

PHOTOCHEMICAL REACTIONS IN THE ATMOSPHERE – A SOURCE OF SECONDARY POLLUTANTS

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In the atmosphere polluting agents are involved in different reactions which lead to secondary pollutants. Secondary pollutants are mainly generated by photochemical and thermal reactions. These reactions occur in the atmosphere and they generate photochemical smog. We studied the variations of primary and secondary pollutants concentrations by photochemical modeling systems. All the test problems (denoted models A-F) were coded in Fortran and are based on the Carbon Bond Mechanism IV consisting of 32 chemical species involved in 70 thermal and 11 photolytic reactions. The numerical integration of the stiff systems was carried out using a Rosenbrock solver.

Introduction

Atmosphere pollution may have natural causes (forest fires, vulcanic eruptions, pollen, dust). It may also be caused by human activities (industrial processes, traffic, agriculture, thermal stations).

Each source/process which causes changes in normal composition of air releases so-called primary polluting agents in the atmosphere. These are compounds which are released in the atmosphere as they are: carbon oxides, nitric oxides, sulphur oxides, hydrocarbons (methane and non methane, volatile organic compounds, aldehydes, ketones, total suspended particulates).

Chemical species resulted from microbial metabolism and organic compounds released by trees in low atmosphere are also considered primary polluting agents.

These compounds are implied in hydroxyl radical production in the atmosphere. As an example, isoprene reacts with HO radicals generating O_3 and other chemical species. These reactions open a new pathway in studying models' predict. But the researchers found that chemicals in air masses that come from the forested area did change with a change in temperature. Forest-generated emissions change a lot with temperature. Isoprene is the forest generated chemical with the largest piece of the emission pie, but it is produced only in during day. Other compounds, terpene respectively, are produced around the clock and are also temperature sensitive (5).

In the atmosphere molecules of primary polluting agents can take part in different reactions (thermal, photochemical) which lead to new compounds – secondary polluting agents; these are more dangerous for human body than the substances which generated them.

Structure of secondary polluting agents differs from the structure of primary polluting agents and it depends on nature and concentration of primary polluting agents, atmospheric conditions (temperature, humidity, solar radiations) and the reaction cycle they take part in. The majority of secondary polluting agents are formed in photochemical reactions which occur in atmosphere and generate photochemical smog. The generation of photochemical smog is conditioned by simultaneous presence of nitric oxides, hydrocarbons and solar radiation. The oxidant capacity of some secondary polluting agents which generate photochemical smog (O_3 , peracyl nitrates) explain the name of oxidant smog.

Sources of primary polluting agents

The main primary polluting agents which are present in the air and generate oxidant smog are: CO, NO, hydrocarbons, sulphur dioxide.

Carbon monoxide (CO)

In the atmosphere there are both natural and anthropogenic sources of CO. Natural emissions are important (they are 10 times more intensive than the emissions generated by human activities). Natural emissions are produced by superior plants, alga, plankton and human breathing. The average natural concentration of CO is $0,1 \text{ mg/m}^3$ air. In atmosphere the lifetime of CO is 30 days.

In urban regions of Europe 90% of CO emission is caused by road traffic.

CO is involved in atmosphere - occurring chemical processes by which it indirectly influences the climate. Interaction of CO with hydroxyl radicals elevates the methane concentration in the atmosphere. In presence of nitric oxides, CO is involved in generating tropospheric ozone.

Nitric oxides (NO_x)

N_2O , NO and NO_2 are nitric oxides which occur in atmosphere. The mixture of NO and NO_2 is represented by NO_x symbol. In the atmospheric air nitric oxides proceed from natural sources and human activity.

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Natural sources: atmospheric nitrogen is fixed as nitrate by plants and bacteria; anaerobic bacteria convert nitrates in N_2 , N_2O and low amounts of NO and NO_2 .

Natural emissions of NO_x are 10 times more intensive than the ones caused by human activity; at soil level the natural concentration of NO_x is $3 - 4 \mu g/m^3$ air. NO_x is formed by reaction between N_2 and O_2 during electric discharges. In stratosphere N_2O is oxidized to NO_2 under the influence of O_3 and UV radiations. In atmosphere the main source of NO_x are the combustion processes (road traffic, thermal stations, industrial processes).

In Europe, almost half of NO_x emissions are generated by road traffic. In urban air, in stable meteo conditions (absence of air currents), high concentrations of NO_x are present. If nitric oxides are generated directly in the air, at high altitudes (by airplanes motors), they contribute to diminution of stratospheric O_3 level. In the presence of sunlight, NO_x together with volatile organic compounds (VOC) are precursors for secondary polluting agents – oxidant smog. Lifetime of NO_x is about one day. A part of NO_x converts into HNO_3 which forms acidic depositions (4).

Volatile organic compounds

This group of primary polluting agents includes different compounds: methane and other organic compounds except methane (NMVOC) – ethane, propane, butane, aldehydes, ketones, alcohols, complex molecules (biphenyl policlorurates, dioxines, furans). NMVOC influence climate changes in two ways: as with CO they indirectly increase atmospheric methane concentrations through reduction of hydroxyl radicals and generation of tropospheric O_3 . Increases in NMVOC concentrations decrease hydroxyl radicals values by decreasing the oxidant atmospheric concentrations of methane.

Toxic organic micropollutants

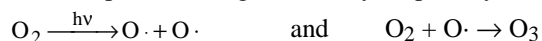
Globally it is considered that VOC natural emissions (metabolism and decomposition of plants) are 5 times higher than the emissions generated by human activity.

Anthropogenic emissions are generated by road traffic, fuel burns, industrial processes, solvents evaporation.

Oxidant smog – mechanism of ozone generation

Mechanisms of O_3 generation are different as the reactions occur in troposphere or stratosphere.

In stratosphere, O_3 is generated by O_2 photolysis in presence of UV radiations with $\lambda < 240$ nm:



In presence of UV radiations with $\lambda < 310$ nm O_3 decomposes: $2O_3 \xrightarrow{h\nu} 3O_2$

In troposphere O_3 is generated by the same reaction: $O_2 + O \cdot \rightarrow O_3$

As solar radiations with $\lambda < 240$ nm can not reach the troposphere, oxygen atom can be generated only by NO_2 photolysis: $NO_2 \rightarrow NO + O$

Reaction rate depends on light intensity; the reaction does not occur during night. NO_2 photolysis does not quantitatively generate O_3 ; O_3 reacts with NO and generates NO_2 . Thus, O_3 generation competes with oxidation of NO to NO_2 . This competition implies generation of radicals with high oxygen content (hydroperoxy and organic peroxy radicals).

Organic compounds and CO are important sources of peroxy radicals. Lifetime of organic compounds is short because they are involved in radical reactions in which hydroxyl radicals take part. These reactions are combustions at low temperatures; in these conditions CH_4 , H_2 and CO are oxidized to CO_2 and H_2O .

The presence of hydrocarbons and nitric oxides in the air increases the availability of free radicals. This mechanism of reaction allows the evaluation of maxim number of O_3 molecules which are generated by a certain compound oxidation. Theoretically, each carbon atom in saturate hydrocarbons generates three molecules of O_3 . For substituted organic compounds (alcohols) carbon atom which is linked to OH is partially oxidized and it is less implied in O_3 generation (1).

The high reactivity of O_3 molecule makes possible its consumption in reactions with other chemical influence O_3 stability which can persist in the atmospheric from several hours to several days.

Tropospheric O_3 tends to concentrate in high populated urban regions in which important amounts of VOC, O_3 precursors, accumulate.

Other chemical species are involved in photochemical decomposition of organic compounds. As the organic molecule is attacked by a free radical, the radical reactions cycle generates O_3 only if NO concentration is 10 - 40 ppt at least. During these reactions, decomposition of peracetyl nitrate is a source of NO_x .

Nitric oxides are not consumed during elementary photochemical processes which generate O_3 . Although, in photochemical systems, the lifetime of nitric oxides is limited because the hydroxyl radicals react very fast with NO_2 and generate $HONO_2$.

If NO_x concentration is higher than the organic compounds concentration, hydroxyl radicals can be consumed stopping O_3 generation. During a photochemical episode, 1 - 3 ozone molecules are generated for each NO molecule. In unpolluted troposphere (free troposphere), O_3 generation is elevated (10 - 100 O_3 molecules for one NO_x molecule). Although, in free atmosphere O_3 generation is limited by NO_x decreased availability (in non-urbane continental regions NO_x concentrations vary between 50 and 1000 ppt; in free troposphere it varies between 10 and 100 ppt) (3,4)..

O₃ stability in atmosphere

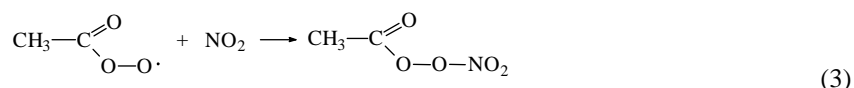
The diminution of O₃ concentration in atmosphere occurs by its decomposition and deposition on the ground, at the surface of seas and oceans, plants. Plants are the main receiver for O₃ which destroys organic molecules in vegetal tissue, especially during day and the intensive vegetation period. Ozone decomposition by photolysis generates O₂ and oxygen atoms which can restart the cycle with generation of new O₃ molecules which can react with water vapors generating hydroxyl radicals or they can react with other molecular species.

Oxidant smog – mechanism of peroxyacyl nitrates generation

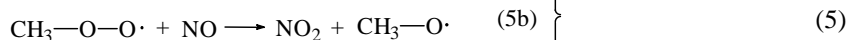
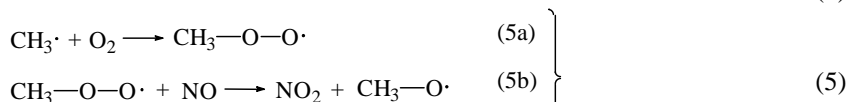
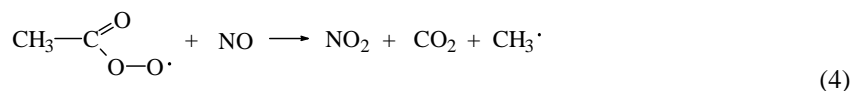
In the atmosphere peroxyacyl nitrates are not generated as they are; they are generated *in situ* by photochemical reactions having NO_x and VOC as precursors.

Depending on organic radical, peroxyacyl nitrates can be: peroxy acetyl nitrates (PAN): CH₃C(O)OONO₂; peroxy propionyl nitrates (PPN): CH₃CH₂C(O)OONO₂; peroxy n-butyryl nitrates (PnBN): CH₃CH₂CH₂C(O) OONO₂ etc. Among these, PAN plays an important in atmospheric chemistry.

The reactions of PAN formation are based on generation of acetyl radicals by radiation of some VOC (hydrocarbons, alcohols, aldehydes). For example:



In addition to the reaction with NO₂, peracetyl radical can also react with NO generating NO₂ and CH₃ radicals. These species generate formaldehyde by oxidation.



PAN decomposition occurs only in the presence of NO. The rate of PAN decomposition increases fast with the temperature. In the atmosphere PAN concentration depends on temperature, NO₂/NO ratio (competition between reaction 3 and 4 and VOC availability and reactivity VOC can generate acetyl radicals). Therefore, the relationship between PAN in the air and the emission of its precursors (VOC and NO_x) is not linear and, in the same time dependent on O₃, VOC and NO_x concentrations.

Acyl radicals having a higher number of carbon atoms (propionyl-, n-butyryl-) generates PPN or PnBN, and not PAN. Ethanol as direct precursor can be oxidized to acetaldehyde.

PPN/PAN ratio can be an index of the impact of using ethanol as an additive for vehicles fuels compared to using gasoline. Both PPN day variation and ratio PPN/O₃ are similar to those for PAN.

PAN stability in the atmosphere

As it has already been shown, PAN stability in the atmosphere is limited (35 minutes). The daytime evolution of oxidant smog composition is expressed by PAN/O₃ ratio. The ratio decreases with increasing temperatures. This confirm of PAN thermal decomposition mechanism (1). This ratio has a maximum value during night (the temperature diminution promotes PAN stability) and a minimum value at now (mid-day), when temperature is higher. A secondary maximum is noticed in the morning when hydroxyl radicals availability is increased (a more intensive road traffic) promoting PAN generation.

Exposure to PAN

PAN impact upon human health, plants and environment in general justifies specialists' interest for the study of this compound. The conversion of human exposure expressed by ppb (µg/person/day). 1 ppb PAN = 4,95 µg/m³ la 25°C and 1 atm and for the 23 m³ of air which are daily represent 114 µg/person/day inhaled. The inhaled doze would be 570 µg/person/day if PAN concentration in inhaled air is 5 ppb.

Comparative numerical study

In this work we studied the variations of primary and secondary polluting agents concentrations by photochemical modeling systems.

All the test problems (denoted models A-F) were coded in Fortran and are based on the Carbon Bond Mechanism IV, consisting of 32 chemical species involved in 70 thermal and 11 photolytic reactions. We used for the numerical integration of the stiff systems a Rosenbrock solver implementing a number of 4-stage (3) pairs. The

problems were run for five days. This time interval is sufficiently large for taking into account several diurnal cycles of the photochemical reactions. The five day interval is split up in 120 one hour subintervals. The unit of time is seconds and the unit for the concentrations is number of molecules per cm^3 . The test problems A-D describe urban scenarios and simulate a heavily polluted atmosphere. The test problems E-F describe a rural atmosphere.

For urban regions (Fig. 1a-h) the models B, C and D were performed by adding emissions of some polluting agents (CO, NO, NO₂, HO radicals, CH₂O, isoprene, O₃, PAN) with some multiplying factors, with respect to the model A, as indicated below:

Model B: NO + 2; NO₂ + 0.4; CO + 4; CH₂O + 0.4; PAR + 4.

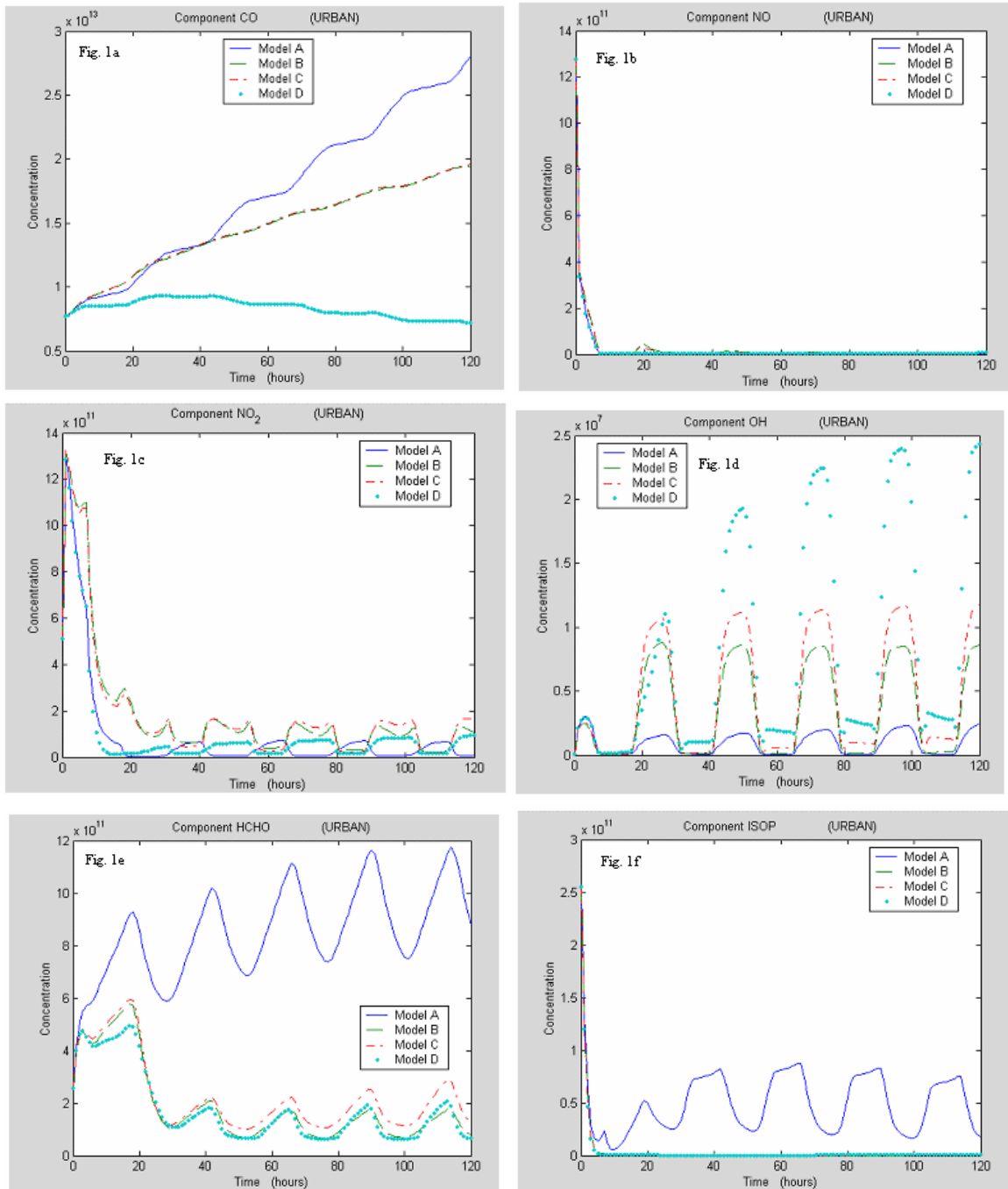
Model C: NO + 2; NO₂ + 0.4; CO + 4; CH₂O + 0.4; PAN + 2; PAR + 4.

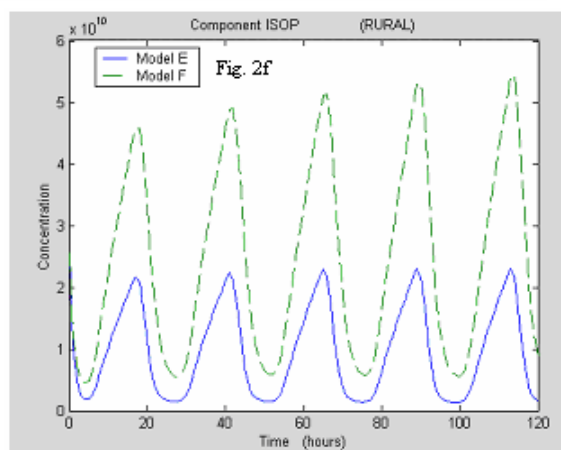
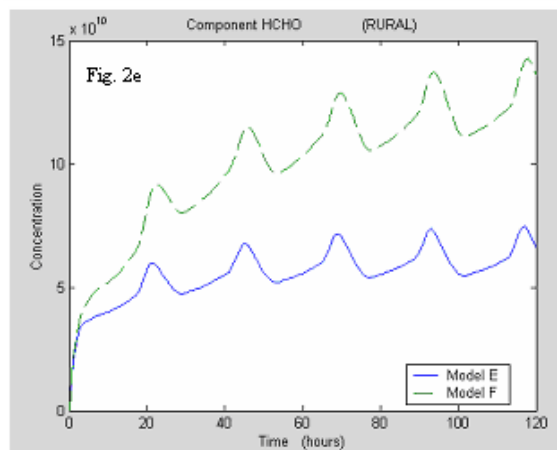
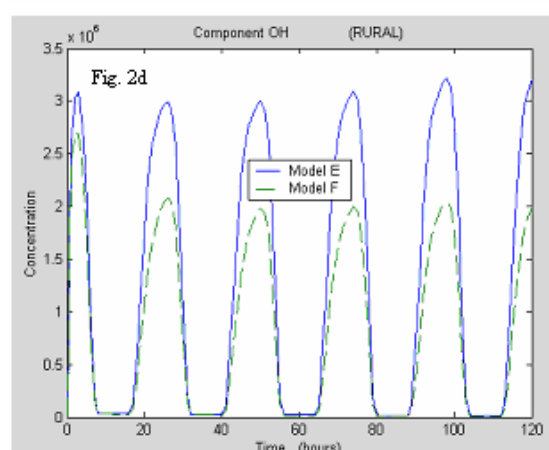
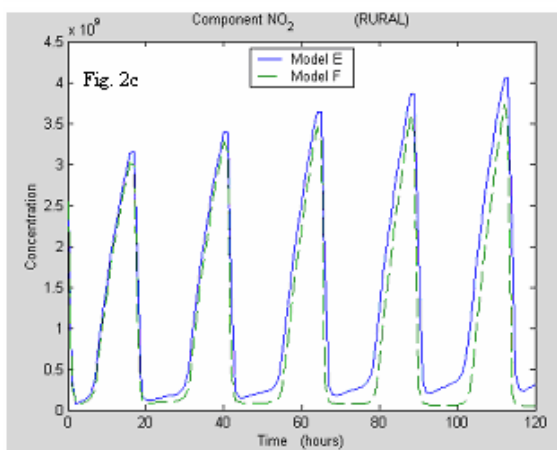
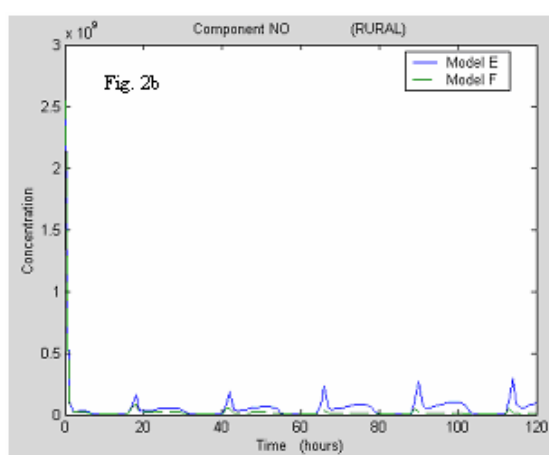
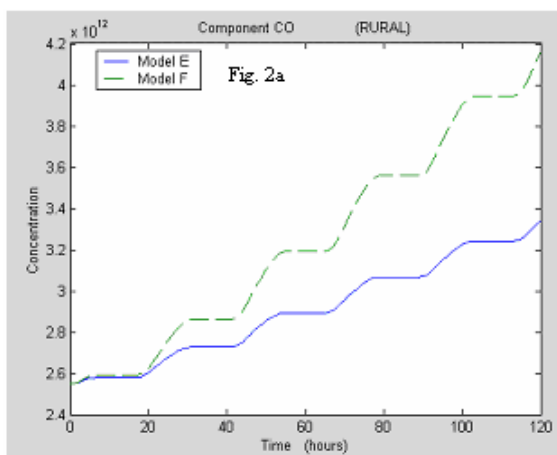
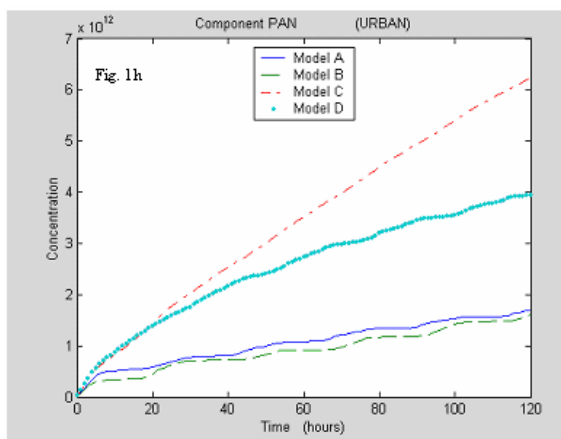
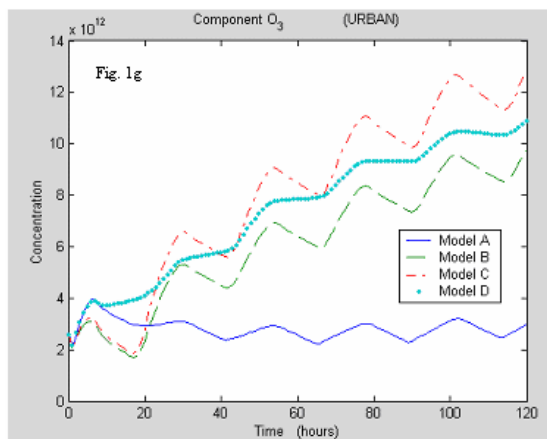
Model D: O₃ + 2; PAN + 2.

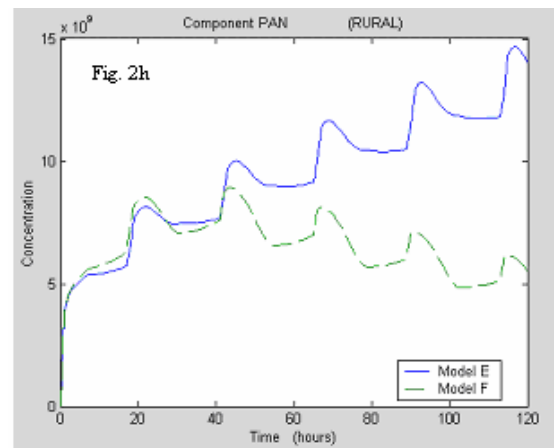
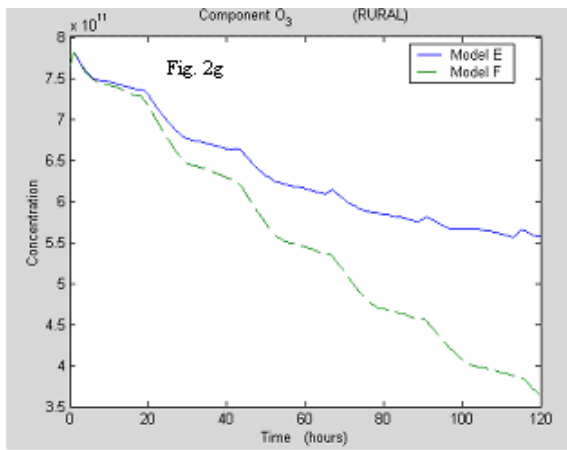
For rural regions (Fig. 2a-h) Model F was constructed from Model E, increasing twice the emissions of the following polluting agents:

Model E: NO + 0.01; NO₂ + 0.01; isoprene + 0.1.

Model F: NO₂ + 0.02; isoprene + 0.2.







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