generic input vector $\mathbf{x}$, $(X_1, \ldots, X_K)$

$$\frac{\hat{Y} - \overline{Y}}{S(Y)} = \sum_{i=1}^{K} SRC(Y, X_i) \frac{X_i - \overline{X}_i}{S(X_i)} \tag{3.3}$$

where $\overline{Y}$ and $\overline{X}_i$ are the averages of $(y_1, \ldots y_N)$, $(x_{1i}, \ldots y_{Ni})$, S are the respective standard deviations, $\hat{Y}$ is the regression model evaluation and the *SRC*'s are computed from the b_i's.

If the regression is effective then the parameters influence can be assessed based on the absolute values of the *SRC* or *SRRC*'s (Iman *et al.*, 1981). These latter are simply obtained by replacing both the output variable values y_i and the input vectors X_i's by the respective ranks. The advantages of using the *SRC*'s (or *SRRC*'s) rather than a simple correlation measure between $\mathbf{y}$ and the X_i's (as done in Thompson and Stewart, 1991) is that with the *SR(R)C*'s the effectiveness of the regression analysis can be quantified. This is done through another statistics, known as the model coefficient of determination R_y^2, which is based on the *SR(R)C*'s and gives the percentage of the original data variance which is explained by the regression model. The validity of the *SRC*'s as a measure of sensitivity is conditional to the degree to which the regression model fits the data, i.e. to R_y^2. When the value of the R_y^2 coefficient computed on the raw values is low, it is usually worth trying the rank equivalent of *SRC*, i.e. the *SRRC*. If the new R_y^2 coefficient (on rank) is higher, then the *SRRC*'s can be used for SA. The transformed (ranked) variables are used in this work because the R_y^2 values associated with the *SRC*'s are generally

lower than that associated to the *SRRC*'s, especially for non-linear models. In the results section both the R_y^2's are given, as their difference is a useful indicator of the non-linearity of the model.

Results from the sensitivity analysis based on the *SRRC* should be interpreted by keeping the regression model in mind. If variable X_i is not evidenced as important for output variable y_r this does not necessarily imply that $\partial y_r / \partial X_i$ is small but only that according to the regression scheme built with the *SRRC*'s the variation of X_i in the range assigned does not produce appreciable effects on y_r, and is hence not given an important weight in the regression model itself. This could either be due to (a) Failure of the *SRRC* to build an effective regression (this would flagged by R_y^2) or (b) A small range of variation of X_i or (c) An effectively small $\partial y_r / \partial X_i$ over the entire range of variation of X_i. The results for the SRRC based SA were interpreted using hypothesis testing, which allows the probability of an erroneous parameter identification to be quantified (Conover, 1980; see note in Table II).

The SA results obtained with the *SRRC*'s were also verified using an independent analysis on a different sample. This was based on a 'measure of importance' S. This test is described in the literature under different forms (Hora and Iman, 1986; Ishigami and Homma, 1989, 1990; Sobol', 1990; Saltelli *et al.*, 1993a; Homma and Saltelli, 1994). The measure of importance is conceptually more powerful that the regression based SA, in that it allows the output variance to be broken down into contributions due to individual parameters or combination of parameters. To make an example, if $y(\mathbf{x})$ is a function of just three parameters, i.e. $\mathbf{x} \equiv (x_1, x_2, x_3)$ and the total variance of $y(\mathbf{x})$ is D, then D can be in principle decomposed as

$$D = D_1 + D_2 + D_3 + D_{12} + D_{13} + D_{23} + D_{123} \tag{3.4}$$

and $S_1 = D_1/D$ is the fraction of the total variance due to the parameter X_1 alone averaged over all the parameters, while $S_{12} = D_{12}/D$ is the fraction of variance due to the coupling of parameters X_1 and X_2, again averaged over all the parameters and so on. In the results section two sensitivity indices have been computed for each variable: the first order term S_i and the total effect term $S_{T,i}$. Using again the example above:

$$\begin{aligned} S_{T,1} &= S_1 + S_{12} + S_{13} + S_{123} \\ S_{T,2} &= S_2 + S_{12} + S_{23} + S_{123} \\ S_{T,3} &= S_3 + S_{13} + S_{23} + S_{123} \end{aligned} \tag{3.5}$$

The computation of the sensitivity indices is detailed in Homma and Saltelli (1994), and involves Monte Carlo integration of multidimensional integrals. To make an example the first-order term $S_i \equiv D_i/D$ is estimated from the Monte Carlo integrals

$$D_i + y_0^2 \approx \frac{1}{N} \sum_{m=1}^{N} y(\mathbf{u}_{im}, x_{im}) y(\mathbf{v}_{im}, x_{im}) \tag{3.6}$$

TABLE II. Output variable: MSA/(SO$_2$ + H$_2$SO$_4$)

R^2_y, raw values and ranks

Time	Polluted		Unpolluted	
5 min	0.494	0.692	0.529	0.819
1 h	0.524	0.732	0.551	0.825
24 h	0.532	0.738	0.554	0.825

Mean, Tchebycheff's bounds[a] and standard deviation

Time	Polluted MEAN	TCHEB	STD	Unpolluted MEAN	TCHEB	STD
5 min	0.0805	0.0514	0.115	0.0389	0.0338	0.0756
1 h	0.0880	0.0530	0.118	0.0441	0.0366	0.0818
24 h	0.0898	0.0534	0.119	0.0448	0.0369	0.0825

Sensitivity analysis, polluted environment SRRC

Time	k_1	k_{10}	k_{18}	k_{19}	k_{-19}	k_{21}	k_{22}	k_{23}	k_{30}	k_{31}	$[O_3]_0$	$[NO]_0$	$[NO_2]_0$
5 min	−0.15	0.15	0.30	0.16	−0.17	−0.23	−0.18	0.30	−0.14	−0.24	0.23	0.31	0.08
1 h	−0.10	0.16	0.30	0.27	−0.24	−0.27	−0.21	0.31	−0.15	−0.21	0.20	0.23	0.15
24 h	−0.10	0.16	0.29	0.28	−0.25	−0.28	−0.21	0.29	−0.16	−0.21	0.19	0.21	0.17

Sensitivity analysis, unpolluted environment SRRC

Time	k_1	k_8	k_{10}	k_{18}	k_{19}	k_{-19}	k_{21}	k_{22}	k_{23}	k_{30}	k_{31}	$[O_3]_0$
5 min	−0.14	0.13	0.20	0.53	0.17	−0.23	−0.35	−0.15	0.25	−0.10	−0.24	0.23
1 h	−0.10	0.10	0.20	0.50	0.24	−0.29	−0.36	−0.17	0.23	−0.11	−0.23	0.19
24 h	−0.10	0.10	0.20	0.50	0.25	−0.30	−0.36	−0.17	0.23	−0.11	−0.22	0.18

[a] The Tchebycheff's theorem based confidence bounds (TCHEB) compensate for the finite sample size employed in the estimation of the mean value. They ensure that there is 95% probability that the true (population) mean value lies within (VALUE plus or minus TCHEB).

[b] Only those variables are given for which the null hypothesis 'There is no correlation between the variable and the output' is rejected for at least one time point at the 0.05 contingency level.

$$y_0 \approx \frac{1}{N} \sum_{m=1}^{N} y(\mathbf{x}_m) \qquad (3.7)$$

$$D - y_0^2 \approx \frac{1}{N} \sum_{m=1}^{N} y^2(\mathbf{x}_m) \qquad (3.8)$$

where again N is the sample size, $\mathbf{x}_m$ is the vector of the input variables sampled for run number m, D is the estimated variance of y and $\mathbf{u}_m$, $\mathbf{v}_m$ denote two different sampled projections of $\mathbf{x}$ in the original space reduced of the variable X_i. An intuitive explanation of Equation (3.6) could be the following: D_i is generated by summing products of two output y values, one obtained with all the input variables sampled and the other with all the variables re-sampled but the variable X_i. If X_i is influential, then high $y(\mathbf{u}_{im}, x_{im})$ values will be preferentially associated with high $y(\mathbf{v}_{im}, x_{im})$ values, and D_i will be high. For a less influential X_i the two y values will be paired more randomly, and D_i will be lower.

Expressions similar to (3.6) can be derived for the higher order terms and for the $S_{T,i}$. Unfortunately one separate sample (of size N) is needed to compute each of the S_i and $S_{T,i}$.

The 'probable error' on S_{Ti}, (δS_{Ti}) as been estimated following Sobol' (1991) and Homma and Saltelli (1994). This is computed in such a way that the true (population) value of S_{Ti} has a 50% chance of falling between the (estimated) $(S_{Ti} \pm \delta S_{Ti})$. The value of δS_{Ti} has been used to select data for entry in the result tables (see also header of Table III). Both S_i and the total effect term $S_{T,i}$ have been computed on the ranks, and have been indicated as S_i^* and $S_{T,i}^*$ respectively. As discussed by Homma and Saltelli (1994) there are similarities between this approach and the FAST technique. In the same article a discussion of the implications of the rank transformation is given.

4. Analysis of the Results

General. The regression based sensitivity analysis (*SRRC*'s) has been conducted for the two cases (polluted and unpolluted). Results are given for three time points: 5 min, 1 h and 24 h. The analysis based on the importance measures (S_i^*, S_{Ti}^*, first-order term and global-effect term) was conducted for the polluted case only, and the simulations were halted at 1 h. This choice can be justified a posteriori on the basis of the relatively small difference between the SA results for 1 h and 24 h.

Three different output functions have been considered:

(1) Ratio between CH_3SO_3H (MSA) and the sum of SO_2 plus H_2SO_4.
(2) The sum of the nitrogen containing species CH_3SOONO_2, $CH_3S(O)O_2NO_2$ and $CH_3S(O)_2O_2NO_2$.
(3) The ratio between SO_2 and H_2SO_4.

TABLE III. Output function: $MSA/(SO_2 + H_2SO_4) \cdot S_T^*$ statistics. Only those variables are given whose S_T^* value is greater than its approximate 'probable error' δS_T^*. The value of the first order term S_i^* is in parentheses. The score correlation coefficients (SCC) between S_T^* and $SRRC$ are also given

Variable	5 m; $SCC = 0.78$		1 h; $SCC = 0.86$	
k_8	0.08	(0.11)	0.07	(0.08)
k_{18}	0.14	(0.12)	0.14	(0.12)
k_{19}	0.10	(0.0)	0.12	(0.06)
k_{-19}	0.14	(0.0)	0.16	(0.03)
k_{21}	0.17	(0.11)	0.18	(0.14)
k_{22}	0.13	(0.03)	0.14	(0.02)
k_{23}	0.27	(0.18)	0.27	(0.18)
$[NO]_0$	0.16	(0.14)	0.15	(0.10)
$[NO_2]_0$	0.11	(0.0)	0.10	(0.01)

The choice of investigating $MSA/(SO_2 + H_2SO_4)$ rather than the conventional MSA/nss-H_2SO_4 compensates for neglecting the heterogeneous chemistry. In reality most of the SO_2 would be rapidly oxidized by in drop reactions.

The relative fractions of H_2SO_4 formed via the SO_2 and SO_3 pathways in both environments were also looked at, as well as the ratio of SO_2 to SO_3 concentrations as function of time when H_2SO_4 formation – either by oxidation of SO_2 or hydration of SO_3 – is excluded. One separate case of size 100 was also run in which the distribution bounds of variable k_{23} were shifted by one order of magnitude.

The average species concentrations at 24 h are also given (molecules/cm^3, Figure 2), together with the average fraction of SO_2 formed through the various pathways. It can be observed that: (1) In both scenarios almost half of SO_2 goes through $CH_3SOO \bullet$; one fifth goes through $CH_3SO_2 \bullet$ and about the same through $CH_3S \bullet$; no more than 15% goes through $CH_3SO \bullet$. (2) The dominating peroxinitrate in both conditions is $CH_3S(O)_2O_2NO_2$. The relative contribution of $CH_3S(O)O_2NO_2$ is larger for the unpolluted case (Fig. 2). CH_3SOONO_2 amount is negligible. (3) The polluted conditions tend to 'pump' more sulphur into the end-products, MSA and H_2SO_4. As SO_2 is mostly (90%) generated through reactions not involving NO_x nor O_3, and there is much more SO_2 than H_2SO_4, then the ratio MSA to $(SO_2 + H_2SO_4)$ increases in the polluted environment.

The main pathways identified as mostly contributing to the output uncertainty are summarised in Figure 1.

Statistics. The dimension of the sample for the *SRRC* based SA was one hundred, i.e. in total KIM has been run 200 times to compute the *SRRC*'s. The base sample for S_i^*, S_{Ti}^* was again 100. The total number of simulation was hence $2 \times 100 \times (1 + 35) = 7200$ (base sample plus one sample per each of the 35
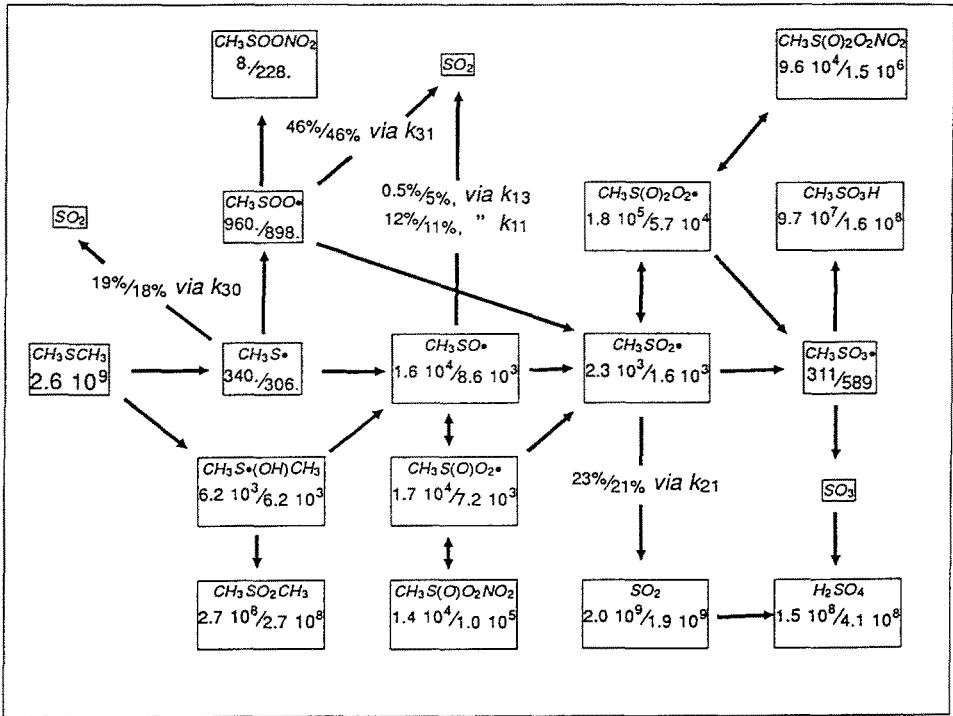
Fig. 2.   Uncertainty analysis. Average concentrations of species in mol · cm^3 (boxes) in the *unpolluted/polluted* scenarios at 24 h. The fraction of SO_2 formed through the various pathways is also given.

variables; different samples being used for S_i^*, S_{Ti}^*). For each output variable the mean as function of time is given together with the Tchebycheff based 95% confidence bounds (Saltelli and Marivoet, 1988). When using *SRRC*'s hypothesis testing has been used to select influential variables: sensitivities are given for those variables which passed the *SRRC* test for significance at the 0.05 contengency level (Conover, 1980). This means that there is 5% probability that a variable is erroneously indicated as influential in the *SRRC*-based analysis (see also notes on Table II). For the S_{Ti}^*-based sensitivity analysis, variables were selected based on the probable error on S_{Ti}^* (see Table III).

4.1. OUTPUT CONSIDERED: CONCENTRATION RATIO MSA/(SO$_2$ + H$_2$SO$_4$)

This analysis looks at which pathways enhances the MSA to (SO$_2$ + H$_2$SO$_4$) ratio (Table II). The values of the R_y^2 on the ranks (between about 0.69 and 0.83) indicate a reliable *SRRC*-based SA. The non-dramatic difference between the R_y^2 on the ranks and that on the raw values indicates a model of moderate non-linearity.

Polluted environment. The ratio is almost constant with time at about 0.1, i.e.

in average a 10% of the total oxidized sulphur is found as MSA. Allowance made for the uncertainty due to the finite sample size there is a 95% probability that the average ratio is in the range ≈ 0.04, 0.16 (using the Tchebyceff's confidence bounds). The standard deviation of this output variable is about 0.12. Considering the large uncertainties in the input data and especially in O_3 and NO_x the uncertainty in the ratio MSA to $(SO_2 + H_2SO_4)$ is mild.

The reaction rate k_{23} is the most important parameter for the polluted conditions, followed by k_{18} and $[NO]_0$. Ozone is also influential, possibly (but not exclusively) because of its association to k_{18}. The negative influence of k_{21} is also easily understood by looking at the reaction scheme (Figure 1). The positive and negative influence of the couple k_{19} and k_{-19} (respectively) is due to the reaction branch which goes through k_{26} (i.e. k_{19} enhances the k_{26} pathway at the expenses of the competing k_{21} pathway, which leads to SO_2). The positive correlation of the output with $[O_3]_0$, $[NO]_0$ and $[NO_2]_0$ confirms the remark (3) above.

S_i^*, S_{Ti}^*-*based sensitivity analysis.* The results are given in Table III. There is a general qualitative agreement between the results in Table II and Table III, i.e. the variables identified tend to be the same, but the relative difference among individual S_T^* values is different – as expected – from that of the *SRRC*'s. In particular for this output variable the kinetic constants appear to account for a much larger fraction of the output variance than the initial conditions. One third of the variance of the system is due to variable k_{23}, either alone or in combination with other variables. The influence of $[NO_2]_0$ is lower and that of $[O_3]_0$ disappears. Although $[O_3]_0$ is influential it does not contribute appreciably to the output variance. This is likely because of its limited range of variation in the input (Table I).

The comparison of the total-effect terms with the first-order ones reveals appreciable coupling of input parameters. It should always be $S_{Ti}^* \geq S_i^*$, and it is mostly so in spite of the random error (different samples were used to estimate the two statistics). The sum of all the first-order terms is about 0.8 for both time points, i.e. close enough to one to make the higher-order terms apparently negligible (see for instance discussion in Liepman and Stephanopoulos, 1985). Yet, because of the large number of variables, and of the large number of potentially non-zero $Si_1 \ldots i_s^*$, the difference between the total and first-order effect terms is remarkable. Variable $[NO_2]_0$ for instance seem to have a zero first-order effect, but to have an impact on the considered output mostly via coupled terms. Similarly for k_{19}, k_{-19}. These results seem to encourage the use of the global effect terms.

Statistics. In Tables III, V and VII the variables are selected based on S_{Ti}^* and its probable error. Value of S_i^* are given in parentheses. The Score Correlation Coefficient (*SCC*) between S_T^* and *SRRC* for each column in Tables III, V, VII are also given. The *SCC* is a measure of the correlation between the prediction of two different SA techniques based on the ranking produced by the two techniques for the same set of variables (Iman and Helton, 1985; Iman and Conover, 1987). They

are useful here to quantify the agreement between the two techniques used in the present work. As discussed elsewhere (Saltelli $et\,al.$, 1993a) the agreement between $SRRC$ and S_i^* (with $SCC \approx 0.8$) can be attributed to the monotonicity of the model.

$Unpolluted\;environment.$ The MSA fraction reduces to less than a 5% of the total sulphur (see point (3) above). It is understandable that $[NO]_0$ and $[NO_2]_0$ disappear from the list of the influential variables. The relative influence of k_{18} is enhanced by the decreased influence of k_{26} and k_{17}. The couple k_{19} and k_{-19} maintain its relevance due to the competition with k_{21}.

The ratio between MSA and non-sea-salt-sulphate measured at remote marine sites at mid and low latitudes (e.g. Putaud $et\,al.$, 1993; Bates $et\,al.$, 1992; Bürgermeister and Georgii, 1991; Salzman $et\,al.$, 1986) can give a hint to what are the true typical values of the MSA to $(SO_2 + H_2SO_4)$ ratio by the oxidation of DMS in the unpolluted marine troposphere, considering that SO_2 is oxidized to H_2SO_4 which, like MSA, will predominantly be found in particles and not in the gas phase.

However, the measured MSA to nss-sulphate ratio does only very roughly reflect the initial formation of MSA vs. SO_2 and H_2SO_4 by the oxidation of DMS because of the influence of dry and wet deposition. This may be particularly relevant in the case of SO_2 where about 50% is removed from the atmosphere by deposition before forming sulphate, according to Langner and Rodhe (1991). Further, some of the MSA will be oxidized to H_2SO_4 in droplets and wet aerosols and finally the contribution of other sources of sulphate than DMS will lower the MSA/nss-sulphate ratio in the real troposphere compared to a hypothetical situation with DMS as the only source of sulphate. Thus it must be considered a pure coincidence that the modelled MSA yield of 4.5% is so close to the measured mean values of the MSA/nss-sulphate ratios, e.g. the value of 3.5% found by both Putaud $et\,al.$ (1993) and Bates $et\,al.$ (1992). However, it can then be stated that there is a qualitative agreement with field observations.

The tendency to a larger formation of MSA (and thus a higher value of the ratio under study) in a more polluted atmosphere is in good agreement with the observation of some authors (Mihalopoulos $et\,al.$, 1992) that attribute this to the influence of higher NO_x levels which is in agreement with the reaction scheme of Figure 1.

4.2. OUTPUT CONSIDERED: SUM OF
$CH_3SOONO_2 + CH_3S(O)O_2NO_2 + CH_3S(O)_2O_2NO_2$ CONCENTRATIONS
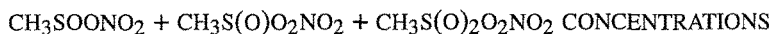
Results are given in Table IV. The sum of the three species increases with time. Values are lower – as expected – for the unpolluted case. R_y^2 values are above 0.84 for both the polluted and the unpolluted case, so that the analysis provided by the $SRRC$ can be considered as reliable. The uncertainty on the mean values is large. As mentioned in Section 2 the rate constants employed in the present study are those

TABLE IV. Output variable: $(CH_3SOONO_2 + CH_3S(O)O_2NO_2 + CH_3S(O)_2O_2NO_2)$

R_y^2, raw values and ranks

Time	Polluted	Unpolluted
5 min	0.522	0.804
1 h	0.464	0.799
24 h	0.451	0.797

Mean, Tchebycheff's bounds and standard deviation

Time	Polluted			Unpolluted		
	MEAN	TCHEB	STD	MEAN	TCHEB	STD
5 min	$2.99 \cdot 10^5$	$4.46 \cdot 10^5$	$9.98 \cdot 10^5$	$7.18 \cdot 10^4$	$9.12 \cdot 10^4$	$2.04 \cdot 10^5$
1 h	$7.82 \cdot 10^5$	$1.50 \cdot 10^6$	$3.36 \cdot 10^6$	$1.09 \cdot 10^5$	$1.31 \cdot 10^5$	$2.94 \cdot 10^5$
24 h	$8.31 \cdot 10^5$	$1.64 \cdot 10^6$	$3.68 \cdot 10^6$	$1.10 \cdot 10^5$	$1.32 \cdot 10^5$	$2.95 \cdot 10^5$

Sensitivity analysis, polluted environment *SRRC*

Time	k_9	k_{14}	k_{-14}	k_{15}	k_{-15}	k_{19}	k_{-19}	k_{20}	k_{-20}	k_{29}	$[OH]_0$	$[NO]_0$	$[NO_2]_0$
5 min	0.12	0.12	−0.14	0.13	−0.09	0.34	−0.34	0.18	−0.16	0.12	0.37	−0.17	0.64
1 h	0.11	0.12	−0.15	0.14	−0.14	0.36	−0.32	0.19	−0.21	0.10	0.34	−0.22	0.63
24 h	0.11	0.12	0.15	0.14	−0.14	0.36	−0.32	0.19	−0.21	0.10	0.34	−0.22	0.63

Sensitivity analysis, unpolluted environment *SRRC*

Time	k_1	k_2	k_{14}	k_{-14}	k_{-15}	k_{19}	k_{-19}	k_{20}	k_{-20}	k_{29}	k_{31}	$[OH]_0$	$[NO_2]_0$
5 min	0.10	0.11	0.11	−0.23	−0.09	0.47	−0.40	0.17	−0.15	0.15	−0.13	0.36	0.28
1 h	0.13	0.12	0.12	−0.24	−0.14	0.47	−0.39	0.17	−0.18	0.12	−0.12	0.34	0.28
24 h	0.13	0.12	0.12	−0.24	−0.14	0.47	−0.39	0.18	−0.18	0.11	−0.12	0.34	0.28

TABLE V. Output function: $CH_3SOONO_2 + CH_3S(O)O_2NO_2 +$
$CH_3S(O)_2O_2NO_2$. S_T^* and S_i^* statistics and SCC (see caption of
Table III)

Variable	5 min; $SCC = 0.89$		1h; $SCC = 0.90$	
k_{-14}	0.06	(0.03)	0.06	(0.02)
k_{19}	0.14	(0.04)	0.14	(0.03)
k_{-19}	0.24	(0.09)	0.25	(0.10)
k_{20}	0.06	(0.02)	0.06	(0.03)
k_{-20}	0.06	(0.01)	0.09	(0.04)
$[OH]_0$	0.10	(0.07)	0.09	(0.06)
$[NO_2]_0$	0.45	(0.34)	0.42	(0.31)

at 298 K; at lower temperature the peroxynitrate would be significantly more stable.

Polluted environment. $[NO_2]_0$ is the most influential variable, followed by the couples k_{19}, k_{-19}, k_{14}, k_{-14} and k_{20}, k_{-20}. This is because there is considerably more $CH_3S(O)_2O_2NO_2$ than $CH_3S(O)O_2NO_2$ and CH_3SOONO_2 (see point (2) above). $[OH]_0$ is influential as it originates all the reaction products (we have not seen $[OH]_0$ in the previous analysis as we were looking at a ratio of reaction products). In spite of the correlation imposed between $[NO]_0$ and $[NO_2]_0$ (0.6 on ranks) $[NO]_0$ has a negative correlation with the output, probably due to the k_{26} pathway.

S_T^*, S_i^*-based sensitivity analysis (Table V). $[NO_2]_0$ and parameter combinations including $[NO_2]_0$ account for more than 40% of the total variance. There is again a qualitative agreement with the *SRRC*'s results. Comparing S_T^* with S_i^* also here reveals significant coupling for k_{19}, k_{-19} and $[NO_2]_0$. For this latter one third of the total effect seems due to the higher order terms.

Unpolluted environment. The decreased ranges of NO_2 and NO result in those two variables loosing importance at the expenses of the couple k_{19} and k_{-19}.

Both in the polluted and in the unpolluted environments the concentration of the sum of the peroxynitrates is of the order of 10^6 molecule/cm^3, i.e. below 1‰ of the DMS concentration. The contribution of CH_3SOONO_2 is negligible. Differences between Table IV and Figure 2 (obtained with different samples) are well within the Tchebycheff bounds.

4.3. OUTPUT CONSIDERED: CONCENTRATIONS RATIO SO_2/H_2SO_4

The ratio decreases with time in both environments, (from 75 to 8 in the polluted case and from 230 to 13 in the unpolluted, Table VI). In general the polluted environment results in a quicker oxidation of sulphur. $CH_3SO_3 \bullet$ seems to be a more important intermediate in the polluted case than in the unpolluted one.

TABLE VI.   Output variable: (SO_2/H_2SO_4)

R_y^2, raw values and ranks

Time	Polluted		Unpolluted	
5 min	0.593	0.765	0.549	0.823
1 h	0.576	0.800	0.590	0.817
24 h	0.606	0.765	0.519	0.839

Mean, Tchebycheff's bounds and standard deviation

Time	Polluted			Unpolluted		
	MEAN	TCHEB	STD	MEAN	TCHEB	STD
5 min	84.6	76.5	171.0	245.0	303.0	676.0
1 h	47.1	41.4	92.5	93.2	69.6	156.0
24 h	8.59	4.30	9.61	13.3	9.41	21.0

Sensitivity analysis, polluted environment SRRC[b]

Time	k_{10}	k_{17}	k_{18}	k_{19}	k_{-19}	k_{21}	k_{22}	k_{23}	k_{26}	k_{29}	k_{31}	$[OH]_0$	$[O_3]_0$	$[NO]_0$	$[NO_2]_0$
5 min	-0.19	-0.11	-0.25	-0.22	0.12	0.24	-0.28	0.34	-0.16	-0.19	0.29	0.04	-0.17	-0.30	-0.11
1 h	-0.17	-0.12	-0.27	-0.29	0.18	0.27	-0.25	0.33	-0.16	-0.22	0.27	0.02	-0.16	-0.22	-0.20
24 h	-0.09	-0.11	-0.24	-0.22	0.13	0.23	-0.10	0.25	-0.12	-0.16	0.27	-0.50	-0.10	-0.18	-0.15

Sensitivity analysis, unpolluted environment SRRC

Time	k_8	k_{10}	k_{18}	k_{19}	k_{-19}	k_{21}	k_{22}	k_{23}	k_{26}	k_{29}	k_{31}	$[OH]_0$	$[O_3]_0$
5 min	-0.12	-0.22	-0.45	-0.22	0.17	0.31	-0.26	0.33	-0.12	-0.17	0.23	0.01	-0.24
1 h	-0.11	-0.22	-0.46	-0.25	0.21	0.32	-0.21	0.33	-0.12	-0.17	0.23	-0.07	-0.18
24 h	-0.05	-0.05	-0.30	-0.19	0.13	0.22	-0.11	0.16	-0.09	-0.09	0.20	-0.68	-0.10

TABLE VII. Output function: SO_2/H_2SO_4. S_T^* and S_i^* statistics and SCC (see caption of Table III)

Variable	5 min; $SCC = 0.78$		1 h; $SCC = 0.87$	
k_8	0.07	(0.09)	0.06	(0.08)
k_{18}	0.07	(0.04)	0.07	(0.04)
k_{19}	0.10	(0.03)	0.11	(0.07)
k_{-19}	0.11	(0.0)	0.13	(0.01)
k_{21}	0.18	(0.15)	0.18	(0.15)
k_{22}	0.15	(0.13)	0.16	(0.14)
k_{23}	0.10	(0.09)	0.09	(0.09)
$[NO]_0$	0.16	(0.10)	0.12	(0.07)
$[NO_2]_0$	0.10	(0.05)	0.09	(0.06)

The increase of SO_2 with time will continue until a steady-state level is reached where the formation rate balances the loss rate (i.e. reaction 25), according to the present reaction scheme. The steady-state concentration can easily be calculated based on the previous analysis, e.g. in the unpolluted case, where only the SO_2, H_2SO_4, MSA and $CH_3SO_2CH_3$ products need to be considered:

$$[SO_2]_{\text{steady state}} = (k_1 + 0.5 \times k_2) \times \frac{0.95 \times [DMS]}{k_{25}} = 532 \text{ ppt.}$$

(The pathway of Reaction 22 to the formation of H_2SO_4 is considered negligible.) The factor 0.95 is introduced because the ratio $[MSA]/([MSA] + [SO_2] + [H_2SO_4])$ is approximately 5%, and k_2 is multiplied by 0.5 as k_3 and k_4 are equal in average. This concentration is about an order of magnitude higher than most measured values at remote sites (e.g. Putaud *et al.*, 1993; Bandy *et al.*, 1992) which may be explained by the existence of heterogeneous loss processes (e.g. on cloud droplets and on the sea-surface); in fact such processes are believed to be more efficient removal mechanisms for SO_2 than the reaction with OH radicals (Langner and Rodhe, 1991). However, also the occurrence of reaction pathways in the oxidation of DMS not leading to formation of SO_2 is compatible with these observations.

The values of R_y^2 are similar to those of the two previous models.

Polluted environment. Positive correlation with the kinetic constants directly related to SO_2 formation k_{21}, k_{31}. Conversely there is a negative correlation with all the kinetic constants and concentrations which promote $CH_3SO_3 \bullet$ and H_2SO_4 formation: k_{-19}, k_{22}, $[NO]_0$. There is a positive influence of k_{23} as this pathway competes with H_2SO_4 formation, and a negative correlation with the oxidizing agents ($[NO_2]_0$, $[O_3]_0$.) which shift the system in Figure 1 toward the formation of more $CH_3SO_3 \bullet$. For the last time point ($t = 24$ h) $[OH]_0$ becomes a very important variable with a negative correlation. This is due to the k_{25} pathway whose relative influence increases with increasing SO_2 concentration.

S_T^*, S_i^* -based sensitivity analysis (Table VII). The importance of $[NO]_0$ and $[NO_2]_0$ is confirmed. For $[NO_2]_0$ 50% of the total effect comes from coupling. Again k_{19} and k_{-19} contribute significantly via higher order terms. According to S_T^* the most important variable is k_{21}, rather than k_{23}.

Unpolluted environment. No qualitative changes in the picture, apart from the decreased influence of NO_2 and NO already observed in the two previously analyses.

4.4. PATHWAYS FOR SO_2 AND H_2SO_4 PRODUCTION

The parameters influencing the relative importance of a pathway to H_2SO_4 not involving SO_2 as an intermediate (i.e. reaction 22) have been investigated by looking at the output variable SO_2/SO_3 in the absence of further reactions of these species (i.e. when k_{25} is set to zero and there is no hydration of SO_3). The results are given in Table VIII(a) and (b) for the polluted and the unpolluted environment. Table VIII(c) gives the SO_2 concentrations predicted by the model. Even here slight differences with Figure 2 are due to the different sample employed.

Polluted environment. The parameters whose uncertainties most strongly influence the uncertainty on SO_2/SO_3 are very much the same as those identified by the analysis of the $[MSA]/([SO_2] + [H_2SO_4])$ output, because of the bifurcation between formation of MSA and of SO_3 is given by the ratio k_{23}/k_{22}. Most important in this case is the uncertainty in the value of k_{23}.

Unpolluted environment. The four most influential k-values highlighted by the analysis are the same as in the polluted case but with a somewhat different ranking, k_{18} (the oxidation of $CH_3SO_2 \bullet$ radicals by ozone) becoming the most important.
   In both environments the yield of SO_3 is only a small fraction of that of SO_2, in the unpolluted case even substantially below 1% of SO_2. In view of the strong interest in the possibility of a direct formation of SO_3 from DMS without the SO_2 intermediate (e.g. Bandy *et al.*, 1992; Lin and Chameides, 1993) it is worthwhile to look further into which are the conditions that would be needed to make reaction 22 become a main reaction pathway, particularly in the unpolluted environment. Obviously, the k-values that we should consider are those indicated by the statistical analysis; thus a fast reaction 18 or 19 or a slow reaction 21 or 23 would favour the formation of the SO_3 intermediate. However, it should be noted that the bond dissociation energy of the $CH_3SO_3 \bullet$ radical is slightly higher than that of $CH_3SO_2 \bullet$ (Yin *et al.*, 1990) and thus if k_{21} is slow then k_{22} would be expected to be even slower and thus probably not an important reaction pathway. Thus, to comply with the hypothesis of Bandy *et al.* (1992), a very fast reaction 18 or reaction sequence 19/26 would be needed to compete efficiently with reaction 21. In this reaction

TABLE VIII(a). Average ratio SO_2/SO_3 as function of time when H_2SO_4 formation is excluded (i.e. when k_{25} is set to zero and there is no hydration of SO_3). Unpolluted environment. The ranking of the influential variables is also summarized in order of decreasing importance (only for variables whose $|SRRC| \geq 0.25$)

Time	Ratio SO_2/SO_3	Mostly influenced by
5 min	382.0	$k_{18}, k_{23}, k_{21}, k_{22}$
1 h	372.0	$k_{18}, k_{23}, k_{21}, k_{19}$
24 h	357.0	$k_{18}, k_{21}, k_{23}, k_{19}$

TABLE VIII(b). Same as Table R.V(a), but for the polluted environment

Time	Ratio SO_2/SO_3	Mostly influenced by
5 min	92.3	$k_{23}, [NO]_0, k_{31}, k_{22}, k_{18}$
1 h	83.3	$k_{23}, k_{19}, k_{31}, k_{21}, k_{22}, k_{18}$
24 h	82.6	$k_{23}, k_{19}, k_{21}, k_{18}, k_{22}$

TABLE VIII(c). Total SO_2 (mol/cm^3)

Time	SO_2 (mol/cm^3) Unpolluted	Polluted
5 min	$7.71 \cdot 10^6$	$7.04 \cdot 10^6$
1 h	$9.36 \cdot 10^7$	$8.53 \cdot 10^7$
24 h	$2.02 \cdot 10^9$	$1.84 \cdot 10^9$

scheme we have not speculated about other possible reactions of the $CH_3S(O)_2O_2 \cdot$ radical leading to formation of $CH_3SO_3 \cdot$ but such reactions may of course take place (e.g. reactions with other peroxyradicals).

4.5. TEMPERATURE DEPENDENCIES

It is an important limitation of the present analysis that it does not include temperature dependencies. This is relevant in the case of the peroxynitrate intermediates, but it should also be noted that the dissociation rates of the $CH_3SO_2 \cdot$ and $CH_3SO_3 \cdot$ radicals are among the reactions rates that would be expected to have a pronounced positive dependence on temperature (as pointed out in the case of k_{22} by Turnipseed and Ravishankara, 1993). Thus the influence of these reaction rates, demonstrated by the present analysis, is in good agreement with the evidence obtained by field measurements of high [MSA]/[H_2SO_4] ratios in particles in cold (arctic) regions (e.g. Berresheim, 1987).

Also the ratio between addition and H-abstraction in the initial steps of the reaction scheme (k_1/k_2) is temperature-dependent and thus dimethyl sulphone, $CH_3SO_2CH_3$ (and the intermediate dimethyl sulphoxide, $CH_3S(O)CH_3$) may be of larger importance at lower temperatures. In fact, a recent field study by Berresheim

TABLE IX(a). Mean output value for the sample with new k_{23} distribution and ratio of this to the mean of the original sample (in parentheses)

Time	MSA/(SO$_2$ + H$_2$SO$_4$)	Peroxynitrates compounds	SO$_2$/H$_2$SO$_4$	SO$_2$/SO$_3$ (when no H$_2$SO$_4$ is formed)
5 min	0.077 (1.97)	$7.18 \cdot 10^4$ (1.00)	835.0 (3.41	$3.13 \cdot 10^3$ (8.19)
1 h	0.088 (2.00)	$1.09 \cdot 10^5$ (1.00)	193.0 (2.07)	$3.13 \cdot 10^3$ (8.20)
24 h	0.090 (2.00)	$1.10 \cdot 10^5$ (1.00)	19.7 (1.48)	$3.13 \cdot 10^3$ (4.62)

TABLE IX(b). Three most influential variables (*SRRC*) for the sample with new k_{23} distribution (above) and for the original sample (below)

Time	MSA/SO$_2$ + H$_2$SO$_4$	Peroxynitrates compounds	SO$_2$/H$_2$SO$_4$	SO$_2$/SO$_3$ (when no H$_2$SO$_4$ is formed)
5 min	k_{18}, k_{21}, k_{31}	$k_{19}, k_{-19}, [OH]_0$	k_{23}, k_{18}, k_{22}	k_{23}, k_{18}, k_{22}
	k_{18}, k_{21}, k_{23}	$k_{19}, k_{-19}, [OH]_0$	k_{18}, k_{23}, k_{21}	k_{18}, k_{23}, k_{21}
1 h	k_{18}, k_{21}, k_{-19}	same as above	$k_{18}, k_{23}, [OH]_0$	k_{23}, k_{18}, k_{22}
	k_{18}, k_{21}, k_{-19}		k_{18}, k_{23}, k_{21}	k_{18}, k_{23}, k_{211}
24 h	same as above	same as above	$[OH]_0, k_{23}, k_{18}$	k_{23}, k_{18}, k_{19}
			$[OH]_0, k_{18}, k_{21}$	k_{18}, k_{21}, k_{23}

et al. (1993) indicates that dimethyl sulphone can be the dominant end-product of the oxidation of DMS in the atmosphere.

4.6. ON THE SENSITIVITY UPON MODEL ASSUMTIONS

As mentioned in the introduction the results of the present study are conditional upon (a) the correctness of the reaction scheme adopted and (b) on the uncertainty ranges assigned to the input data. While the impact of (a) is difficult to assess, it is fairly simple to produce an example of the impact of (b) based on a test example.

The reaction constant k_{23} is probably the most uncertain of all the rate constants in Table I and the range of values is almost purely based on intuition. The choice of values made in the present work could be argued upon by comparing the CH$_3$SO$_3 \bullet$ radical to the OH$\bullet$ radical. CH$_3$SO$_3 \bullet$ could be thought to react at least as fast as OH$\bullet$ with most organic compounds and thus have an atmospheric lifetime similar to or shorter than that of OH. If this is taken as the most realistic estimate, then both the lower and the upper limit of k_{23} in Table I are too low.

Another numerical experiment has been then performed in which both limits were increased by an order of magnitude for the unpolluted environment scenario. The results are shown in the Table IX.

It is seen that the MSA/$(SO_2 + H_2SO_4)$ ratio increases to reach a value close to 10%. The SO_3 intermediate is now less than 1/1000 of SO_2 because Reaction (23) is more efficiently competing with Reaction (22).

The value of 10% for the MSA/$(SO_2 + H_2SO_4)$ ratio lies close to the maximum values of the MSA/nss-sulphate ratio measured in field experiments. Considering the factors influencing the MSA/nss-sulphate ratio, discussed in Section 4.1, it could be that the highest measured MSA/nss-sulphate ratios most truly reflect the initial yields of MSA, SO_2 and H_2SO_4 by the oxidation of DMS and thus this value from the model output cannot be rejected as unrealistically high.

The consequences of the simplifications and omissions made in the model should also be considered. In the case of the peroxyradical chemistry, not included in the model, the relevant reactions to be considered would have included:

$$ROO\cdot + HO_2 \rightarrow ROOH + O_2 \tag{4.1}$$
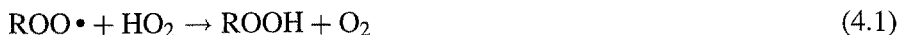
which would lead to formation of hydroperoxide species. In the case of the most abundant S-containing peroxyradical, which according to the results of the present model (Figure 2) is $CH_3S(O)_2OO\cdot$, the product would be $CH_3S(O)_2OOH$. This product would easily react subsequently in liquid phase (after sticking to particles or cloud droplets) to form MSA. Other RO_2-reactions to be expected by analogy to alkyl RO_2 radical chemistry are

$$2ROO\cdot \rightarrow 2RO\cdot + O_2 \tag{4.2}$$

and

$$RCH_2OO\cdot + RO_2\cdot \rightarrow RCHO + ROH + O_2 \tag{4.3}$$
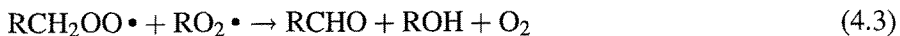
Both reactions would favour the formation of MSA from $CH_3S(O)_2OO\cdot$ (see Figure 1). HO_2 radicals are also likely to react rapidly with $CH_3SO_3\cdot$ to form MSA. Thus these qualitative considerations indicate that the reactions involving HO_2 and alkylperoxyradicals are likely to lead to formation of MSA.

The present analysis indicates that the lowest yields of MSA will be reached at low NO_x levels. However, as the above-mentioned peroxyradical reactions achieve their maximum importance at low [NO] this chemistry may to some extent compensate for the effect of low $[NO_x]$ on MSA by providing additional pathways to the formation of this species.

Another assumption made to simplify the model is to neglect the diurnal variation of concentrations of trace species such as OH, DMS, NO, NO_2, etc. This is clearly an unrealistic assumption, particularly in the case of OH. OH shows a strong diurnal variation with presumably negligible values at night-time. However, if a time-dependent variation of [OH] were introduced, most output parameters would remain the same after 24 h, as when applying a constant value of [OH] equal to the diurnal average value. This is due to the fact that, apart from the reaction with SO_2, OH is only involved in the initial reaction steps and does not influence

the branching ratios between the reaction pathways in our model. The estimate of the influence of Reaction (25) (OH + SO$_2$) may suffer from the present approximation, but this error is of little consequence compared to those of neglecting heterogeneous reactions and dry deposition.

It can be objected that there is probably a positive correlation between [OH] and [NO] values as both species are photochemically formed. This would enhance the importance of reactions involving NO, because their maximum rates would be obtained during the hours of the day where the largest quantity of DMS is oxidized. The overall result of this would correspond to increasing the average NO concentration, but as this concentration is already treated as a highly uncertain parameter in the present analysis it does not seem necessary to include an algorithm for diurnal variations in the numerical treatment.

It is difficult to evaluate the implications of omitting the NO$_3$ radical chemistry in the model as the global distribution of NO$_3$ is very uncertain and thus the importance of this chemistry is equally uncertain. However, it seems likely that the reaction of DMS with NO$_3$ radicals is of relevance at polluted coastal sites (Mihalopoulos *et al.*, 1992). A hydrogen-abstraction pathway, leading to the same products as those formed by the reactions initiated by hydrogen-abstraction by OH radicals (Reaction 1), has been found to be the predominant pathway in the reaction of NO$_3$ radicals with DMS (Jensen *et al.*, 1992; Butkovskaya and LeBras, 1994). Thus the occurrence of the reaction with NO$_3$ would enhance the importance of the hydrogen-abstraction pathway.

5. Conclusions

A part of the numerical experiments described in this note was the comparison between experimental and field data with model predictions. Because of the large uncertainty in the input data the comparison was made on a Monte Carlo basis, looking at the averages computed by the model. The fact that the averages were found to agree with observation was taken as a confirmation that the interval of uncertainty selected for the input data was not unrealistic.

Given the uncertainties involved such a comparison between prediction and observation could only be done on a Monte Carlo basis.

The main result of this work is nevertheless the identification of which kinetic parameters would deserve – on a priority basis – a more accurate determination. This identification is, obviously, only valid to the extent that the reaction scheme and the values and the uncertainties attributed to the various parameters are accepted as discussed in the previous sections. The most important pathways have been highlighted in Figure 1.

(1) Pathways to formation of SO$_2$ and H$_2$SO$_4$. The present analysis highlights some kinetic parameters as being particularly relevant to the understanding of the recently proposed pathway to formation of H$_2$SO$_4$ in the atmosphere (Bandy *et al.*,

1992; Lin and Chameides, 1993) involving SO_3 rather than SO_2 as an intermediate. These parameters are:

(a) k_{23} and k_{22}, i.e. the reactions of the $CH_3SO_3 \bullet$ radical to form either SO_3 or MSA.

(b) k_{18}, i.e. the rate constant of a reaction leading to formation of $CH_3SO_3 \bullet$.

(c) k_{19}, i.e. the first step of an alternative pathway to the formation of $CH_3SO_3 \bullet$.

(d) k_{21}, i.e. a pathway to the formation of SO_2.

The average ratio between SO_3 and SO_2 is low (less than 2% yield of SO_3 in the polluted environment conditions and less than 0.3% in the unpolluted), so the present analysis does not attribute a major role to the SO_3-forming pathway. To the knowledge of the authors, no reports on laboratory studies of these reactions, apart from Reaction 21, are available in the literature.

Further, the analysis shows that reactions of the $CH_3S \bullet$ and, in particular, of the $CH_3SO_2 \bullet$ radicals are potentially very important sources of SO_2. Bearing in mind, that such reactions are only known as a hypothetical possibility, this result underlines the need for further investigations of this issue.

(2) The ratio $MSA/(SO_2 + H_2SO_4)$. The parameters which affect this ratio are the same which were identified in the previous paragraph. A comparison between model output and measured values of the ratio shows a qualitative agreement, although the uncertainties on k_{23} and k_{22} are considerable.

(3) Peroxynitrate intermediates. The most abundant peroxynitrate compound is, according to the present analysis, $CH_3S(O)_2O_2NO_2$. The concentrations at 298 K are below 1% of the DMS concentration but they are expected to be higher at lower temperatures and thus possibly of importance in atmospheric transport. Also heterogeneous reactions of these species on water droplets are of potential relevance as a source of MSA (Van Dingenen *et al.*, 1994).

We hope that this analysis will serve to identify some of the key questions to be answered by further research into the intricate atmospheric chemistry of DMS.

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References

Andreae, M. O. and Raemdonck, H., 1983, Dimethyl sulphide in the surface ocean and the marine atmosphere: a global view, *Science* **221**, 744–747.

Alcamo, J. and Bartnicki, J., 1990, The uncertainty of atmospheric source-receptor relationship in Europe, *Atmospheric Environment* **24A** (8), 2169–2189.

Bandy, A. R., Scott, D. L., Blomquist, B. W., Chen, S. M., and Thornton, D. C., 1992, Low yields of SO$_2$ from dimethyl sulfide oxidation in the marine boundary layer, *Geophys. Res. Lett.* **11**, 1125–1127.

Barnes, I., 1993, Private communication.

Barnes, I., Bastian, V., and Becker, K. H., 1988, Kinetics and mechanisms of the reaction of OH radicals with dimethyl sulphide, *Int. J. Chem. Kin.* **20**, 415–431.

Barnes, I., Bastian, V., Becker, K. H., and Niki, H., 1987, FTIR spectroscopic studies of the CH$_3$S + NO$_2$ reaction under atmospheric conditions, *Chem. Phys. Lett.* **140**, 451–457.

Bates, T. S., Calhoun, J. A., and Quinn, P. K., 1992, Variations in the methanesulfonate to sulfate molar ratio in submicrometer particles over the South Pacific Ocean, *J. Geophys.* **97**, 9859–9865.

Bates, T. S., Charlson, R. J., and Gammon, R. H., 1987, Evidence for the climatic role of marine biogenic sulphur, *Nature* **329**, 319–321.

Berresheim, H., 1987, Biogenic sulfur emissions from the Subantarctic and Antarctic oceans, *J. Geophys. Res.* **92**, 13245–13262.

Berresheim, H., Eisele, F. L., Tanner, D. J., McInnes, L. M., Ramsey-Bell, D. C., and Covert, D. S., 1993, Atmospheric sulfur chemistry and cloud condensation nuclei (CCN) concentrations over the Northeastern Pacific Coast, *J. Geophys. Res.* **98**, 12701–12711.

Bürgermeister, S. and Georgii, H. W., 1991, Distribution of methane sulfonate, nss-sulfate and dimethylsulfide over the Atlantic and over the North Sea, *Atmos. Environ.* **25A**, 587–595.

Charlson, R. J., Langner, J., Rodhe, H., Leovy, C. B., and Warren, S. G., 1991, Perturbation of the northern hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols, *Tellus* **43AB**, 152–163.

Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G., 1987, Oceanic phytoplancton, atmospheric sulphur, cloud albedo and climate, *Nature* **326**, 655–661.

Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley Jr., J. A., Hansen, J. E., and Hofman, D. J., 1992, Climate forcing by anthropogenic aerosols, *Science* **255**, 423–440.

Conover, W. J., 1980, *Practical Non-parametric Statistics*. 2nd edn., Wiley, New York.

Cukier, R. I., Levine, H. B., and Schuler, K. E., 1978, Nonlinear sensitivity analysis of multiparameter model systems, *J. Comput. Phys.* **26**, 1–42.

Cukier, R. I., Fortuin, C. M., Schuler, K. E., Petschek, A. G., and Schaibly, J. K., 1973, Study of the sensitivity of coupled reaction systems to uncertainties in rate coefficients, part I. Theory, *J. Chem. Phys.* **59**(8), 3873–3878.

De More, W. B., Golden, D. M., Howard, C. J., Hampson, R. F., Kolb, C. E., Kurylo, M. J., Molina, M. J., Ravishankara, A. R., and Sander, S. P., 1992, Chemical kinetics and photochemical data for use in stratospheric models, *JPL Publ.* 92–20.

Dominé, F., Ravishankara, A. R., and Howard, C. J., 1992, Kinetics and mechanisms of the reactions of CH$_3$S, CH$_3$SS, CH$_3$SO and CH$_3$SSO with O$_3$ at 300 K and low pressures, *J. Phys. Chem.* **96**, 2171–2178.

Draper, N. R. and Smith, H., 1981, *Applied Regression Analysis*, Wiley, New York.

Foley, J. A., Taylor, K. E., and Ghan, S. J., 1991, Planktonic dimethylsulfide and cloud albedo: an estimate of the feedback response, *Climatic Change*, 1–15.

Good, A. and Thynne, J. C. J., 1967, Reactions of free radicals with sulphur dioxide, *J. Chem. Soc. Faraday Trans.* **63**, 2708–2727.

Hatakeyama, S., Izumi, K., and Akimoto, H., 1985, Yield of SO$_2$ and formation of aerosol in the photooxidation of DMS under atmospheric conditions, *J. Phys. Chem.* **90**, 4148–4156.

Helton, J. C., 1993, Uncertainty and sensitivity analysis techniques for use in performance assessment for radioactive waste disposal, *Reliability Engineering and System Safety* **42**, 327–367.

Helton, J. C., Garner, J. W., McCurley, R. D., and Rudeen, D. K., 1991, Sensitivity analysis techniques and results for the performance assessment at the waste isolation pilot plant, *Sandia Laboratories Report* SAND90-7103.

Homma, T. and Saltelli, A., 1991, PREP (Statistical Pre-Processor); Program description and user guide, *CEC/JRC Sci. Techn. Rep.* EUR 13922 EN, Luxembourg.

Homma, T. and Saltelli, A., 1994, Global sensitivity analysis of nonlinear models. Importance measures and Sobol' sensitivity indices, CEC/JRC Sci. Techn. Rep. EUR 16052 EN, Luxembourg.

Hora, S. C. and Iman, R. L., 1986, A comparison of maximum/bounding and Bayesian/Monte Carlo for fault tree uncertainty analysis, *Sandia Laboratories Report* SAND85-2839.

Hynes, A. J., Wine, P. H., and Semmes, D. H., 1986, Kinetics and mechanism of OH reactions with organic sulfides, *J. Phys. Chem.* **90**, 4148–4156.

Iman, R. L. and Conover, W. J., 1987, A measure of top-down correlation, *Technometrics* **29** (3), 351–357.

Iman, R. L. and Conover, W. J., 1982, A distribution free approach to inducing rank correlation among input variables, *Comm. Statist.* **B11** (3), 311–334.

Iman, R. L. and Helton, J. C., 1985, A comparison of uncertainty and sensitivity analysis techniques for computer models, *Sandia Laboratories Report*, SAND84-1461.

Iman, R. L. and Helton, J. C., 1988, An investigation of uncertainty and sensitivity analysis techniques for computer models, *Risk Analysis* **8** (1), 71–90.

Iman, R. L., Helton, J. C., and Campbell, J. E., 1978, Risk methodology for geological disposal of radioactive waste: sensitivity analysis techniques, *Sandia Laboratory Report*, SAND78-0912.

Iman, R. L., Helton, J. C., and Campbell, J. E., 1981, An approach to sensitivity analysis of computer models, Parts I and II, *J. Quality Tech.* **13** (3, 4), 174–183 and 232–240.

Ishigami, T. and Homma, T., 1989, An importance quantification technique in uncertainty analysis, *Japan Atomic Energy Research Institute Report* JAERI-M 89-111.

Ishigami, T. and Homma, T., 1990, An importance quantification technique in uncertainty analysis for computer models, *Proc. ISUMA '90, 1st Int. Symp. Uncertainty Modelling and Analysis*, University of Maryland, USA, December 3–5, 1990, pp. 398–403.

Jensen, N. R. and Hjorth, J., 1995, Evidence for the formation of a stable intermediate in the tropospheric oxidation of DMS, *Geophys. Res. Lett.*, in press.

Jensen, N. R., Hjorth, J., Lohse, C., Skov, H., and Restelli, G., 1991, Products and mechanism of the reaction between NO_3 and dimethylsulphide in air, *Atmos. Environ.* **25A**, 1897–1904.

Jensen, N. R., Hjorth, J., Lohse, C., Skov, H., and Restelli, G., 1992, Products and mechanisms of the gas phase reactions of NO_3 with CH_3SCH_3, CD_3SCD_3, CH_3SH and CH_3SSCH_3, *J. Atmos. Chem.* **14**, 95–108.

Kiehl, J. T. and Briegleb, B. P., 1993, The relative roles of sulphate aerosols and greenhouse gases in climate forcing, *Science* **260**, 311–314.

Koga, S. and Tanaka, H., 1993, Numerical study of the oxidation process of dimethylsulfide in the marine atmosphere, *J. Atmos. Chem.* **17**, 201, 228.

Langner, J. and Rodhe, H., 1991, A global three-dimensional model of the tropospheric sulfur cycle, *J. Atmos. Chem.* **13**, 225–263.

Langner, J., Rodhe, H., Crutzen, P. J., and Zimmerman, P., 1992, Anthropogenic influence on the distribution of tropospheric sulphate aerosol, *Nature* **359**, 712–716.

Lelieveld, J. and Heintzenberg, J., 1992, Sulphate cooling effect on climate through in-cloud oxidation of anthropogenic SO_2, *Science* **258**, 117–120.

Liepman, D. and Stephanopoulos, G., 1985, Development and global sensitivity analysis of a closed ecosystem model, *Ecological Modelling* **30**, 13–47.

Lin, X. and Chameides, W. L., 1993, CCN formation from DMS oxidation without SO_2 acting as an intermediate, *Geophys. Res. Lett.* **20** (7), 579–582.

Mellouki, A., Jourdain, J. L., and Le Bras, G., 1988, Discharge flow study of the $CH_3S + NO_2$ reaction mechanism using $Cl + CH_3SH$ as the CH_3S source, *Chem. Phys. Lett.* **2, 3**, 231–236.

Mihalopoulos, N., Nguyen, B. C., Boissard, C., Campin, J. M., Putaud, J. P., Belviso, S., Barnes, I., and Becker, K. H., 1992, Field study of dimethylsulfide oxidation in the boundary layer: Variations of dimethylsulfide, methanesulfonic acid, sulfur dioxide, non-sea-salt sulfate and Aitken nuclei at a coastal site, *J. Atmos. Chem.* **14**, 459–477.

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.

Putaud, J.-P., Belviso, S., Nguyen, B. C., and Mihalopoulos, N., 1993, Dimethylsulfide, aerosols and condensation nuclei over the tropical Northeastern Atlantic Ocean, *J. Geophys. Res.* **98**, 14863–14871.

Restelli, G. and Angeletti, G. (eds.), 1993, *Proc. Int. Symp. Dimethylsulfide, Oceans, Atmosphere and Climate, Belgirate (I)*, Kluwer, Dordrecht.

Saltelli, A., Andres, T., and Homma, T., 1993a, Sensitivity analysis of model output. An investigation of new techniques, *Comp. Statistics Data Analysis* **15**, 211–238.

Saltelli, A. and Homma, T., 1991, SPOP; Program description and user guide, *CEC/JRC Scient. Techn. Report* EUR 13924 EN, Luxembourg.

Saltelli, A. and Homma, T., 1992, Sensitivity analysis for model output. Performance of black-box techniques on three international benchmark exercises, *Comp. Statistics Data Analysis* **13**, 73–94.

Saltelli, A., Homma, T., Raes, F., Wilson, J., and Van Dingenen, R., 1993b, Modelling of the sulphur cycle. From DMS to cloud particles, see Restelli and Angeletti 1993 (eds.).

Saltelli, A. and Marivoet, J., 1988, Safety assessment for nuclear wate disposal. Some observations about actual risk calculations, *Radioactive Waste Management and the Nuclear Fuel Cycle* **9** (4), 309–321.

Saltelli, A. and Marivoet, J., 1990, Nonparametric statistics in sensitivity analysis for model output; A comparison of selected techniques, *Reliability Engineering and System Safety* **28**, 229–253.

Saltzman, E. S., Savoie, D. L., Prospero, J. M., and Zika, R. G., 1986, Methane sulfonic acid and non-sea-salt sulfate in pacific air: Regional and seasonal variations, *J. Atmos. Chem.* **4**, 227–240.

Schaibly, J. K. and Schuler, K. E., 1973, Study of the sensitivity of coupled reaction systems to uncertainties in rate coefficients. Part II, Applications, *J. Chem. Phys.* **59** (8), 3879–3888.

Schwartz, S. E., 1988, Are global cloud albedo and climate controlled by marine phytoplankton? *Nature* **336**, 441–445.

Shaw, G. E., 1993, Bio-controlled thermostasis involving the sulphur cycle, *Climatic Change* **5**, 297–303.

Sobol', I. M., 1990, Sensitivity estimates for nonlinear mathematical models, *Matematicheskoye Modelirovaniye, 1990*, **2** (1), 112–118 (in Russian), translated in *Math. Model. Comput. Experiments* **1** (4), 407–414 (1993).

Sobol', I. M., 1991, Quasi Monte Carlo methods, *Progress in Nuclear Energy* **24**, 55–61.

Spiro, P. A., Jacob, D. J., and Logan, J. A., 1992, Global inventory of sulphur emissions with $1° \times 1°$ resolution, *J. Geophys. Res.* **97**, 6023–6036.

Thompson, A. M. and Stewart, R. W., 1991, Effects of chemical kinetics uncertainties on calculated constituents in a tropospheric photochemical model, *J. Geophys. Res.* **96**, D7, 13,089–13,108.

Turnipseed, A. A., Barone, S. B., and Ravishankara, A. R., 1992, Observation of CH_3S addition to O_2 in the gas phase, *J. Phys. Chem.* **96**, 7502–7505.

Turnipseed, A. A., Barone, S. B., and Ravishankara, A. R., 1993, Reactions of CH_3S and CH_3SOO with O_3, NO_2 and NO, *J. Phys. Chem.* **97**, 5926–5934.

Turnipseed, A. A. and Ravishankara, A. R., 1993, The atmospheric oxidation of dimethyl sulfide: Elementary steps in a complex mechanism, see Restelli and Angeletti 1993 (eds.).

Tyndall, G. S. and Ravishankara, A. R., 1989, Kinetics and mechanisms of the reactions of CH_3S with O_2 and NO_2 at 298 K, *J. Phys. Chem.* **94**, 5839–5847.

Tyndall, G. S. and Ravishankara, A. R., 1991, Atmospheric oxidation of reduced sulfur species, *Int. J. Chem. Kinet.* **23**, 483–527.

Vajda, S., Valko, P., and Turányi, T., 1985, Principal component analysis of kinetic models, *Int. J. Chem. Kinetics* **17**, 55–81.

Van Dingenen, R., Jensen, N. R., Hjorth, J., and Raes, F., 1994, Peroxynitrate formation during the night-time oxidation of dimethylsulphide: its role as a reservoir species for aerosol formation, *J. Atmos. Chem.*, **18**, 211–237.

Wigley, T. M., 1989, Possible climate change due to SO_2-derived cloud condensation nuclei, *Nature* **339**, 365–339.

Yin, F., Grosjean, D., and Seinfeld, J. H., 1990, Photooxidation of dimethyl sulfide and dimethyl disulfide, I. Mechanism development, *J. Atmos. Chem.* **11** (4), 309–364.

Yin, F., Grosjean, D., Flagan, R. F., and Seinfeld, J. H., 1990b, Photooxidation of dimethyl sulfide and dimethyl disulfude, II. Mechanism evaluation, *J. Atmos. Chem.* **11** (4), 365–399.