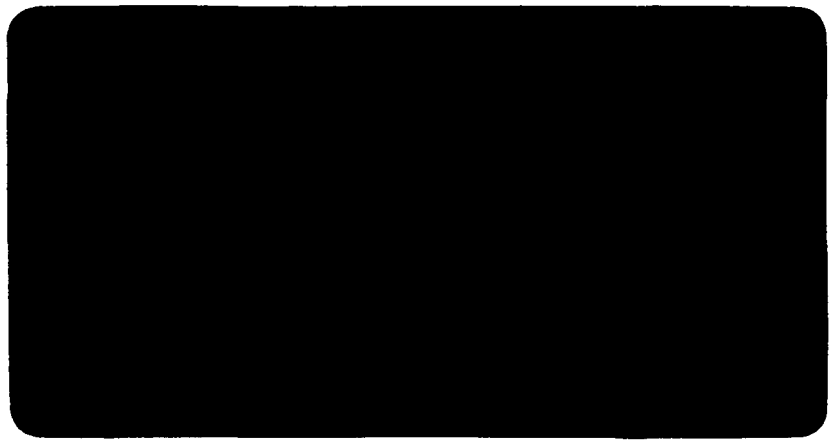
NASA CR-166818

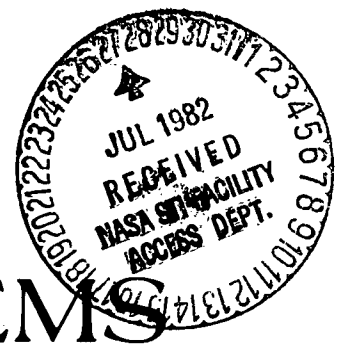
SSAI

(NASA-CR-166818) OZONE UNCERTAINTIES STUDY ALGORITHM (OUSA) Final Technical Report (Science Systems and Applications, Inc.) 24 p HC A02/MF A01 CSCL 04A

N82-29793

Unclas G3/46 26419





SCIENCE SYSTEMS AND APPLICATIONS, INC.

10210 Greenbelt Road, Suite 140
Seabrook, MD 20801
Telephone (301) 794-6633
794-6634

OZONE UNCERTAINTIES STUDY ALGORITHM (OUSA)

A Final Technical Report
Prepared by Om P. Bahethi
For
NASA/GSFC Contract: NAS5-26083

SCIENCE SYSTEMS AND APPLICATIONS, INC.
10210 Greenbelt, Rd., Suite 140
Seabrook, MD 20706
(301) 794-6633

ABSTRACT

This report describes an algorithm to carry out sensitivities, uncertainties and overall imprecision studies to a set of input parameters for a one dimensional steady state ozone photochemistry model. This algorithm can be used to evaluate steady state perturbations due to point source or distributed ejection of H2O, CLX, and NOX, besides, varying the incident solar flux. This algorithm is operational on IBM OS/360-91 computer at NASA/Goddard Space Flight Center's Science and Applications Computer Center (SACC).

CONTENTS

CONTENTS

LIST OF ILLUSTRATIONS

1. INTRODUCTION

Rundel, Butler and Stolarski (1) have carried out stratospheric ozone uncertainties studies using a Monte-Carlo method. This algorithm uses an atmosphere covering altitudes 0-60 km for user specified thicknesses of 1.25 to 5.0 km. The algorithm incorporates odd oxygen, nitrogen, hydrogen and chlorine chemistry and utilitizes 58 chemical reactions described in Table 1. The fixed (user input) profiles of N2, O2 and CO2 (stable molecules) are used. The concentrations of N2O, H2O, H2 and CH4 are determined from self consistent diffusion calculations with fixed boundary conditions for the above species. The OX, and CO are calculated by solving differential equations using boundary conditions chosen to reproduce the atmospheric measurements.

For analyzing the uncertainties of stratospheric perturbations, this algorithm uses techniques of decoupling iterations. The differential equations solved are:

a. diffusion equations

b. local photo-chemical equations for species or ratio of species.

This algorithm is capable of carrying out uncertainties studies for an altitude range of 0-60 km in steps of 1.25 km. Table 1 shows the basic chemistry of the odd oxygen, nitrogen, hydrogen, chlorine compounds together with the methane oxidation chain.

In general the steady state distribution of an atmospheric trace gas (j) is calculated by solving the continuity equation:

$$\nabla \cdot \phi_j = P_j(\{n_k\}) - L_j(\{n_k\}), \quad (1)$$

where n_{kj} is he number density of the jth specie. ϕ_j is the flux vector, Pj and Lj are the chemical production and loss terms. $\{n_k\}$ denotes the set of

TABLE 1. REACTIONS USED IN OUSA ALGORITHM

	Reactions	Reaction Number
1.	$Cl + O_3 \rightarrow ClO + O_2$	(42)
2.	$ClO + O \rightarrow Cl + O_2$	(43)
3.	$ClO + NO \rightarrow Cl + NO_2$	(46)
4.	$Cl + H_2 \rightarrow HCL + H$	(40)
5.	$Cl + NO_2 \rightarrow HCl + O_2$	(41)
6.	$Cl + CH_4 \rightarrow HCl + CH_3$	(44)
7.	$Cl + H_2O_2 \rightarrow HCl + HO_2$	(13)
8.	$HCl + OH \rightarrow Cl + H_2O$	(45)
9.	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	(52)
10.	$ClONO_2 + O \rightarrow ClO + NO_3$	
11.	$ClONO_2 + OH \rightarrow HOCl + NO_3$	(25)
12.	$O + O_2 + M \rightarrow O_3 + M$	(2)
13.	$O + O_3 \; O_2 + O_2$	(4)
14.	$NO + O_3 \rightarrow NO_2 + O_2$	(15)
15.	$NO_2 + O_3 \rightarrow NO_3 + O_2$	(16)
16.	$OH + O_3 \rightarrow HO_2 + O_2$	(9)
17.	$HO_2 + O_3 \rightarrow OH + O_2 + O_2$	(10)
18.	$H + O_3 \rightarrow HO + O_2$	(22)
19.	$NO_2 + O \rightarrow NO + O_2$	(17)
20.	$NO_2 + O + M \rightarrow NO_3 + M$	(19)
21.	$OH + O \rightarrow H + O_2$	(7)
22.	$HO_2 + O \rightarrow OH + O_2$	(11)
23.	$H_2O_2 + O \rightarrow OH + HO_2$	(55)
24.	$HNO_3 + O \rightarrow OH + NO_3$	(48)
25.	$CH_2O + O \rightarrow HCO + OH$	(37)
26.	$N_2O + O(^1D) \rightarrow NO + NO$	(1)
27.	$H_2O + O(^1D) \rightarrow OH + OH$	(5)
28.	$H2 + O(^1D) \rightarrow OH + OH$	(26)

29. $CH_4 + O(^1D) \rightarrow OH + H$ (21)

30. $CH_4 + O(^1D) \rightarrow H_2 + CH_2O$ (54)

31. $O(^1D) + M \rightarrow O(^3P) + M$ (14)

32. $NO + NO_3 \rightarrow NO_2 + NO_2$ (49)

33. $N + NO \rightarrow N_2 + O$ (35)

34. $N + O_2 \rightarrow NO + O$ (36)

35. $N + O_3 \rightarrow NO + O_2$ (56)

36. $NO + HO_2 \rightarrow NO_2 + OH$ (3)

37. $NO_2 + OH + M \rightarrow HNO_3 + M$ (18)

38. $OH + HNO_3 \rightarrow NO_3 + H_2O$ (20)

39. $OH + H_2O_2 \rightarrow HO_2 + H_2O$ (47)

40. $OH + HO_2 \rightarrow O_2 + H_2O$ (6)

41. $OH + OH \rightarrow O + H_2O$ (12)

42. $HO + H_2 \rightarrow H + H_2O$ (50)

43. $OH + CH_4 \rightarrow CH_3 + H_2O$ (29)

44. $OH + CH_2O \rightarrow HCO + H_2O$ (38)

45. $OH + CH_3Cl \rightarrow Ch_2Cl + H_2O$ (32)

46. $OH + CO \rightarrow CO_2 + H$ (28)

47. $OH + OH + M \rightarrow H_2O_2 + M$ (23)

48. $H + O_2 + M \rightarrow HO_2 + M$ (8)

49. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (24)

50. $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ (30)

51. $CH_3O_2 + NO \rightarrow CH_3O + NO_2$ (31)

52. $CH_3O_2 + NO_2 \rightarrow CH_3O + NO_3$ (53)

53. $CH_3O_2 + HO_2 \rightarrow CH_3OOH + NO_2$ (33)

54. $CH_3O + O_2 \rightarrow CH_2O + HO_2$ (34)

55. $HCO + O_2 \rightarrow CO + HO_2$ (39)

56. $CH_4 + O(^1D) \rightarrow CH_3 + OH$ (27)

57. $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ (21)

58. $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ (51

all reactants which enter into the chemistry of the jth specie. The net upward eddy flux is approximated by

$$\Phi_j = -K_j [M] \frac{df_j}{dz} , \qquad (2)$$

where K_j is the vertical eddy coefficient. [M] is the density of air and $f_j = \frac{x_j}{M}$ denotes the volume mixing ratio of a given constituent x_j.

2. COMPUTATION PROCEDURE

Figure 1 illustrates the flow-chart of the calculations of ambient constituents concentrations in the model and the method used for chemical families and obtaining self-consistent finally conveged species by iteration. The calculations sequence consists of:

1. Initial (starting)values of O3, HOX, NOX, CLX.....etc.
2. Calculate column content of O3
3. Calculate J-coefficients
4. Calculate O/O3, O(1D)/O3, O3/OX (photo-chemical equilibrium)
5. Calculate new OX (diffusion)
6. Calculate N2O (diffusion)
7. Calculate HOX (OH, H, HO2, H2, O2 photo-chemical equilbrium)
8. Calculate CH4, H2, H2O (diffusion)
9. Calculate CH4 - oxidation products (photo-chemical equilbrium)
10. Calculate CO (diffusion)
11. Calculate CCl4, CH3Cl, CF2Cl2, CFCL3 (diffusion)
12. Calculate CLX (diffusion)
13. Calculate CL, CLO, HCL, CLONO2, from CLX (photo-chemical equilibrium)
14. Calculate odd nitrogen (diffusion)
15. Calculate NO, NO2, NO3, HNO3 from odd nitrogen

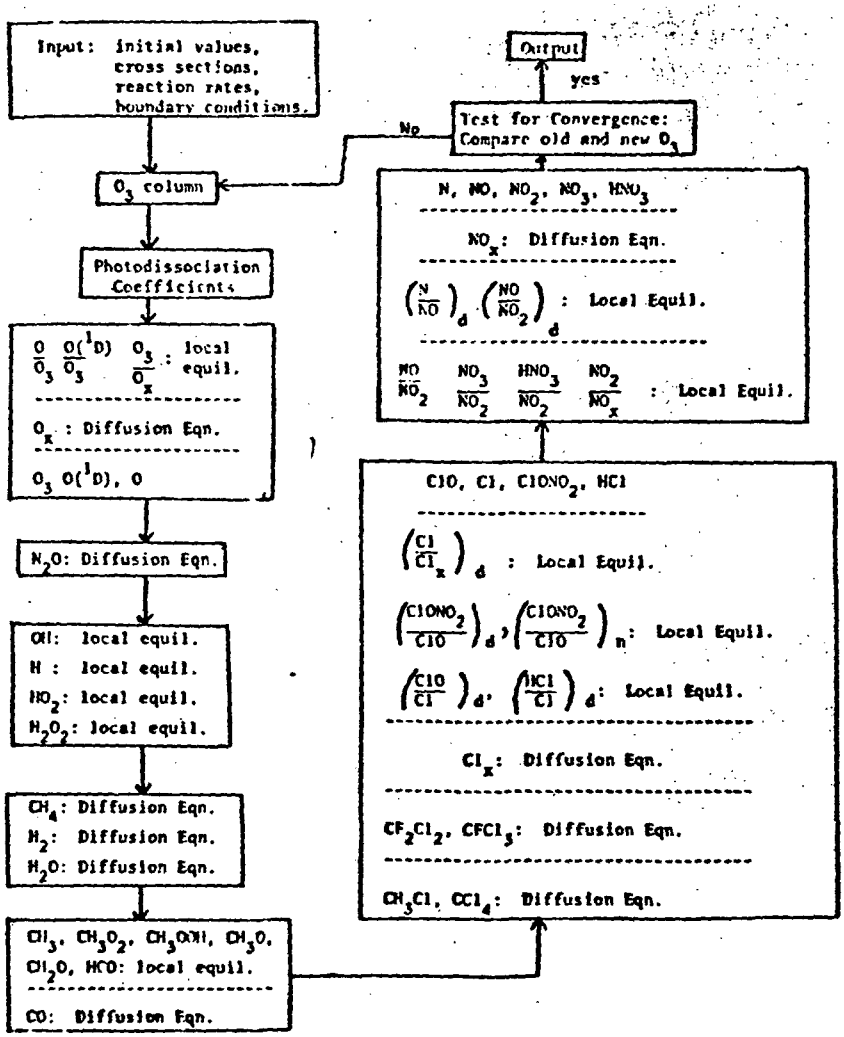


Figure 1. Flow-chart of OUSA Algorithm Computations

16. Recycle to 2.

Imprecision of rate constants used for the reactions in Table 1 may range from small (10 to 15%) to large (up to factor of 10) variation from the mean values. Such a large degree of variation is most coveniently dealt with by using logarithmic variation. Monte-Carlo calculation necessitates a probability function for each reaction rate. OUSA algorithm uses a Gaussian distribution in log-k (reaction rate) and the probability distribution is given by

$$P(\log k) \propto e^{-(\log k)^2/2\sigma}, \qquad (3)$$

where σ is the standard deviation.

2.2 Subroutine Main (OUSA)

This subroutine is a driver program calling most of the subroutine detailed in Figure 2. The subroutines called by this routine are:

1. Images
2. ERRSET*
3. INPUT
4. DIFFUS
5. OUT1
6. GGNRF
7. COMPK
8. O3COL
9. JCOEFF
10. OX
11. N2OD
12. HOX
13. CH4D
14. CH4
15. CLX
16. NOX
17. CVAL
18. OUT2
19. OUTPUT
20. RDPERT (FLUXBC, POINT, DIST, SOLAR, MIXING)
21. OUT3

*ERRSET - is system routine to prevent printout due to underflows.

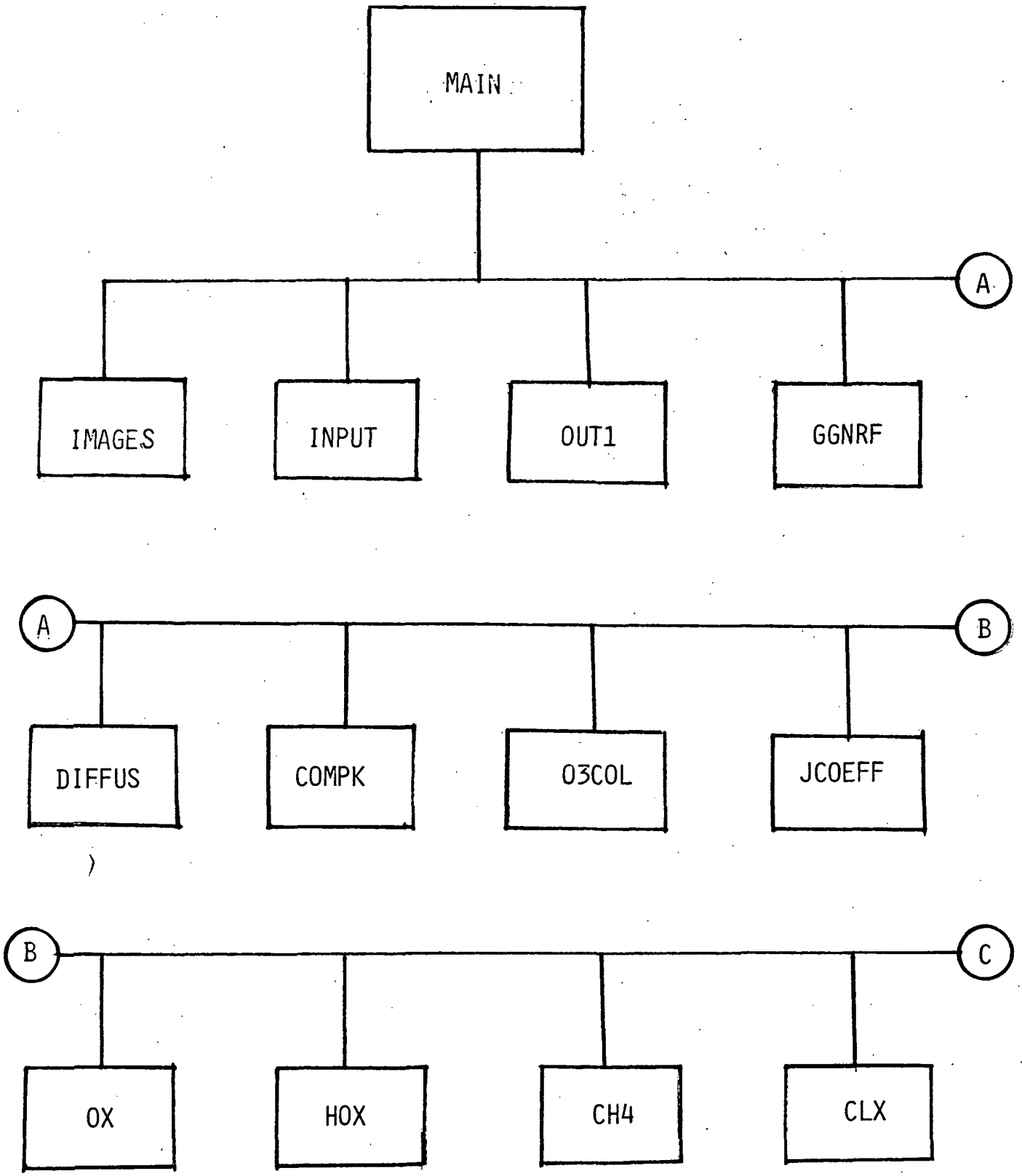


Figure 2 - Block Diagram For OUSA Algorithm

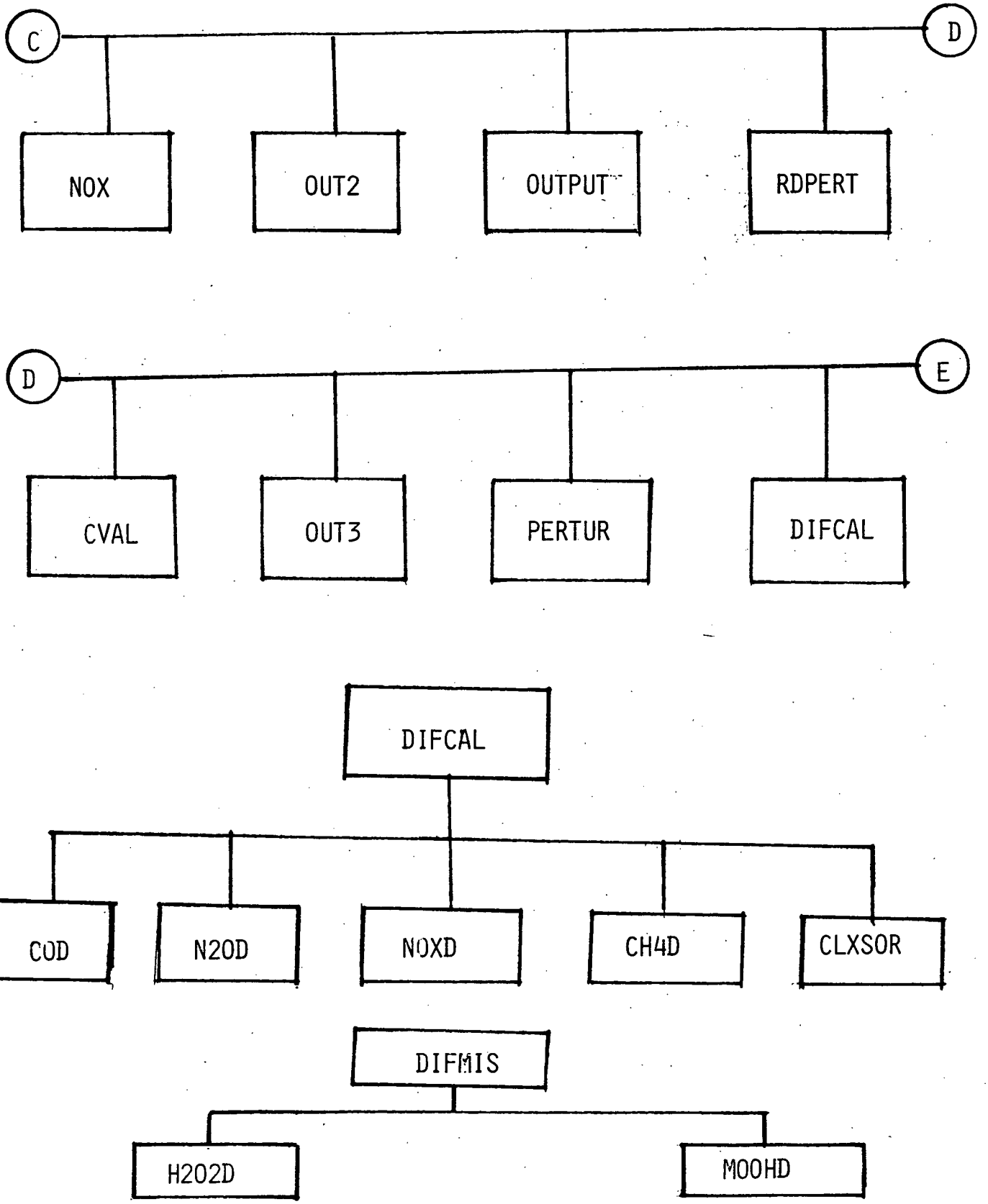


Figure 2 - Block Diagram For OUSA Algorithm

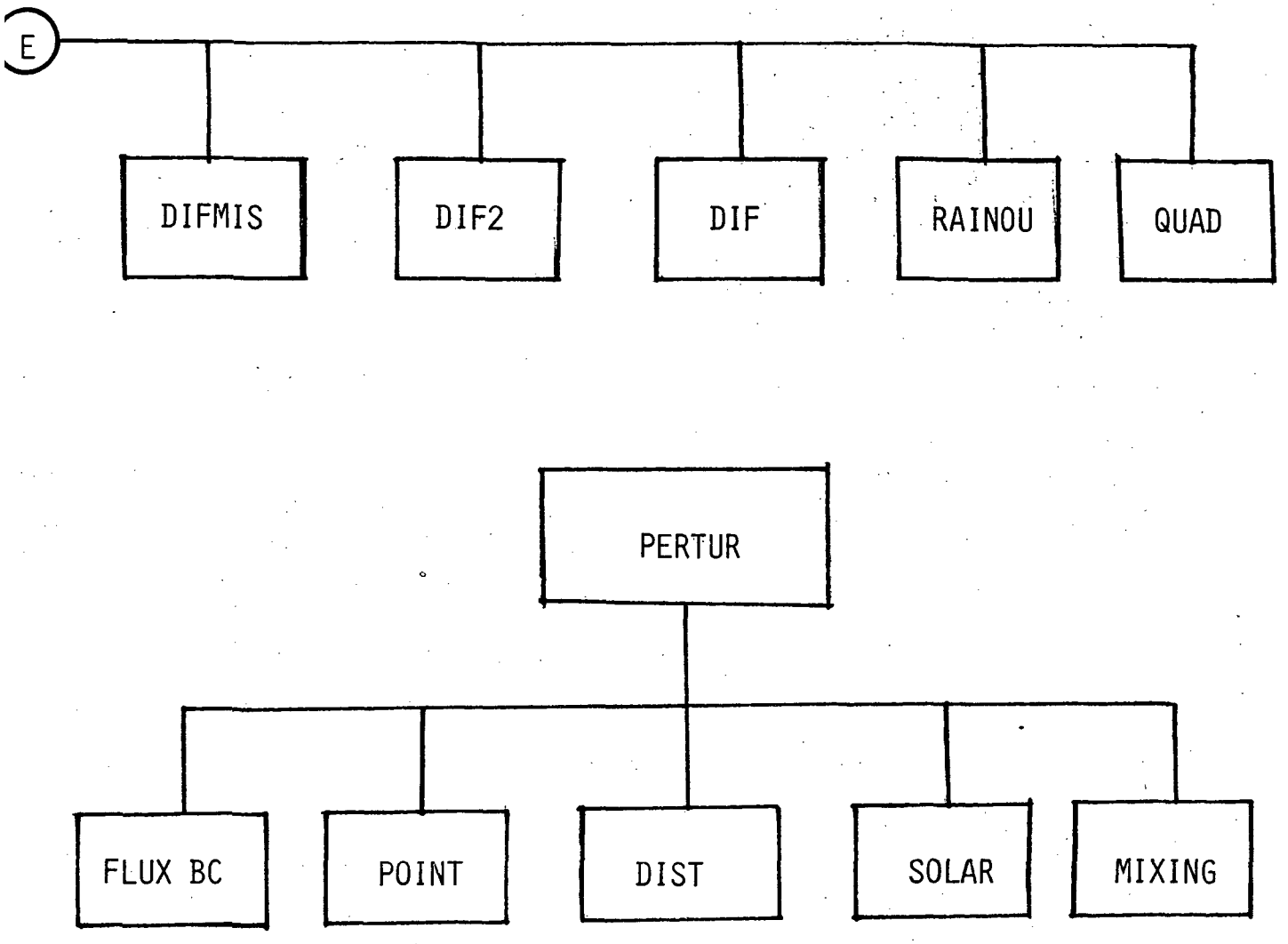


Figure 2 Block Diagram For OUSA Algorithm

Besides calling for input and output operations via subroutines; INPUT, OUT1, OUT2, OUT3, and OUTPUT, this program initiates the routines to provide normal distribution of random number (DO LOOP 111). It provides the initial values of various species, productions parameters, reactions dissociation rates etc.,.

The statements 16300-18100 carryout computations for the ambient atmosphere and the convergence of ozone amounts at each atmospheric levels. Depending upon the input print out criterion, the various species concentration and mixing ratios are printed and the uncertainity studies species are stored on a magnetic tape.

The statements 20700-31200 repeat the computations identical to the ambient atmosphere (detailed in the preceding paragraph) for a perturbed atmosphere by using the following selection of perturbations, invoked via the subroutine RDPERT:

1. Flux boundary
2. Point Sources
3. Distributed Sources
4. Variation of Solar Irradiance
5. Variations of Mixing Ratios.

The unformatted output of this program is stored on the magnetic tape (unit-8) and is used with the program STATIS for computing the statistics of Monte-Carlo simulations of ozone uncertaintity studies.

2.3 Subroutine IMAGES

This subroutine is employed to obtain the echo-check of the input data specified for a given data unit. For the OUSA algorithm the input

resides on unit 5 and 11. It consists of initial atmospheric parameters and perturbations related parameters.

2.4 Subroutine INPUT

This subroutine provides the initial atmospheric parameters for the execution of OUSA algorithm. Table 2 shows the INPUT parameters together with their explanations.

2.5 Subroutine DIFFUS

The main purpose of this subroutine is to compute the diffusion related parameters and the molecular number density at all the levels of the atmosphere using Mo (number density at bottom) values.

2.6 Subroutine COMPK

This subroutine is used for calculating two body and three body reaction rates in accordance with a NASA report (2). Depending on the algorithm central line option or uncertainty (Monte-Carlo) simulations, these reaction rates are multiplied by a log-normal random distribution.

2.7 Subroutine OUT1

This subroutine is employed to print the initial atmospheric constituents, as a function of altitude and parameters related to "run" setup, the reaction rates related variables, diffusion parameters etc.,.

2.8 Subroutine O3COL

This subroutine is employed for calculating the columnar ozone amounts at the various levels of the atmosphere.

2.9 Subroutine JCOEFF

The photo-dissociation coefficients for various reactions shown in

TABLE 2. INPUT PARAMETERS

1.	NOPERT	-Number of kind of perturbations
2.	IRAND	-Number of Monte Carlo simulation for each perturbation
3.	IMIX	-Flag for printing of mixing ratio boundary i.e., if IMIX=0 print
4.	IFLX	-Flag for printing for flux boundary conditions i.e., if IFLX=0, then print
5.	ZBOT	-Altitude of bottom of atmosphere
6.	ZINC	-Altitude increment (in km) for each level of atmosphere
7.	NZ	-Number of atmospheric levels
8.	M(1)	-Molecular number density at the bottom of the atmosphere
9.	NTROP	-Level number for the troposheric layer
10.	TT(1)	-Input temperature at various levels
11.	K1, A1, B1, K3, K4, K2	-These are eddy diffusion parameters
12.	VOLN	-Diffusion related parameter
13.	FLXFAC	-Flux factor
14.	TEST	-Convergence test value for the ozone amount at each level
15.	FBC(I)	-Boundary values of fluxes

	MR(I)	-Boundary values of mixing ratios
17.	IOPT(I)	-Options for flux and mixing ratio boundary conditions
18.	QCOI(I), QCH4(I),QH2(I) QH2O(I), QCLX(I), QN2O(I)	-Values of carbon monoxide, methane, hydrogen, water, sun chlorine specie, nitricoxide,
19.	RAIN(I), SOL(I)	-Rain out and solubility parameters as a function of height
20.	S1(I)....S17(I) J(1,I)....J(22,I)	-Absorption cross sections and rates as a funtion of height
21.	K(I), E(I), I=1,60	-Rates and energy parameters for reactions
22.	U(I), USEN(I), USENH(I); I=1,60	-Reactions rates uncertainty parameters

Table 1 are calculated using the solar flux and absorptions cross-section. The solar spectrum is divided into 25 regions beyond 3200A°. These calculations are done by assuming no attenutions of incident solar radiation. The incident solar flux below 3200 A is assumed to be absorbed by 02 and 03 and the attenuation due to other species is assumed to be optically thin. The photo-disociation coefficients are diurnally averaged by using Rundel's technique (3).

2.10 Subroutine OX

This subroutine computes the daytime and 24 hour averages for concentration of O, O(1D), and 03. After each entry to this subroutine, the loss and production terms (CCi and DDi) are computed and upper and lower boundary conditions are set. The diffusion computations are then accomplished by using subroutine DIF.

2.11 Subroutine DIFCAL

This subroutine is used for computing the steady state values of various species by taking into account eddy diffusion. This routine has following entry points to carry out diffusion computation of various species:

	ENTRY POINTS	PURPOSE
1.	COD	Carbon monoxide
2.	N2OD	Nitrous oxide
3.	NOXD	Odd nitrogen
4.	CH4D	Methane
5.	CLXSOR	Carbon tetra-chloride
6.	CLXPER	CFC13 and CF2C12

7.	CLXDIF	Odd chlorine
8.	OXD	Odd oxygen

The calculations for diffusion of hydrogen and water are carried out after the completion of methane diffusion.

After each entry to the above points the loss and production terms (CCi and DDi) are computed and upper and lower boundary conditions are set. The diffusion computations are then accomplished by using subroutine DIF.

2.12 Subroutine DIF

This subroutine solves the differential equation by using the Nicholson method. Depending on the upper and lower boundary conditions for each specie, the differential equation is then solved for the all the atmospheric levels. The variable Ri (i=1, NZ) returns the mixing ratio values for the specie desired in diffusion computation.

2.13 Subroutine CH4

This subroutine is used for obtaining the values of CH3, CH3O2, H2CO, and HCO species. In order to carry out diffusion computation for the methyl hydrogen peroxide (CH3COOH) and for carbon monoxide, this subroutine makes call to entries MOOHD and COD via subroutine DIFMIS.

2.14 Subroutine NOX

This subroutine carries out the NOX (N, NO, NO2, NO3, N2O5, CLONO2 and HNO3) computation using local photo-equilibrium and CLONO2/NO2, HNO3/NO2, NO3/NO2, NO/NO2, and NO2/odd nitrogen ratio computations. N2O5 day-day and night-night effects are also used in these computations. This subroutine also calls for the entry to DIF program to perform

diffusion calculations for the odd nitrogen.

2.15 Subroutine HOX

This subroutine carries out the HOX (OH + HO2 + HCO + H) related computations using steady state values and day-night effects. This subroutine also invokes the entry point H2O2D to DIFMIS subroutine where the hydrogen peroxide diffusion calculations are carried out.

2.16 Subroutine CLX

This subroutine carries out source calculations for CLX solving differential equations for each source molecule assuming a fixed mixing ratio at specified height and zero flux at the top of the atmosphere. This subroutine calls for the entry points CLXSOR (selection for CCl4 and CH3Cl) and CLXPER (for Flouro-Carbon-11 and Flouro-Carbon 12) diffusion calculations in subroutine DIFCAL. This subroutine accounts for the day effects of HOCL/CL, CLO/CL and day night effects for CLONO2 and CLO. It is assumed that HCL concentrations do not vary on a 24 hour time scale. The day is approximated by 12 hours of constant insolation and night as 12 hours of complete darkness. It is also assumed that CL/CLO approaches a rapid equilibrium.

2.17 Subroutine DIF2

This subroutine is used for calculating diffusion of water.

2.18 Subroutine DIFMIS

This subroutine is used for calculating the hydrogen peroxide and methyl hydrogen peroxide diffusion.

2.19 Subroutine OUT2

This subroutine prints out the number density and mixing ratio as a

function of height for the converged ambient atmosphere iterations.

2.20 Subroutine OUTPUT

This subroutine carries out OX loss and production terms and prints them as a function of height.

2.21 Subroutine CVAL

This subroutine carries out mixing ratio calculation for a large number of molecular species.

2.22 Subroutine RAINOU

This subroutine computes rainout concentrations of water, odd N, H2O2 and odd CL.

2.23 Subroutine OUT3

This subroutine prints out the densities and mixing ratios for various constituents for converged perturbed atmosphere.

2.24 Subroutine RDPERT

This subroutine provides user-option perturbation parameters input for flux boundary conditions, injection of various specie at different altitudes, specie profile changes, solar insolation variation, and mixing ratio boundary parameters alterations.

2.25 Subroutine PERTUR

This subroutine enters the user specified perturbations input parameters. The values of these input parameters are printed out as well.

2.26 Subroutine GGNRX

This is an IBM OS/360 assembly language program to obtain fast

normal random number generation. It calls for assembler control section GGNRF (N,A), where A sets the seed for N normal random number generation.

3. REFERENCES

1. Rundel, R.D., Butler, D.M., and Stolarski, R.S., Uncertainty Propogation in a Stratospheric Model 1. Development of Concise Stratospheric Model, J. Geo. Phys. Res. 83 , 3036 (1878).

2. The Stratosphere Present and Future - NASA Technical Report RP-1049 (1979), Edited by R.D. Hunson.

3. Rundel, R.D., Determination of Diurnal Average Photo-Dissociation Rates, J. Atmos. Sci. 34, 639 (1977).

4. PROGRAM JOB CONTROL LANGUAGE (JCL) CARDS

The following listing details the IBM OS/360 Job Control Language (JCL) cards needed to successfully compute the OUSA program. Various subroutines detailed in section 2 are preserved under the library Z10PB LIB OM03. The input data is stored on member DATA3 and perturbation parameters are accessible through the member PERTZERO. The output of this run are stored on a magnetic tape for future statistical analysis.

```
//Z10PBRUN JOB (L40041195A,T,0PB001,H01H03),059,MSGLEVEL=1                00
//*COMP-RUN                                                               00
//FORT EXEC FORTRANH,PARM='MAP,XREF'                                      00
//SOURCE.SYSIN DD DISP=SHR,DSN=Z10PB.LIB.OM03(DMAIN)                      00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DIMAGES)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DIN)                              00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DDIFFUS)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DCOMPK)                           00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DOUT1)                            00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DO3COL)                           00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DQUAD)                            00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DJCOEFF)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DOX)                              00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DDIFCAL)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DDIF)                             00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DCH4)                             00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DNOX)                             00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DHOX)                             00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DCLX)                             00
```

```
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DDIF2)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DDIFMIS)                        00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DOUT2)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DOUTPUT)                        00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DCVAL)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DRAIN)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DOUT3)                          00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DRDPERT)                        00
//       DD DISP=SHR,DSN=Z10PB.LIB.OM03(DPERTUR)                        00
/*                                                                      00
//ASMG EXEC ASMG                                                        00
//SOURCE.SYSIN DD DISP=SHR,DSN=Z10PB.LIB.OM03(GGNRF)                    00
/*                                                                      00
//TROPO EXEC LOADER,PROG=LINKER,PARM='SIZE=380K,EP=MAIN',REGION.GO=380K 00
//GO.SYSLIB DD DISP=SHR,DSN=SYS2.IMSLS                                  00
//GO.FT05F001 DD DISP=SHR,DSN=Z10PB.LIB.OM03(DATA3),LABEL=(,,,IN)       00
//GO.SYSUDUMP DD SYSOUT=A,SPACE=(CYL,(2,2))                             00
//GO.FT08F001 DD DSN=Z10PB.BAHETHI,DISP=(NEW,KEEP),UNIT=(6250,,DEFER),  00
//    LABEL=(4,NL,,OUT),DCB=(RECFM=VBS,LRECL=3244,BLKSIZE=16224,DEN=3),  00
//    VOL=SER=DB0002                                                    00
//GO.FT11F001 DD DISP=SHR,DSN=Z10PB.LIB.DATA(PERTZERO),LABEL=(,,,IN)    00
/*                                                                      00
//NOTIFY  EXEC NOTIFYTS,MSG='TROP DONE'                                 00
//                                                                      00
```

5. FORTRAN LISTING OF ALGORITHM

SEE THE ENCLOSED COMPUTER PRINTOUT

6. INPUT PARAMETERS

SEE THE ENCLOSED COMPUTER PRINTOUT

7. OUTPUT FROM TEST RUN

SEE THE ENCLOSED COMPUTER PRINTOUT