

## 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<sub>3</sub> 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<sub>3</sub>, 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 mg/m<sup>3</sup> 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<sub>x</sub>)

N<sub>2</sub>O, NO and NO<sub>2</sub> are nitric oxides which occur in atmosphere. The mixture of NO and NO<sub>2</sub> is represented by NO<sub>x</sub> 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)..

### O<sub>3</sub> stability in atmosphere

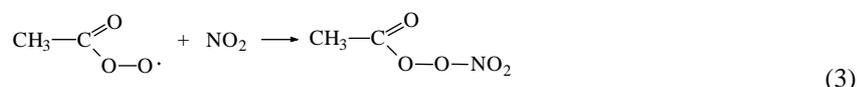
The diminution of O<sub>3</sub> concentration in atmosphere occurs by its decomposition and deposition on the ground, at the surface of seas and oceans, plants. Plants are the main receiver for O<sub>3</sub> which destroys organic molecules in vegetal tissue, especially during day and the intensive vegetation period. Ozone decomposition by photolysis generates O<sub>2</sub> and oxygen atoms which can restart the cycle with generation of new O<sub>3</sub> 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

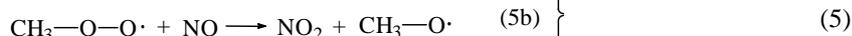
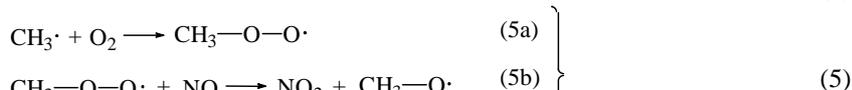
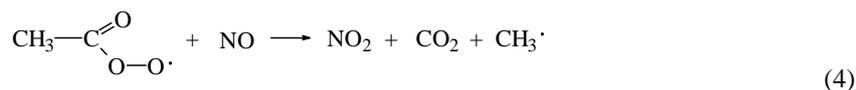
In the atmosphere peroxyacyl nitrates are not generated as they are; they are generated *in situ* by photochemical reactions having NO<sub>x</sub> and VOC as precursors.

Depending on organic radical, peroxyacyl nitrates can be: peroxy acetyl nitrates (PAN): CH<sub>3</sub>C(O)OONO<sub>2</sub>; peroxy propionyl nitrates (PPN): CH<sub>3</sub>CH<sub>2</sub>C(O)OONO<sub>2</sub>; peroxy n-butyryl nitrates (PnBN): CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C(O) OONO<sub>2</sub> 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 NO<sub>2</sub>, peracetyl radical can also react with NO generating NO<sub>2</sub> and CH<sub>3</sub> 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, NO<sub>2</sub>/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<sub>x</sub>) is not linear and, in the same time dependent on O<sub>3</sub>, VOC and NO<sub>x</sub> 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/O<sub>3</sub> 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/O<sub>3</sub> 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/m<sup>3</sup> la 25°C and 1 atm and for the 23 m<sup>3</sup> 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  $\text{cm}^3$ . 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, NO<sub>2</sub>, HO radicals, CH<sub>2</sub>O, isoprene, O<sub>3</sub>, PAN) with some multiplying factors, with respect to the model A, as indicated below:

Model B: NO + 2; NO<sub>2</sub> + 0.4; CO + 4; CH<sub>2</sub>O + 0.4; PAR + 4.

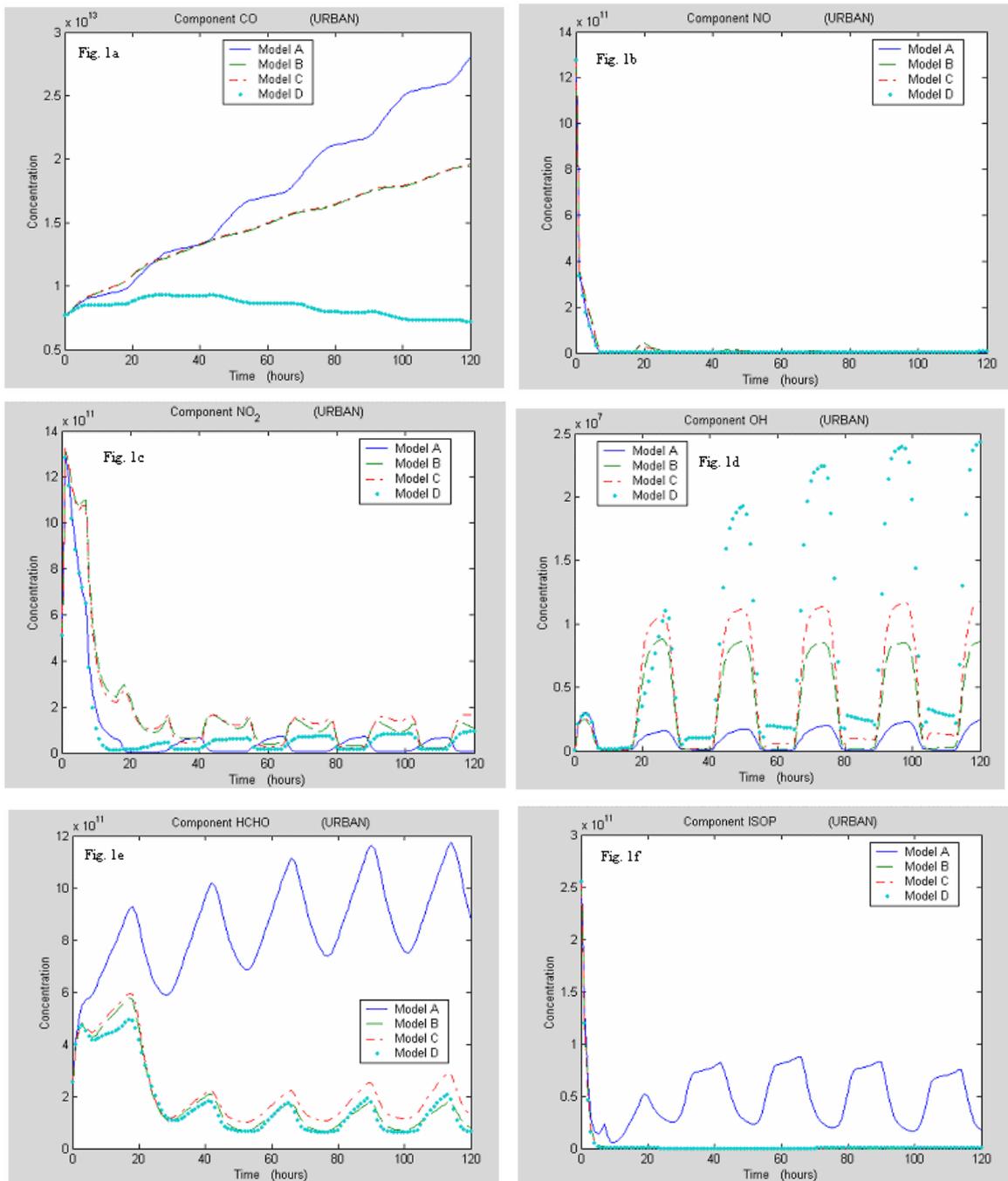
Model C: NO + 2; NO<sub>2</sub> + 0.4; CO + 4; CH<sub>2</sub>O + 0.4; PAN + 2; PAR + 4.

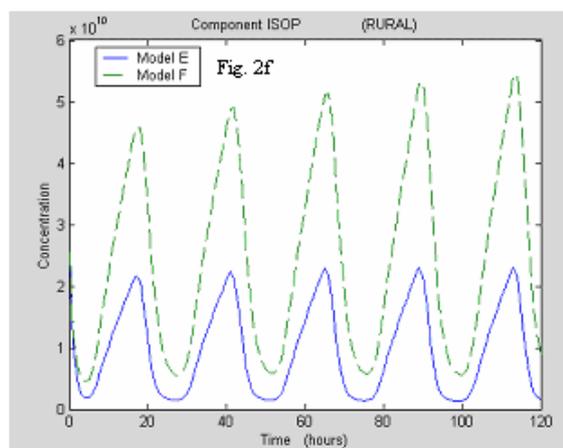
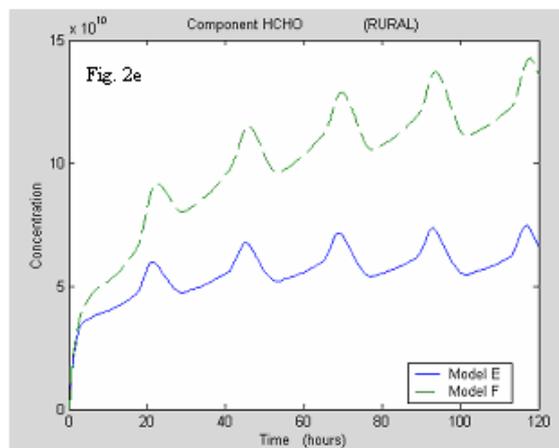
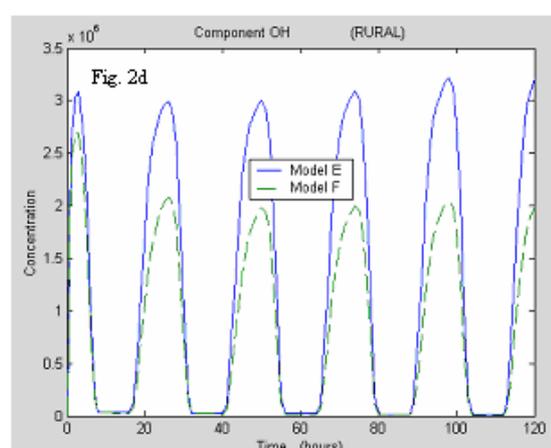
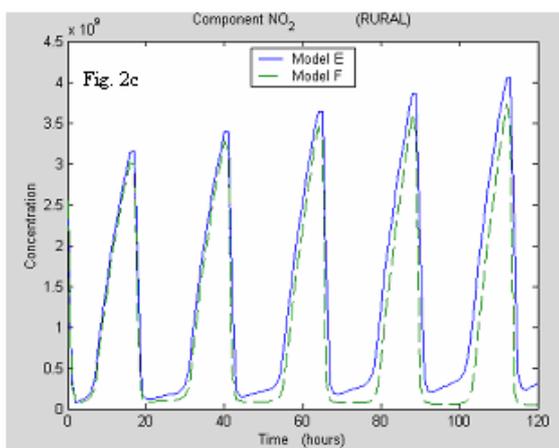
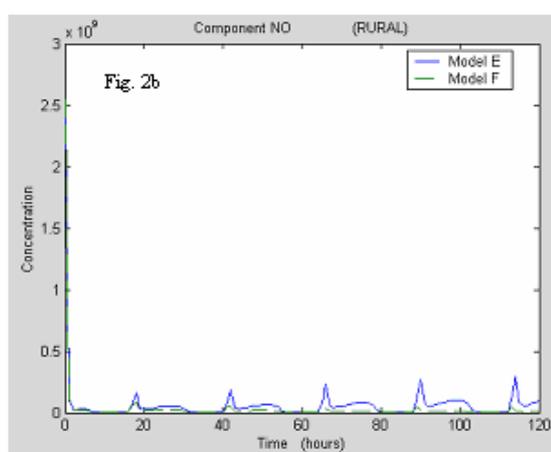
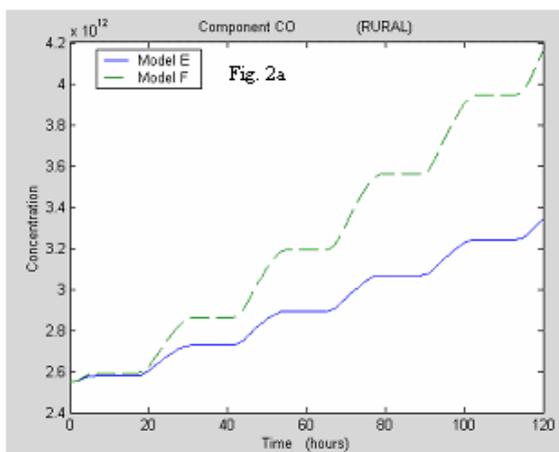
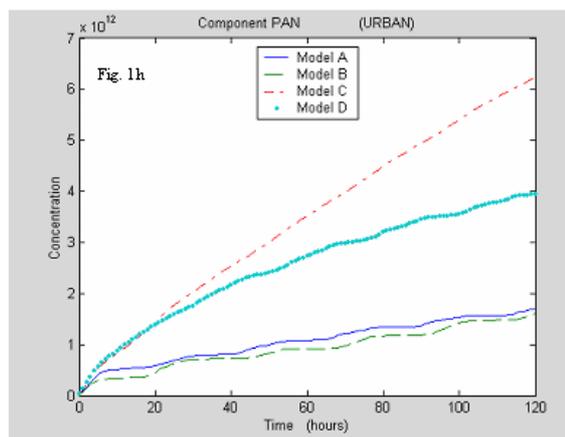
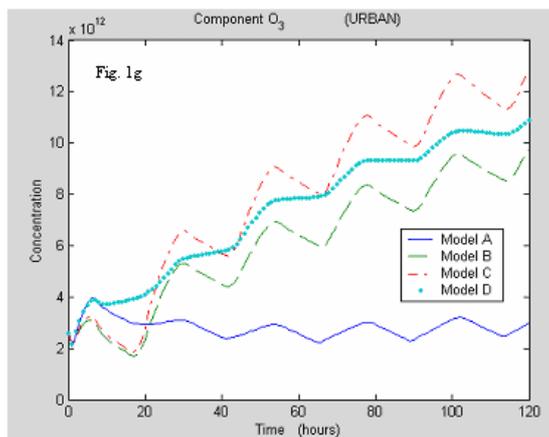
Model D: O<sub>3</sub> + 2; PAN + 2.

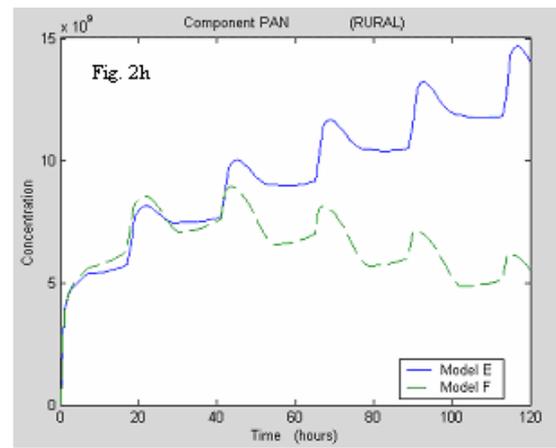
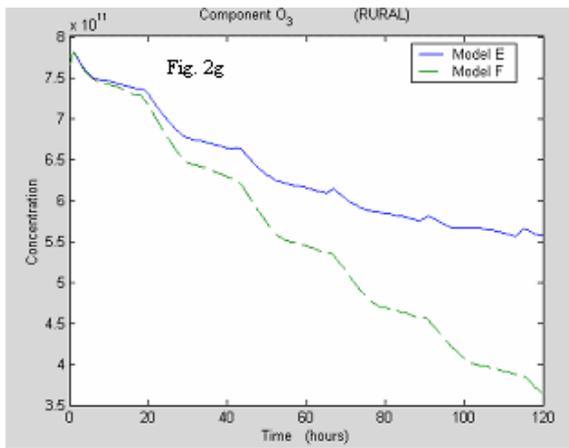
For rural regions (Fig. 2a-h) Model F was constructed from Model E, increasing twice the emissions of the following polluting agents:

Model E: NO + 0.01; NO<sub>2</sub> + 0.01; isoprene + 0.1.

Model F: NO<sub>2</sub> + 0.02; isoprene + 0.2.







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