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Geographical Distribution and Seasonal Variation of Surface Emissions  
and Deposition Velocities of Atmospheric Trace Gases

by

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B E L G I S C H   I N S T I T U U T   V O O R   R U I M T E - A E R O N O M I E

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## FOREWORD

The paper "GEOGRAPHICAL DISTRIBUTION AND SEASONAL VARIATION OF SURFACE EMISSIONS AND DEPOSITION VELOCITIES OF ATMOSPHERIC TRACE GASES" has been submitted in July 1991 to "Journal of Geophysical Research-Atmospheres". The author is Research Assistant of the Belgian National Fund for Scientific Research.

## AVANT-PROPOS

L'article "GEOGRAPHICAL DISTRIBUTION AND SEASONAL VARIATION OF SURFACE EMISSIONS AND DEPOSITION VELOCITIES OF ATMOSPHERIC TRACE GASES" a été soumis en juillet 1991 à la revue "Journal of Geophysical Research-Atmospheres". L'auteur bénéficie d'un mandat d'"Aspirant" du Fonds National de la Recherche Scientifique (FNRS).

## VOORWOORD

Het artikel "GEOGRAPHICAL DISTRIBUTION AND SEASONAL VARIATIONS OF SURFACE EMISSIONS AND DEPOSITION VELOCITIES OF ATMOSPHERIC TRACE GASES" werd in juli 1991 voorgelegd bij het tijdschrift "Journal of Geophysical Research-Atmospheres". De auteur heeft een mandaat van "Aspirant" bij het Nationaal Fonds van Wetenschappelijk Onderzoek (NFWO).

## VORWORT

Die Arbeit "GEOGRAPHICAL DISTRIBUTION AND SEASONAL VARIATIONS OF SURFACE EMISSIONS AND DEPOSITION VELOCITIES OF ATMOSPHERIC TRACE GASES" wurde in Juli 1991 zum "Journal of Geophysical Research-Atmospheres" eingegeben. Der Verfasser ist ein "Aspirant" des Belgisches FNRS.

GEOGRAPHICAL DISTRIBUTION AND SEASONAL VARIATION OF SURFACE EMISSIONS  
AND DEPOSITION VELOCITIES OF ATMOSPHERIC TRACE GASES

by

Jean-François MÜLLER<sup>(1)</sup>

Abstract

The geographical distributions on the global scale of trace gas surface emission and deposition are established on the basis of a variety of technical, geographic and climatic data. 5° x 5° resolution maps of the sources and deposition velocities are constructed, which can be used as surface boundary conditions in a three-dimensional chemical/transport model of the troposphere. Special attention is devoted to emissions of CO, NO<sub>x</sub> and several non-methane hydrocarbons (NMHC), and to the fossil fuel emissions of methane. Anthropogenic sources, i.e. the emissions produced or controlled by human activities, represent about 75% or more of the total surface emissions of CO, CH<sub>4</sub>, SO<sub>2</sub> and NO<sub>x</sub>, and about two thirds of the total production of atmospheric CO (from surface sources and atmospheric oxidation of hydrocarbons). The possibility arises that methane releases from natural gas exploitation in the USSR are substantially larger than accounted for in previous studies, implying possible important consequences for the methane budget.

Résumé

Les distributions géographiques à l'échelle globale des émissions et vitesses de déposition à la surface de plusieurs importants gaz en trace ont été établies sur base de diverses données techniques, géographiques et climatiques. Des cartes des sources et des vitesses de déposition d'une résolution de 5° x 5° ont été construites, qui peuvent être utilisées comme conditions à la limite inférieure dans un modèle tri-dimensionnel de la chimie et du transport des gaz en trace dans la troposphère. Une attention particulière a été portée aux émissions de CO, NO<sub>x</sub> et plusieurs hydrocarbures non-méthaniques, et aux émissions de méthane dues aux combustibles fossiles. Cette étude montre que les sources anthropogéniques, c.à.d. les émissions produites ou contrôlées par les activités humaines, représentent environ 75% ou d'avantage des émissions de surface de CO, CH<sub>4</sub>, SO<sub>2</sub> et NO<sub>x</sub>, et environ deux tiers de la production totale de CO atmosphérique (provenant des sources à la surface et de l'oxydation atmosphérique des hydrocarbures). Il apparaît que les émissions de méthane provenant de l'exploitation du gaz naturel en Union Soviétique ont été probablement fortement sous-estimées par les précédentes études, ce qui nous amène à reconsidérer certains aspects importants de notre connaissance du bilan du méthane.

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## Samenvatting

De geografische verdelingen op globale schaal van de emissie van verscheidene belangrijke sporegassen en de snelheid waarmee zij neerslaan op de oppervlakte werden opgesteld op basis van verschillende technische, geografische en klimatische gegevens. Kaarten van de bronnen en van de snelheid van het neerslaan werden gemaakt met een resolutie van  $5^\circ \times 5^\circ$ . Deze kunnen gebruikt worden als lagere grensvoorwaarden voor een driedimensionaal model van de chemie en het transport van de sporegassen in de troposfeer. Er werd in het bijzonder aandacht gegeven aan de emissie van CO, NO<sub>x</sub> en verscheidene niet-methanische koolwaterstoffen en aan de emissie van methaan door fossiele brandstoffen. Deze studie toont aan dat de antropogenische bronnen, d.w.z. de emissie veroorzaakt of gecontroleerd door de menselijke activiteiten, 75% of meer vertegenwoordigen van de CO-, CH<sub>4</sub>-, SO<sub>2</sub>- en NO<sub>x</sub>-emissies aan de oppervlakte en ongeveer twee derde van de totale productie van atmosferische CO (afkomstig van bronnen aan de oppervlakte en de atmosferische oxydatie van koolwaterstoffen). Het blijkt dat de methaanemissie afkomstig van het ontginnen van aardgas in de Sovjet Unie hoogstwaarschijnlijk sterk werd onderschat bij voorafgaande studies, hetgeen tot gevolg heeft dat zekere belangrijke aspecten van onze kennis over de methaanbalans moeten herzien worden.

## Zusammenfassung

Die globale geographische Verteilung der Emission und Niederschlag von Minderheitgasen wird aus verschiedenen technischen, geographischen und klimatologischen Angaben aufgestellt. Landkarten mit  $5^\circ \times 5^\circ$  Spaltung werden für die Emissions- und Niederschlagsgeschwindigkeiten aufgebaut. Diese Resultaten können als unteren Grenzen für Dreidimensionalen Modellen der Troposphäre gebraucht werden. Emissionen von CO, NO<sub>x</sub>, verschiedene NMHC und CH<sub>4</sub> sind vorgestellt. Anthropogenische Emissionen sind 75% oder mehr der totalen Emissionen von CO, CH<sub>4</sub>, SO<sub>2</sub> und NO<sub>x</sub> und ungefähr zwei Drittel der globalen Produktion von atmosphärischen CO. Es ist möglich, dass die CH<sub>4</sub> Emission aus Gaswirtschaftsführung in USSR grösser ist als früher vorgesehen und dadurch wichtiger Einfluss auf dem CH<sub>4</sub> Budget hat.

## 1. Introduction

Global warming, acidic precipitation and photochemical smog formation are examples of environmental threats requiring a rapid improvement in our understanding of the chemical processes in the atmosphere. In this respect, global scale, three-dimensional models are necessary to best represent the many aspects of atmospheric chemistry. For example, the rapid increase in the atmospheric concentration of greenhouse gases such as methane is probably due to increasing emissions of these compounds as well as changes in the concentration of other atmospheric trace gases (e.g., carbon monoxide and the hydrocarbons), through complex interactions involving a large number of chemical compounds. Qualitative and quantitative understanding of processes involved requires (1) quantification of the fluxes (sources and sinks) of the tropospheric pollutants at the earth's surface and (2) the analysis of the atmospheric fate of these pollutants (transport, chemical transformations, sticking on aerosols or water droplets). This paper addresses the first point, and presents latitude-longitude maps of the major sources of tropospheric trace gases. These include carbon monoxide (CO), hydrocarbons (HCs), nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>). Four categories of emissions are distinguished: the technological sources (mainly fossil fuel burning); biomass burning; plant foliage (primarily in the case of isoprene and monoterpenes); and other natural sources. The latter category groups the emissions of methane by anaerobic environments and various soil and ocean emissions. Surface deposition velocity distributions are proposed for ozone and for most of the above-mentioned species. Seasonal variations are determined for all four source categories, and for the deposition velocities. The maps are derived on a 5° × 5° resolution latitude-longitude grid, and are suitable for use as surface boundary conditions in three-dimensional models of the atmosphere.

The methodology and data used to deal with the different source categories and the results are presented in the following sections (2–6); the emissions estimates are then summarized and briefly discussed in Section 7.

## **2. Technological Sources**

Technological sources include fossil fuel burning, industrial processes and waste disposal. They are the major contributor to the current increase in pollutants levels on the global scale, and represent the largest part of the emissions in the most densely populated and industrialized areas. These sources are therefore the chief contributor to ozone smog formation and to precipitation acidity in these regions.

As a result of the increasing concern for air pollution in North America, Japan and a large number of West European countries, the emissions of trace gases in these countries generally either decrease or increase more slowly than the use of products causing the emissions (e.g., Amann [1990]). The emission factors of these gases are thus reduced as a result of emission controls and regulations. An example of such reduction in the emission factors is provided by the evolution of the emissions of  $\text{SO}_x$ ,  $\text{NO}_x$ , CO and HCs in the U.S. since the early 1970's, as a consequence of the implementation of the Clean Air Act Amendments (Table 1). Less detailed, but generally similar patterns are found in the evolution of the emissions in other countries which are member of the Organization of Economic Co-operation and Development (OECD), i.e., Northern America (United States and Canada), Western Europe, Japan, Australia and New Zealand. OECD has gathered and published emission data of the main pollutants for most of its member countries (Table 2) [OECD (1989); Lübkert and de Tilly (1990)]. When data are lacking, emissions were estimated by the method used by Hameed and Dignon [1988], i.e., assume a linear relationship between the emissions and fossil fuel consumption, derived from the data for



TABLE 2. OECD emission estimates of NO<sub>x</sub>, SO<sub>x</sub>, CO, and VOCs in 1980, in thousands of tons (derived from OECD, 1989). SO<sub>x</sub> and NO<sub>x</sub> emissions are expressed as SO<sub>2</sub> and NO<sub>2</sub>, respectively.

	SO <sub>x</sub>	NO <sub>x</sub>	CO	VOC
Canada	4650	1900	9928	2100
U.S.	23900	20300	76100	22700
Japan	3400	3600	13600	3100
Australia	1600	940	4000	618
New Zealand	100	90	600	55
Austria	350	210	1126	251
Belgium	856	317	839	339
Denmark	452	245	832	197
Finland	584	284	660	163
France	3550	2561	6620	1972
West Germany	3200	3000	11708	2490
Greece	800	127	740	130
Iceland	6	13	30	8
Ireland	217	70	497	62
Italy	3500	1600	5850	1566
Luxembourg	24	23	60	11
Netherlands	462	553	1450	493
Norway	150	203	608	159
Portugal	266	166	800	159
Spain	2543	937	4200	843

TABLE 2. (continued)

Sweden	502	318	1250	410
Switzerland	126	196	711	311
United Kingdom	4800	2264	4999	2241

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the other OECD countries and the fossil fuel use statistics of the United Nations [U.N., 1986]. The assessment of the trace gas emissions in other regions of the world, with limited pollutant control and estimate, requires (1) an estimation of the pollutants emission factors from the various known sources and (2) the use of appropriate statistics for fossil fuel consumption and industrial productions responsible for the emissions. The emission factors for SO<sub>x</sub>, NO<sub>x</sub> and CO were taken from different published estimates [Cullis and Hirschler, 1980, 1989, 1990; Logan et al., 1981; Logan, 1983] and are summarized in Table 3a–c. Oil and coal burning are the largest contributors to the emissions of these compounds, followed by metallurgy, oil refining and waste disposal. The corresponding energy use and industrial productions statistics from the United Nations and other institutes [U.N., 1986, 1988; OECD/IEA, 1989; Europa Yearbook, 1985; American Iron and Steel Institute, 1987] , which are summarized in Table 4a–b, gives the global totals and the relative share for the four large regions of the world, i.e., North America, other OECD countries, central-planned countries of Europe and Asia, and the rest of the world. Because of the lack of data, the emissions associated with waste were assumed to be proportionate to the electricity consumption, to account for the fact that high waste production is associated with populated areas of industrial countries [e.g., Bingemer and Crutzen, 1987].

OECD data provides the total hydrocarbon emissions, but with no distinction between the different compounds. Furthermore, these statistics do not include two major sources of methane, namely coal mining and natural gas losses [Ehhalt, 1974; Sheppard et al., 1982; Crutzen, 1987; Cicerone and Oremland, 1988; Okken, 1989; Levander, 1990]. Additional information is thus required to estimate these emissions. The emissions due to fossil fuel use and industrial activities, such as solvent use and chemical manufacturing [e.g., Duce et al., 1983; Rudolph, 1990; Middleton et al, 1990], are minor sources of

TABLE 3. SO<sub>x</sub>, NO<sub>x</sub>, and CO emission factors, in kg (SO<sub>2</sub>, NO<sub>2</sub>, or CO)/ton of product, except if indicated (sources, see text).  
15(6) means 15 × 10<sup>6</sup>.

		SO <sub>x</sub>
<b>Coal</b>		
	Hard coal	48.2
	Lignite	35.6
	Coke and briquettes	5.4
<b>Oil</b>		
	Gasoline	0.72
	Gas-diesel fuel oils	4.47
	Residual fuel oils	36.0
	Petroleum coke	13.5
	Refining	2.0
<b>Ore Smelting</b>		
	Copper (smelted)	2000
	Copper (refined)	300
	Lead	400
	Zinc	200
<b>Other Sources</b>		
	Sulphuric acid	24
	Sulphur	2
	Paper/pulp	2
	Refuse (world source)	8(5) tons/yr

TABLE 3. (continued)

		NO <sub>x</sub>
Coal		
	Hard coal	5.9
	Lignite	2.9
Oil		
	Gasoline	27
	Diesel	30-56
	Combustion (stationary)	2.3-10
	Natural Gas	6.4 g/m <sup>3</sup>
	Industry (world source)	5(6) tons/yr
		CO
Coal		
	Hard coal	27
	Lignite	3.7
Oil		
	Gasoline	360
	Diesel vehicles	26-35
	Combustion (stationary)	4
	Natural Gas	6.4 g/m <sup>3</sup>
Industrial Processes		
	Pig iron, production	80
	Pig iron, foundry	72.5
	Steel production	69.5 kg/m <sup>3</sup>
	Petroleum refining	39.2
	Ammonia production	100
	Miscellaneous (world source)	15(6) tons/yr

TABLE 3. (continued).

<u>Refuse (world source)</u>	<u>12(6) tons/yr</u>
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TABLE 4. Energy use and industrial productions (in 1986) by region and category, used to assess the technological emissions of trace gases (United Nations, 1986; 1988).

	World	North America (%)	Other OECD (%)	Central Planned (%)	Others (%)
Area (km <sup>2</sup> )	1.48(8)	13	9	23	55
Population	4.83(9)	6	10	30	54

*(a) Energy Consumption (millions Terajoules)*

Total	283.1	29	22	34	15
Solid fuels	90.4	20	17	51	12
Hard coal	78.7	22	17	48	13
Lignite	11.7	8	17	71	3
Liquid fuels	113.8	30	28	20	22
Gasoline	30.2	47	22	15	16
Diesel-oil	30.7	23	36	17	24
Residual fuel-oil	28.7	12	26	33	29
Natural Gas	61.4	30	18	41	11
Electricity (non-fuel)	17.6	48	27	12	12
Electricity (total)	36.1	31	29	26	14

*(b) Industrial Productions (millions of metric tons, except where indicated)*

Steel	715	13	34	40	13
Pig iron (total)	497	10	35	42	13

TABLE 4. (continued)

Pig iron (foundry)	8.5	14	38	33	15
Ammonia	86	19	11	63	7
Carbon black	4.1	32	43	9	16
Copper, smelted	8.5	17	22	25	36
Copper, refined	9.4	21	28	26	25
Coal	4419	19	14	56	11
Natural gas (Terajoules)	66.5(3)	30	12	42	16

methane, but important contributors to NMHC emissions. About 27 teragrams (Tg) hydrocarbons were emitted in North America in 1980, of which about only 10% in mass was methane [Placet and Streets, 1987; Middleton et al, 1990]. The same fraction was assumed for the other countries. Hydrocarbon emissions in non-OECD countries were assumed to be proportional to fossil fuel consumption, with a proportionality factor inferred from the (pre-Clean Air Act) 1970 U.S. emissions [U.S. EPA, 1986] and fossil fuel use. To estimate the methane emissions from coal, we assumed constant ratios of methane release to hard coal and lignite production. These ratios,  $6.6 \text{ m}^3 \text{ CH}_4$  per ton of hard coal and  $1.4 \text{ m}^3 \text{ CH}_4$  per ton of lignite, were taken from the study of Levander [1990]. Fung et al. [1990] reported estimates of the natural gas venting/flaring rate at the extraction ranging from about 1% in North America to as high as 61% in the Middle East, while the loss rate associated with the transmission through pipelines varied between 1% for Canada to around 3% in West Germany. Assuming that 20% of the flared or vented gas escapes to the atmosphere, losses at natural gas and oil extraction sites are estimated to  $15 \text{ Tg}(\text{CH}_4)/\text{yr}$  globally, in good agreement with the value reported by Levander [1989]. In contrast with this, Levander reports much lower values for the losses during the distribution, ranging from 0.05% to 1%. However, these figures of Levander as well as those of Fung et al., by assuming that natural gas loss rates are uniform throughout Europe and USSR, probably largely underestimate the contribution of the Soviet Union and possibly other Eastern European countries. Yablokov [1989] reports that more than 100 billions of cubic meters of gas are lost each year in the USSR during its transport from the gas wells to the consumers, of which about 17 billions cubic meters are torched. This implies a loss rate to the atmosphere of 14%, much higher than the estimated loss rate of other large natural gas producers. As this estimate may be excessive, we consider it as an upper limit and assume in the following an intermediate loss rate of 8% for all central-

planned countries. We used the Fung's estimates for other regions. Although the composition of natural gas varies with the extraction site, the methane release from natural gas losses can be estimated by assuming that, on the average, methane represents about 80% in volume of the gas released at the gas wells. The other hydrocarbons (primarily ethane, propane and butane) account for about 10%, and non-hydrocarbon compounds account for the remainder (these latter compounds are extracted from natural gas in processing plants).

With these emissions levels estimated for each country, the geographical distribution of these sources can be addressed. The emissions resulting from fossil fuel use and waste disposal are assumed to be distributed according to population. The emissions from industrial or mining activities are generally concentrated into relatively small specific areas whose locations have to be determined from published economic maps or other sources of information. This was done for iron siderurgy (CO source), petroleum refining (CO, NO<sub>x</sub>, SO<sub>x</sub> and HCs sources), copper refining and sulfuric acid manufacturing (SO<sub>x</sub> sources), hard coal, lignite and natural gas extraction (HC's sources) [e.g., Encyclopedia Britannica, 1982; Encyclopedia Americana, 1988; Goode's World Atlas, 1976; National Geographic Atlas of the World, 1981; Neue Welt Atlas, 1977; Times Atlas of the World, 1975; Europa Yearbook, 1985].

The time variation of the emissions throughout the year was determined by considering the seasonal variation of fossil fuel consumption or production and the temperature dependencies of the automobile emission factors as assessed by a study performed by the Energy and Environmental Analysis [EEA, 1981] for U.S. cars. This study reported relatively large variations of the CO and HCs emission factors with temperature for gasoline-powered vehicles, with a minimum around 20°C and higher values

for lower or higher temperatures. The  $\text{NO}_x$  emissions varied much less by comparison. All emissions from diesel-powered vehicles were found to be insensitive to temperature. We expect thus little or no temperature dependency of the  $\text{SO}_x$  emission factors (not measured by EEA) since gasoline vehicles emit only negligible amounts of  $\text{SO}_x$ . The International Energy Agency [OECD/IEA, 1989] gives the 1976–1988 quarterly fossil fuel use and natural gas production for all OECD members. Seasonal variations in other countries can then be estimated assuming a simple latitude dependency for the amplitude of the time variation which best fit the OECD/IEA data. As the consumption of oil used for transportation can be expected to have only little dependency on the time of the year, the seasonal variation in oil consumption has to be associated primarily with the other oil uses. The seasonal variation adopted for the global energy use agrees well with the figures given by Marland [1987], who investigated the seasonal variation of the anthropogenic  $\text{CO}_2$  emissions. An exception is the particular case of oil whose use for electricity generation and heating has much declined during the mid and late 1980s, leading to a decrease in the overall seasonal variability of the consumption of oil.

In summary, three different types of pollutants sources have been considered, with distinct seasonal variations. The transportation source varies according to its known temperature dependency; monthly emissions were computed using climatological surface temperatures [Trenberth and Olson, 1988]. The seasonal variation of the other fossil-fuel sources was assumed to be identical to that of fossil fuel use consumption or production. Finally, the remaining emissions were assumed to be constant as a function of time.

Our emission estimates of the global emissions of  $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and NMHC are summarized in Table 5. Two examples of the emission distributions are shown in Figures 1 and 2 ( $\text{CH}_4$  and  $\text{CO}$  emissions). The geographical distribution of the

TABLE 5. Anthropogenic emissions of NO<sub>x</sub>, SO<sub>x</sub>, CO, CH<sub>4</sub>, and NMHC. Global emissions (millions of tons) and repartition (in percent) among four large regions. SO<sub>x</sub> and NO<sub>x</sub> emissions are expressed as SO<sub>2</sub> and NO<sub>2</sub>, respectively. See text for details.

	World (Tg/yr)	North America (%)	Other OECD (%)	Central Planned (%)	Others (%)
CO <sub>2</sub>	5560	26	22	36	16
NO <sub>x</sub>	72	30	25	30	15
transportation	28	34	32	16	18
combustion	39	29	20	39	13
other sources	5	12	29	30	29
SO <sub>x</sub>	184	15	15	52	19
transportation	3	32	33	14	21
combustion	151	13	14	57	15
other sources	30	16	23	29	32
CO	383	22	16	42	20
transportation	200	28	15	32	25
combustion	74	13	16	54	16

TABLE 5. (continued).

other sources	109	16	18	51	15
<b>CH<sub>4</sub></b>	<b>132</b>	<b>19</b>	<b>16</b>	<b>48</b>	<b>17</b>
natural gas	65	11	8	60	21
coal mining	17	19	14	56	11
landfills	40	31	29	26	14
other sources	10	23	17	42	18
<b>NMHC</b>	<b>98</b>	<b>20</b>	<b>15</b>	<b>47</b>	<b>18</b>
natural gas	14	11	8	60	21
other sources	84	23	17	42	18

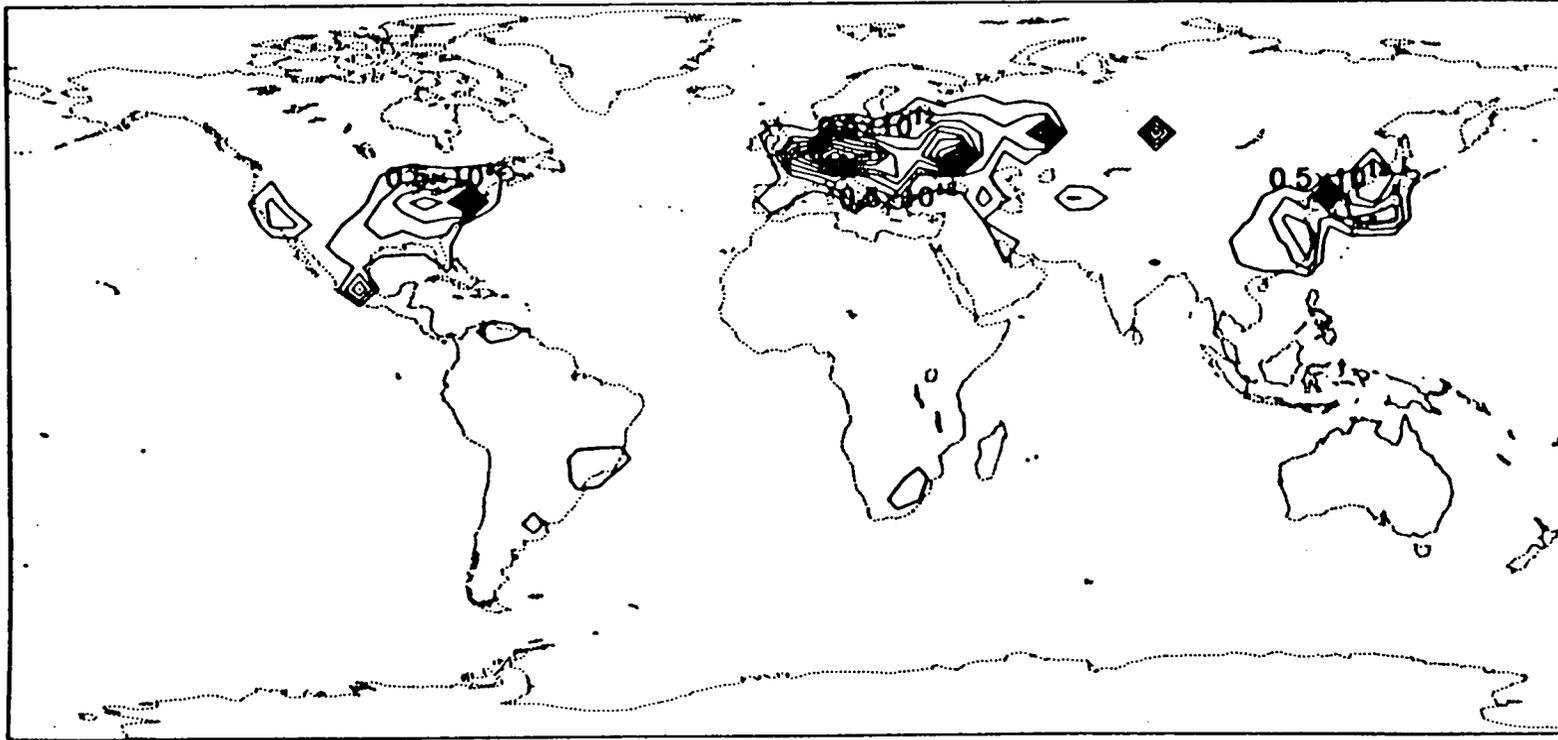


Fig. 1.- Annual mean distribution of the anthropogenic emissions of methane (molec/cm<sup>2</sup>/s).

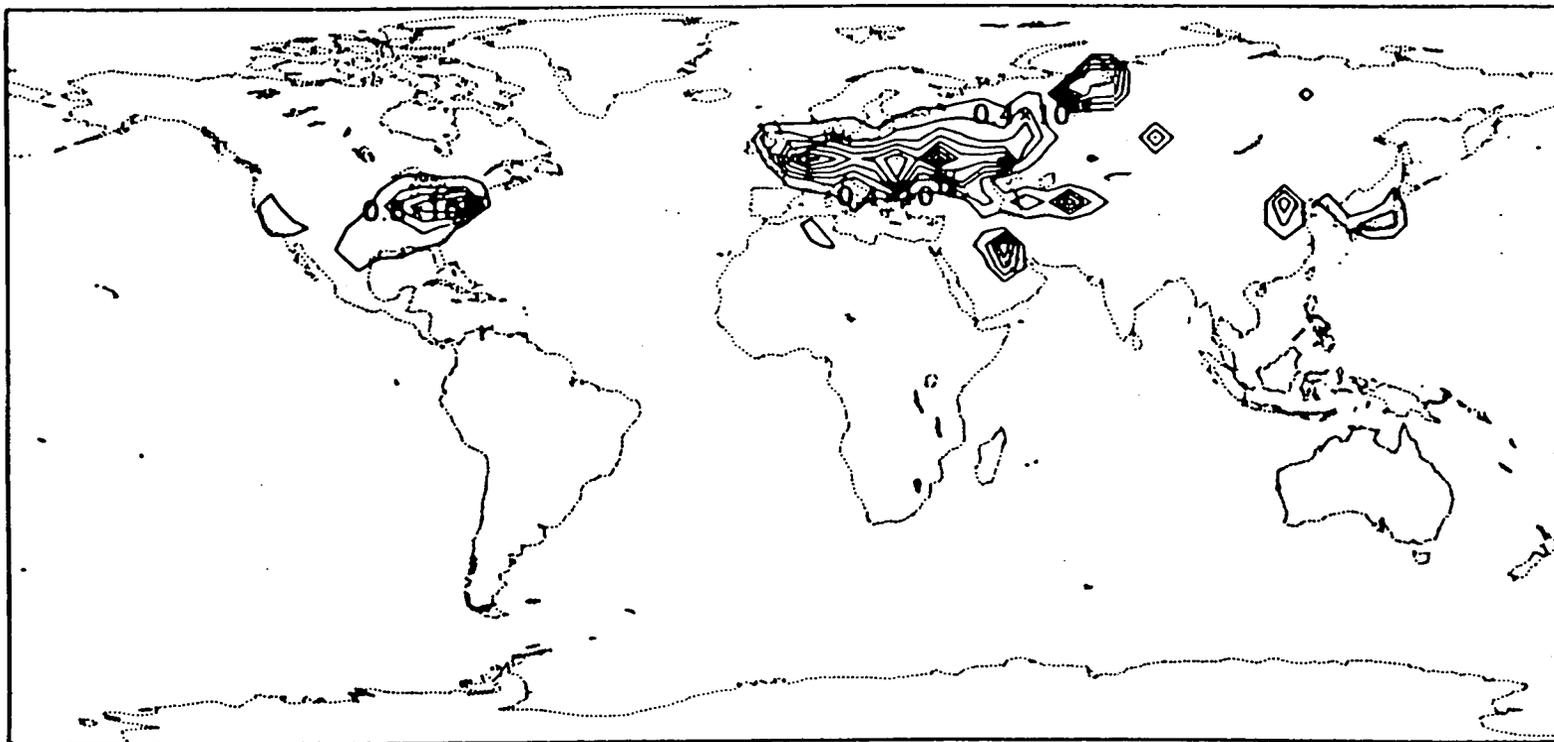


Fig. 2.- Annual mean distribution of the anthropogenic emissions of carbon monoxide (molec/cm<sup>2</sup>/s).

emissions shows different patterns for the different compounds. While 55% of the global source of  $\text{NO}_x$  is concentrated in OECD countries (central-planned countries 30%), only 35% of the methane emitted is provided by the same region. Central-planned countries totalize 52 and 48% of the sulphur oxide and methane emissions, respectively. This is explained by the fact that these regions extract and use large amounts of coal and natural gas, and that natural gas loss rates are expected to be particularly large in these regions. Of the 132 Tg of methane emitted per year globally, waste disposal, natural gas losses, coal mining and other sources contribute to 40, 65, 17 and 10 Tg/yr, respectively. The fossil (i.e., radiocarbon-depleted) part of this source is 92 Tg/yr. This is higher than previous estimates of the fossil anthropogenic source of methane (e.g., Ehhalt [1974], Cicerone and Oremland [1988]). Assuming a total source of 400–600 Tg  $\text{CH}_4$ /yr, the fossil source that we estimate represents about 15–25% of this source. Recent measurements indicate that the contribution of fossil sources is most probably between one sixth and one third of the total contribution: 23–32% according to Lowe et al. [1988] and Manning et al. [1990], 18–24% according to Wahlen et al. [1989],  $16 \pm 12\%$  according to Quay et al. [1991]. Besides coal mining and natural gas leakage, other sources have been proposed by different authors which could emit significant amounts of fossil methane, such as asphalt pavements and wetlands (see, e.g., Cicerone and Oremland [1988] for a discussion). Emissions from asphalt, however, appear to be a negligible source [Tyler et al., 1990]. Our work suggests that the fossil fuel sources alone could possibly explain the observed fossil methane content of the atmosphere. Much work needs, however, to be done to better constrain the magnitude of the individual sources which are still very uncertain. In particular, specificities of the situation in the Soviet Union and Eastern Europe need to be further investigated.

### 3. Biomass Burning

Biomass burning is associated with deforestation, savannah burning, slash and burn agriculture, forest wildfires, wood used as fuel, and burning of agricultural wastes [e.g., Logan et al., 1981; Seiler and Crutzen, 1980; Crutzen et al., 1989]. Since most of these processes are controlled by humans, the emissions ( $\text{CO}_2$ , CO,  $\text{NO}_x$ , HCs, and other compounds) caused by the combustion of biomass can be considered as anthropogenic emissions. They play a dominant role in the chemistry of the tropical troposphere, where the largest part of the source is located, and contribute a large part of the budgets of CO,  $\text{NO}_x$ , and some hydrocarbons, not to mention  $\text{CO}_2$ .

Crutzen et al. [1989] used detailed data on deforestation, biomass densities and agricultural practices to estimate the contribution of biomass burning in the tropics to the budget of trace gases. They developed maps of the annual emissions of  $\text{CO}_2$  caused by forest and savannah fires in the tropics with a resolution of  $5^\circ \times 5^\circ$ . They expressed the amount of burned biomass ( $M$ , in tons/yr) as

$$M = A \times B \times \alpha \times \beta \quad (1)$$

where  $A$  is the surface area burned each year (hectares),  $B$  is the biomass density of vegetation (tons dry matter per hectare),  $\alpha$  is the fraction of biomass which is above ground and  $\beta$  is the fraction of the above-ground biomass that is burned. The amount of CO emitted is then computed by assuming that the ratio of CO to  $\text{CO}_2$  produced by the combustion of biomass is 10% in volume. The emission ratios of the other trace gases to  $\text{CO}_2$  are also assumed to be constant ( $\text{NO}_x$  0.2%,  $\text{CH}_4$  1.3%, NMHC 1.4%). The estimated total emissions resulting from forest and savannah fires in the tropics amount to about 2000 Tg  $\text{CO}_2\text{-C/yr}$ , 200 Tg  $\text{CO-C/yr}$ , 26 Tg  $\text{CH}_4\text{-C/yr}$ , 28 Tg  $\text{NMHC-C/yr}$  and 5

Tg NO<sub>x</sub>-N/yr. The uncertainty in these numbers is estimated to be roughly a factor of three.

The study of Crutzen et al. [1989] has been adopted to establish our inventory, but it has been extended to account for the other contributions to biomass burning. Estimates of the forest damage caused by fire in individual states of the U.S., the other OECD countries and several eastern European countries (GDR, Poland, Czechoslovakia, Hungary) are available from statistics of U.S. Forest Service [1986], OECD [1989] and UN [1988]. These data give the area of forest burned annually in the early 1980s. Table 6 lists the area of burned forests for these countries, averaged over the period for which data are available. It must be noted, however, that the data show a very large interannual variability of fire damage and also strong transient trends in some countries (for example, the burned area of Canadian forests decreased by about a factor of 5 between 1981 and 1985). Therefore, the time-average used to derive the geographical distribution of forest fires cannot be thought as representative of any particular year. A global geographical distribution of forests on a 5° × 5° grid was derived from the World Ecosystems Database of Olson et al. [1983; 1985]. This database distinguishes about sixty different ecosystems ranked by carbon content and distributed on a 0.5° resolution grid. The forest map derived from this database was used to estimate the percentage of the forest coverage that is burned each year in the countries for which data are available. They range from less than 0.01% (e.g., in northern Europe) to a few percents (in Mediterranean countries, and in some states in the U.S.). These data were used to estimate the extent of forest fires in other non-tropical countries, following the assumption that similar fire frequencies occur in similar climatic environments. The forest map and the estimates of the forest fire frequencies were then used to assess the distribution of fires. It was assumed that the fires are distributed as the forest coverage within each country. The global surface area of burned forests in extra-

TABLE 6. Burned area of forests (in thousands km<sup>2</sup>) in the early 1980s in countries of the temperate and boreal regions.

	Burned Area		Burned Area
Austria	1.2	France	420
Belgium & Luxembourg	0.5	Greece	480
Denmark	0.1	Italy	680
Finland	6	Portugal	430
Federal Republic of Germany	9	Spain	1800
Iceland	0	Turkey	95
Ireland	6	Yugoslavia	180
Netherland	0.7	South Europe	4085
Norway	2.7		
Sweden	50	Canada	24400
Switzerland	9	United States	14900
United Kingdom	7	North America	39300
Czechoslovakia	1.7		
Hungary	30	Japan	50
Poland	110	New Zealand	14
German Democratic Republic	8		
North Europe	242		

tropical (i.e., temperate and boreal) regions is found to be about 120,000 km<sup>2</sup> each year. The biomass densities necessary to compute the CO<sub>2</sub> emissions resulting from these fires were taken from Whittaker and Likens [1975] and NAS [1975], and the coefficients  $\alpha$  and  $\beta$  of the equation (1) were assumed to be constant and equal to 0.75 and 0.35, respectively. Using the same emission factors for the trace gases other than CO<sub>2</sub> as those used by Crutzen et al. [1989], the global yearly emissions resulting from this extra-tropical source is estimated to amount to 320 Tg CO<sub>2</sub>-C/yr, or about one sixth of the tropical source found by Crutzen et al. [1989].

The forest and savannah fire emissions show a strong seasonality (in both tropical and extratropical regions). Most emissions take place during the dry season in the tropics and during the summer in the other regions. Observations of trace gases in the tropics [Kirchhoff, 1989; Marenco et al., 1990] show that a delay separates the period of minimum precipitation and the period of most intense burning. This delay is particularly pronounced in South America, where most fires occur at the end of the dry season. To parameterize this time variation, we first define a function of the monthly mean precipitation ( $P_m$ , in mm/month, obtained from the climatology of Shea [1986]) and temperature ( $T_m$ , in Celsius, from Trenberth and Olson [1988]) as

$$f_m = f(T_m, P_m) = \frac{T_m}{P_m} \quad (2)$$

when  $T_m$  is positive, and equal to zero below freezing. Although  $f(T, P)$  is maximum when temperature is highest (i.e., during the summer) in temperate and boreal regions, it varies basically like  $1/P_m$  in the tropics where temperature changes much less than precipitation. We assume that the fraction of annual emissions occurring during the month  $m$  is proportional to the function

$$g_m = f_m \times (1 + a \times n_m) \quad (3)$$

where  $n_m$  is the number of consecutive months preceding the month  $m$  for which the function  $f$  is larger than the annual mean of  $f$ . The factor  $a$  in (3) has to be chosen to reproduce the seasonality of the emissions estimated from the observations of trace gases. The larger this factor is, the more pronounced the delay between the burning period and the period of maximum drought. Its value was set to 2 for Latin America and 0.5 in other regions.

The use of wood as fuel is another significant contribution to global biomass burning. We used the world statistics for fuelwood use from the FAO [1987] to estimate the distribution of the emissions resulting from this source. According to FAO, 1715 millions cubic meters of fuelwood is used each year. It was assumed that fuel wood use within each country is distributed as the product of population density and forest coverage. To compute the resulting CO<sub>2</sub> emissions requires us to distinguish between hardwood and coniferous wood, which have different volume mass, i.e., 750 kg/m<sup>3</sup> and 625 kg/m<sup>3</sup>, respectively. Maps of hardwood and coniferous forests were obtained from the ecosystem database of Olson et al., and used to estimate the emissions. Following Crutzen et al. [1989], we assume that 90% of wood carbon is released as CO<sub>2</sub>. The emissions are found to amount to around 465 Tg CO<sub>2</sub>-C/yr on the global scale, about two thirds of which take place in the tropical regions.

Finally, the source resulting from agricultural waste burning was assumed simply to be proportional to the population density. The global emissions from this source is estimated to be 355 Tg CO<sub>2</sub>-C/yr, based on Crutzen et al. [1989].

In summary, biomass burning emissions on the global scale amounts to 3140 Tg CO<sub>2</sub>-C/yr, of which 2000 Tg results from forest and savannah fires in the tropics. The distribution of the emissions for the months of March and September are given in Figures 3a and 3b. The emissions of the other trace gases were computed by using the emission ratios (trace gas/CO<sub>2</sub>) reported by Crutzen et al., except for NO<sub>x</sub>: the nitrogen content of the burned biomass and the conversion efficiency factor were taken to Galbally [1985], and result in NO<sub>x</sub> to CO<sub>2</sub> ratios of 0.25 and 0.1% for the forests and for other environments, respectively. The global emissions of trace gases by biomass burning are estimated to be 730 Tg CO/yr, 54 Tg CH<sub>4</sub>/yr, 51 Tg NMHC/yr and 5.5 Tg NO<sub>x</sub>-N/yr. Crutzen et al. estimate the uncertainty of their CO<sub>2</sub> emissions from biomass burning in the tropics to be a factor of three. Robinson [1989] argues that this error estimate is probably too low; and because of important variations in the trace gas normalized emission ratios, for example with combustion and fire intensity (e.g., Andreae et al. [1988], Cofer et al. [1988]) the trace gas emission uncertainties are probably larger than the factor of three proposed by Crutzen et al.

#### 4. Foliage Emissions

Isoprene and monoterpenes are emitted primarily by foliage [e.g., Sanadze, 1961; Rasmussen, 1964, 1972]. Laboratory experiments have shown that plant emissions generally increase with increasing temperature, and that isoprene emissions are very sensitive to radiation intensity, and are probably associated with photosynthesis. Little or no isoprene is emitted in the dark [Rasmussen and Jones, 1973; Tingey et al., 1979, 1981]. While isoprene is generally the dominant hydrocarbon compound emitted by deciduous trees, conifers emit primarily terpene type compounds. Emission patterns are

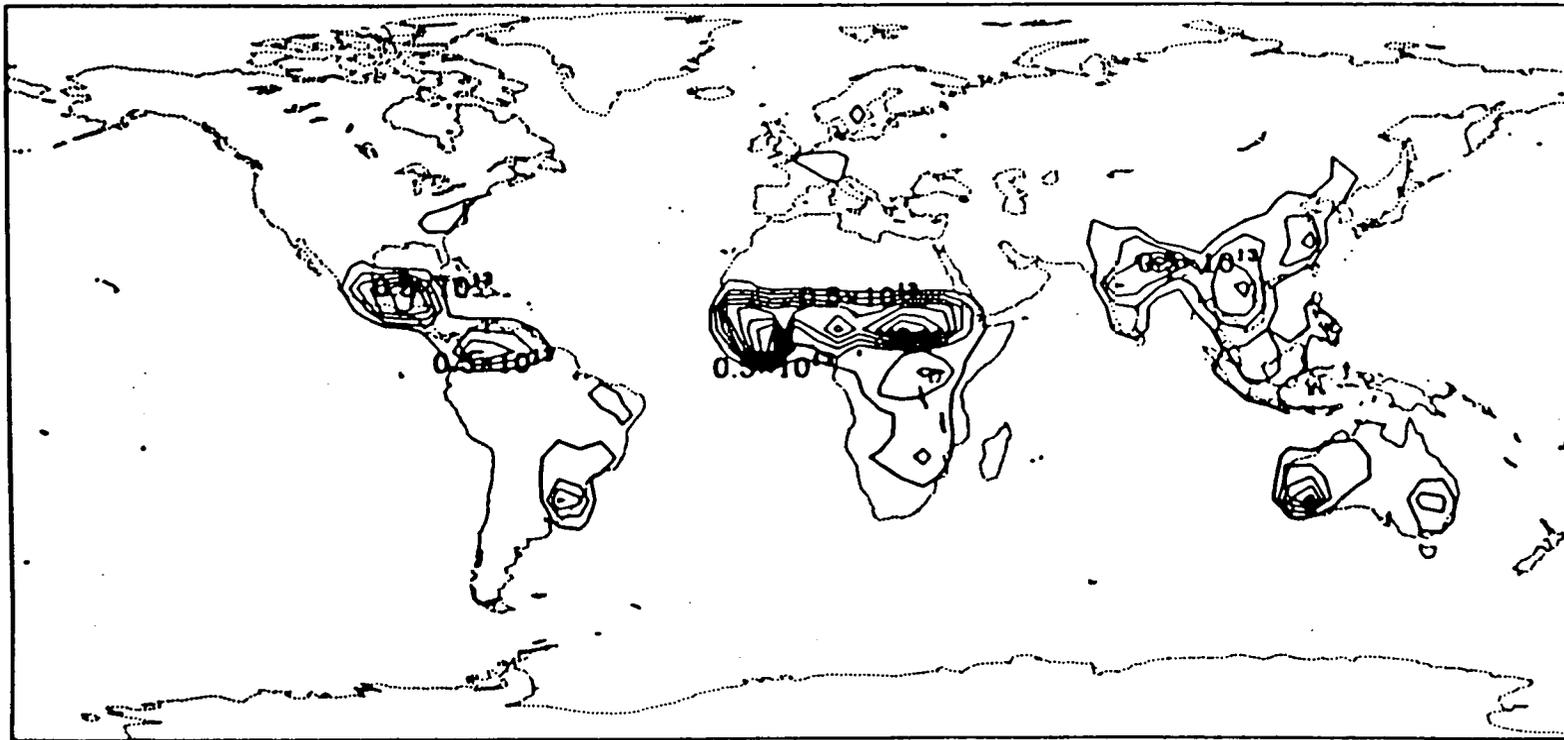


Fig. 3a.- Biomass burning emissions of CO<sub>2</sub>, for the month of April (molec/cm<sup>2</sup>/s).

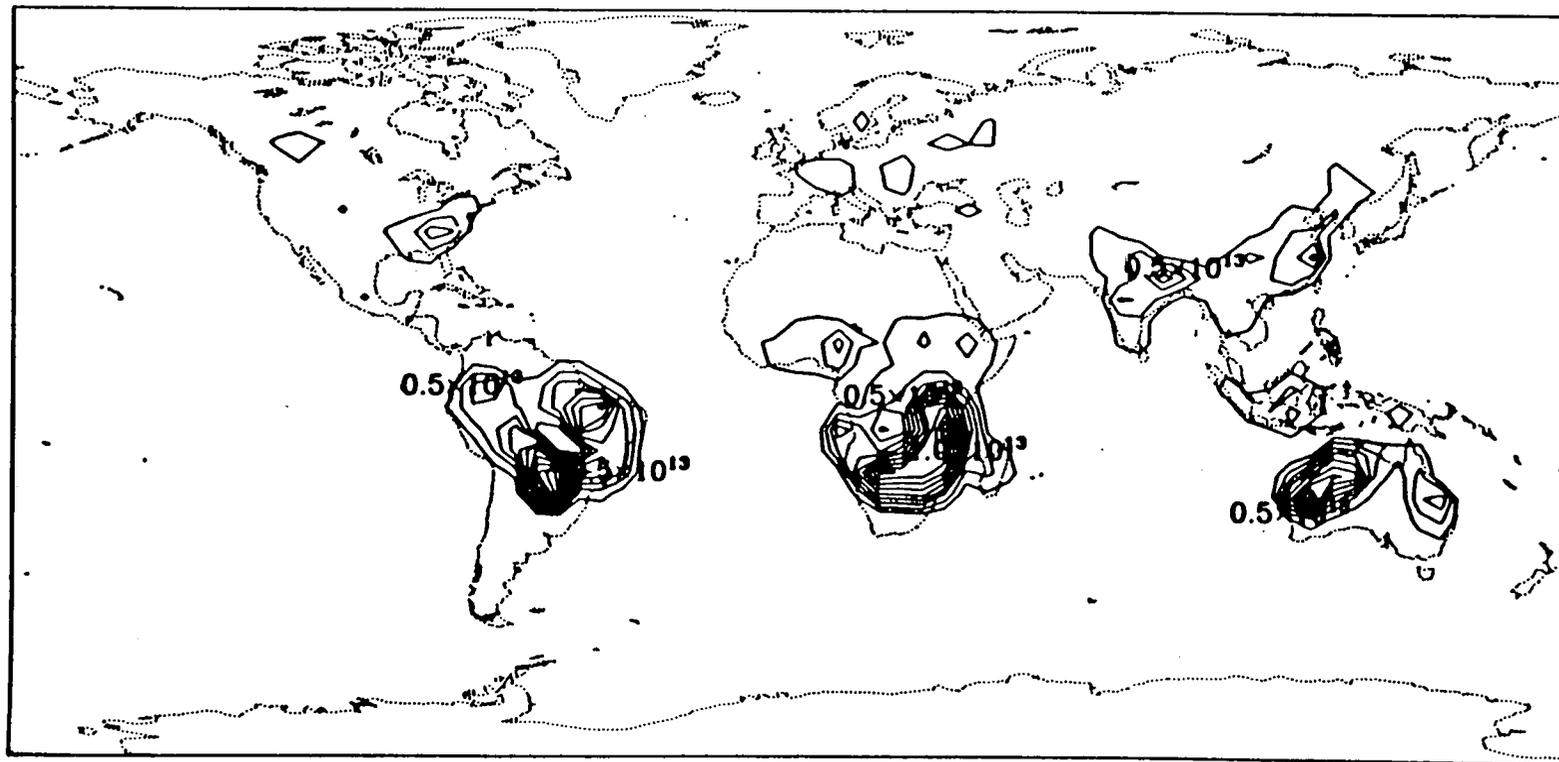


Fig. 3b.- Biomass burning emissions of CO<sub>2</sub>, for the month of October (molec/cm<sup>2</sup>/s).

affected by a number of environmental factors and show considerable variability [e.g., Zimmerman, 1979b; Evans et al, 1982a, b; Lamb et al., 1985].

Four classes of compounds were considered in this study: isoprene, terpenes, aromatics and paraffins. Since emission rates are highly dependent on vegetation type, the use of a global land-surface data set was necessary to develop the inventory. The Ecosystem Database of Olson was used for this purpose. Broad classes were defined by grouping Olson's ecosystems which have similar plant composition and biomass densities (Table 7). Parameterizations using the temperature algorithms of Lamb et al. [1987] and the Net Primary Productivity (NPP) were developed to compute the emissions. The NPP was calculated as a function of precipitation and temperature according to the empirical relationships adopted in the Miami model [Lieth, 1973, 1975]. Typical NPP values computed by this method for each broad ecosystem are given in Table 7. These values are based on U.S. averaged ecosystem productivity for temperate ecosystems and global averages for the other ecosystems. The daytime hydrocarbon emission rate  $ER_d(T)$  at temperature  $T$  is related to the emission rate at  $30^\circ$  ( $ER_{30}$ ) by

$$ER_d(T) = ER_{30} \times 10^{0.0416(T-30)} \quad (4a)$$

for isoprene and

$$ER_d(T) = ER_{30} \times 10^{0.0568(T-30)} \quad (4b)$$

for the terpenes, according to the algorithms developed by Lamb et al [1987]. Here  $T$  is in Celsius, and  $ER_d(T)$  and  $ER_{30}$  are expressed for example in  $\mu\text{g}$  per hour and per gram of leaf biomass. The emission rates standardized at  $30^\circ$  for the different broad ecosystem classes were estimated from Zimmerman [1979a, b] and Lamb et al. [1987] for the non-tropical ecosystems. The conversion to emission rates expressed per unit area was made

TABLE 7. Standard NMHC emission rates and typical Net Primary Productivity by ecosystem complex. Ecosystems are from the Olson's World Ecosystem Database (version WE2.0). The ecosystem complexes include similar ecosystems which are assumed to have standard emission factors.

Ecosystem Complex		Standard Emission		Standard NPP g/m <sup>2</sup> /yr
		rate (in $\mu\text{g}/\text{m}^2/\text{h}$ )		
WE2.0	Description	Isoprene Aromatics	Terpenes Paraffins	
8, 17, 50,	desert and semidesert	100	50	200
51, 69, 70, 71		30	40	
44, 49, 53	tundra, boreal wetlands	70	300	200
		100	100	
21, 22, 27,	coniferous forest	200	8000	1000
62, 63		300	575	

TABLE 7. (continued)

20, 60, 61	mixed coniferous-deciduous forest	1000	6000	1000
	(boreal)	380	575	
25, 26	deciduous forests	4000	1000	1400
		470	575	
23, 24, 54	deciduous forest, with conifers	2500	2500	1300
	(non-boreal)	425	575	
30, 31, 37, 38, 39, 56b, 58b	croplands, pasture	250	150	1100
		100	150	
55	field/wood (snowy)	500	2000	1000
		180	300	
58c	field/wood (non snowy, non tropical)	1500	500	1300
		210	300	

TABLE 7. (continued).

57	forest/field (snowy)	700	4000	1200
		280	450	
56c	forest/fields (non snowy, non tropical)	2500	1000	1550
		330	450	
2, 40, 41b, 46, 47, 42, 52, 65-69	scrub/grass (non tropical)	500	1000	700
		200	300	
36, 45, 72	wetlands (non boreal)	250	130	1500
		100	200	
6, 28, 29, 32, 33, 56a, 58a	tropical forests	2500	350	2100
		200	200	
43	savanna	1000	350	1500
		150	150	

TABLE 7. (continued).

41a, 48, 59	other tropical ecosystems	600	300	1100
		100	100	

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by multiplying them by the leaf biomass density of the ecosystems vegetation. Typical values of the leaf biomass densities were taken from the estimates of Whittaker and Likens [1975], and NAS [1975]. The spatial variability of biomass density within each broad ecosystem was modeled by assuming that leaf biomass density is proportional to the NPP within the ecosystem. This is a good assumption if the biomass turnover time, as well as the ratio of leaf biomass to standing biomass, are roughly constant in each ecosystem. The hydrocarbon emission rate is then expressed as follows:

$$ER = \sum_k \left[ C_k \times \frac{NPP}{NPP_k^s} \times ER_k^s \times f(T) \times g \right] \quad (5)$$

Here  $ER$  is the average emission rate,  $C_k$  is the fractional cover of ecosystem number  $k$ ,  $NPP_k^s$  and  $ER_k^s$  are the standard NPP and emission rate of the ecosystem  $k$  ( as given in Table 7),  $f(T)$  is the Lamb et al. temperature function, and  $g$  is a function to account for the variations of the day and night lengths, depending on latitude and month.

The hydrocarbons emission rate for tropical forests was estimated from the results of the Atmospheric Boundary Layer Experiments (ABLE 2A) measurements performed in July and August 1985 in the region of Manaus, Amazonia (Zimmerman et al. [1988]). We compute from these data that the isoprene and terpenes emission rates for tropical forest are expressed as  $2080 \times \frac{NPP}{NPP_o}$  and  $270 \times \frac{NPP}{NPP_o} (\mu g / m^2 / h)$  respectively, where  $NPP_o = 0.18 \text{ kg} / m^2 / \text{month}$  is the summer NPP predicted by the Miami model for this region. The daytime emission rates at 30°C for tropical forests given in Table 7 were computed by using these results, the daytime temperature observed during the ABLE 2A experiment (around 28°C) and the algorithms of Lamb et al.

The isoprene emissions in other tropical ecosystems were estimated by accounting for the fact that grass emits significantly less isoprene than tree and shrub species [see e.g., Zimmerman, 1979*a, b*; Evans et al., 1982*b*; Winer et al., 1983]. The values of the ratio of herbaceous NPP to total (herbaceous + woody) NPP were estimated by Esser [1984], and used to correct the emissions. It is typically 0.4 for forests, and closer to unity in other environments.

The 30°C emission rates are listed in Table 7. Winter as well as nighttime isoprene emissions were assumed to be zero. The other hydrocarbon nighttime emissions were assumed to be 0.75 times the daytime emissions.

The climatological precipitation and temperature fields of Shea [1986] and Trenberth and Olson [1988] were used to compute monthly mean emission rates. As precipitation is expected to be the primary factor limiting the emissions in tropical ecosystems (see e.g., Ayers and Gillet, 1988; Greenberg et al., 1985), the seasonal variation of the emissions in these regions was assumed to be similar to that of the NPP. We used the approach of Taylor et al. [1990] and assumed that the NPP algorithms of the Miami model remain valid approximations when annual mean climatological data are replaced by monthly mean data. Precipitation or relative humidity were assumed to play a negligible role in determining seasonality in temperate and boreal regions, in accordance with the results of e.g., Guenther et al. [1991] which showed that the emissions are only slowly dependent on relative humidity.

The results are summarized in Table 8, with the monthly and annual global emissions of isoprene, monoterpenes, aromatics and paraffins compounds, and their partition among the hemispheres and among the tropical and non-tropical regions. The biosphere emits about 250 Tg of isoprene, 147 Tg of monoterpenes, 42 Tg of aromatics

TABLE 8. Estimated global emissions of biogenic hydrocarbons in 1980 (teragrams).

Monthly Emissions					
	Isoprene	Terpenes	Aromatics	Paraffins	Total NMHC
Jan	18.4	8.0	2.9	3.5	32.8
Feb	18.2	8.0	2.9	3.5	32.6
Mar	19.3	8.6	3.1	3.6	34.6
Apr	20.3	9.8	3.2	3.9	37.2
May	21.8	12.7	3.6	4.5	42.6
June	23.0	17.0	4.1	5.3	59.4
July	24.9	21.8	4.8	6.3	57.9
Aug	24.2	20.0	4.7	6.1	55.0
Sept	22.1	14.4	3.9	4.9	45.4
Oct	20.4	10.4	3.3	4.1	38.3
Nov	18.5	8.2	2.9	3.5	33.1
Dec	18.4	7.9	2.9	3.4	32.6

Yearly Emissions					
	Isoprene	Terpenes	Aromatics	Paraffins	Total NMHC
Northern Hemisphere	132	105	25	32	294
Southern Hemisphere	117	42	17	20	197
Tropical ecosystems	208	81	33	38	360
Other ecosystems	41	66	10	14	132
Total	250	147	42	52	491

and 52 Tg of paraffins annually. As expected, isoprene is the dominant compound in tropical regions, and monoterpenes are the primary compounds in the other regions (Figures 4a and 4b). Total hydrocarbon emissions amount to about 500 Tg/yr, in relatively good agreement with the range of most previous estimates, given the large uncertainties associated with these estimates: Rasmussen [1972] predicts a global source of NMHC from vegetation of 230–440 Tg/yr, while Zimmerman et al. [1978] estimate the world source of isoprene and monoterpenes to be 350 and 480 TgC/yr, respectively. For comparison with other studies, we computed also the NMHC emissions predicted by our model for more specific regions. Isoprene and total NMHC emissions from the contiguous United States are estimated to be of 11 and 36 Tg/yr, respectively, to be compared with the recent estimates proposed by Lamb et al. [1987] of about 5 and 31 Tg/yr, respectively. We compute the isoprene emissions from tropical Australia to be on the order of 8 Tg/yr, at the lower end of the range of 6–100 TgC/yr proposed by Ayers and Gillet [1988] for this region.

## 5. Other Natural Emissions

Nitric oxide (NO) emissions from soils are believed to play an important role in some remote continental environments such as the tropical forests where the fossil-fuel source is weak [e.g., Galbally, 1985; Kaplan et al., 1988; Bakwin et al., 1990a]. NO may be produced biologically (nitrification and denitrification processes) or abiologically (decomposition of  $\text{NO}_2^-$ ). The variability in the emissions is extremely high. NO production is found to be dependent on soil temperature, vegetation cover, soil type, soil nitrate concentration, water content, and several other variables. Williams et al. [1987] derived an empirical NO/temperature relationship, based on measurements made over a grassland site in Colorado:

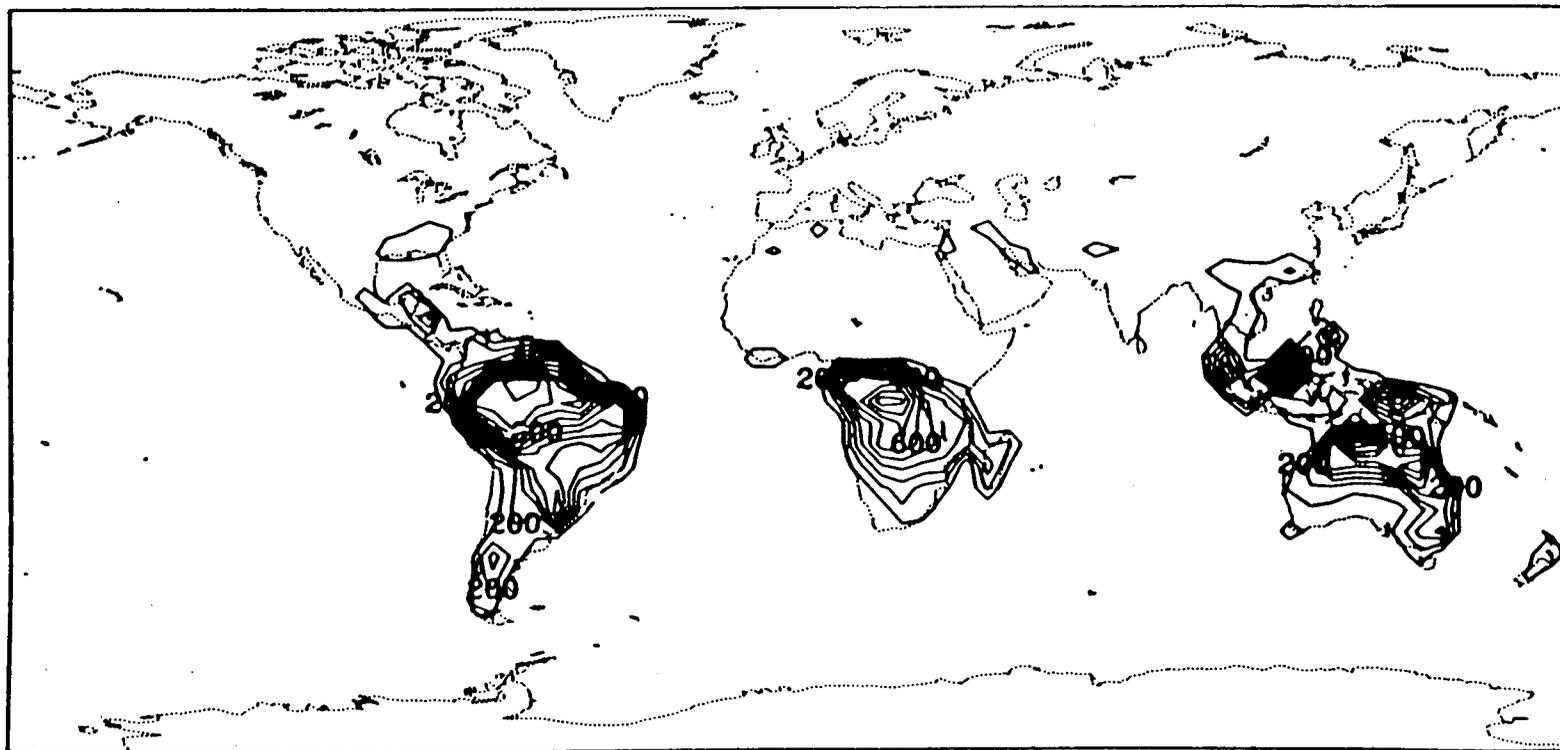


Fig. 4a.- Annual mean distribution of the foliage emissions of isoprene in January ( $\mu\text{g}/\text{m}^2/\text{hour}$ ).

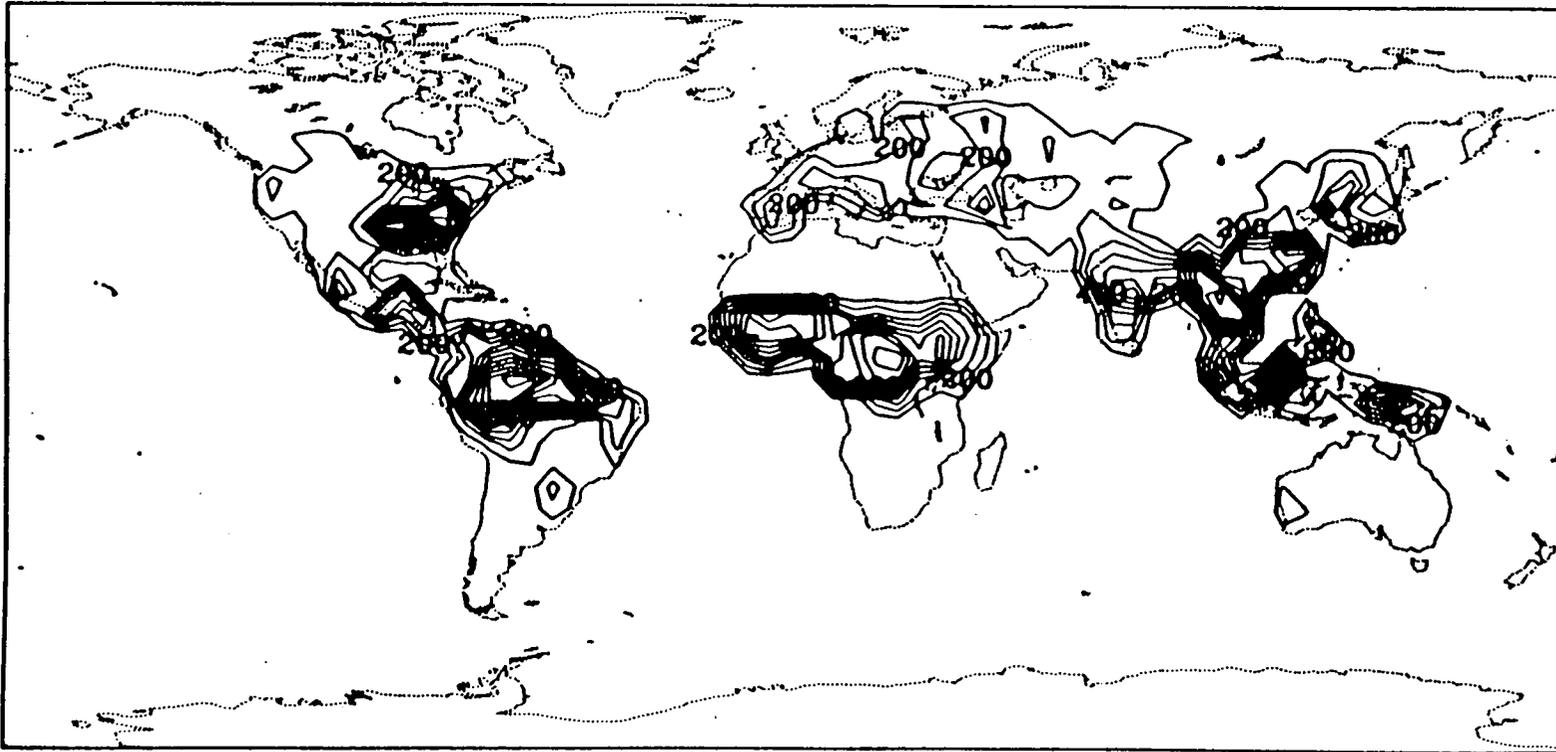


Fig. 4b.- Annual mean distribution of the foliage emissions of isoprene in July ( $\mu\text{g}/\text{m}^2/\text{hour}$ ).



Fig. 4c.- Annual mean distribution of the foliage emissions of monoterpenes in January ( $\mu\text{g}/\text{m}^2/\text{hour}$ ).

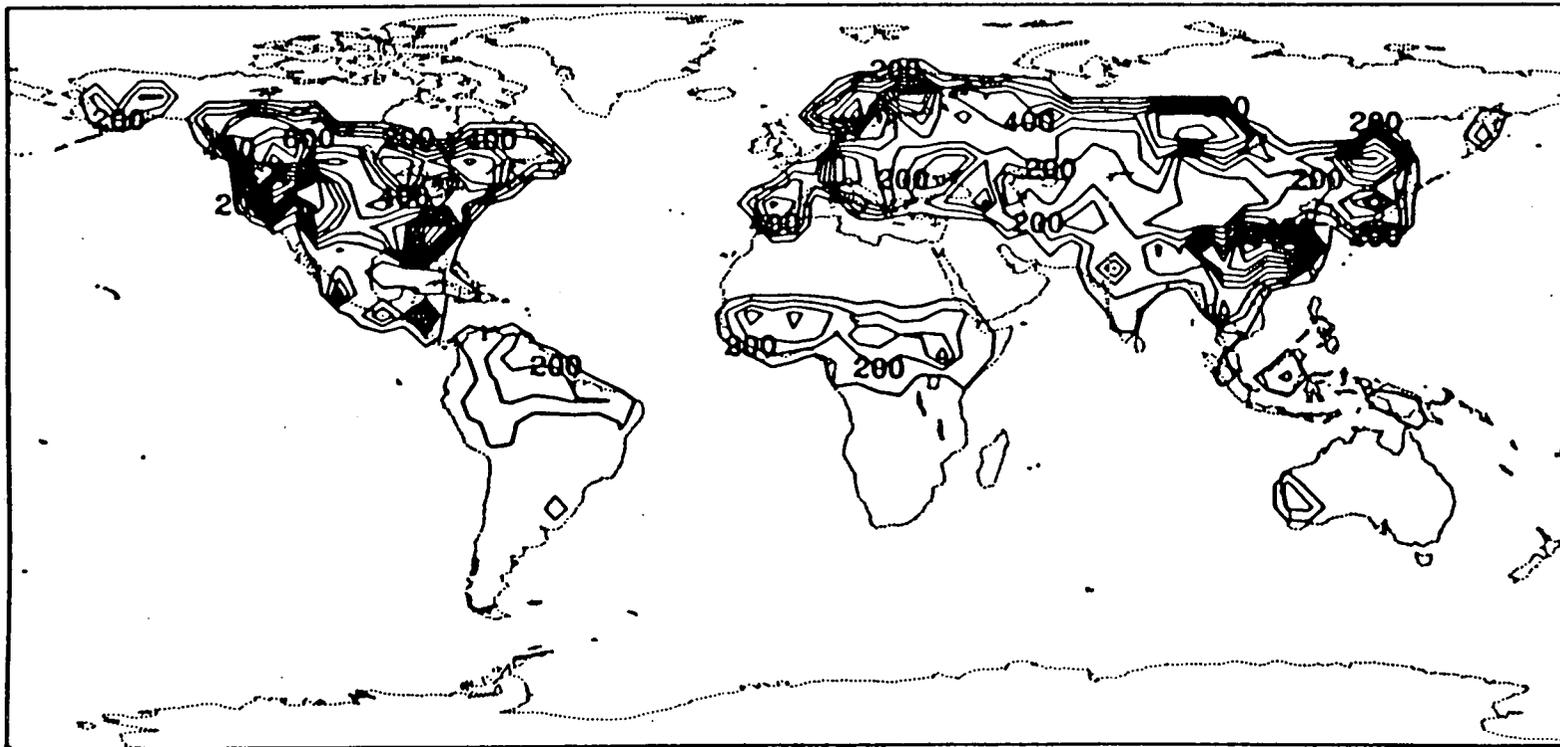


Fig. 4d.- Annual mean distribution of the foliage emissions of monoterpenes in July ( $\mu\text{g}/\text{m}^2/\text{hour}$ ).

$$\log_{10}(\text{NO flux}) = 0.049 \times T_A - 0.83 \quad (6)$$

where  $T_A$  is the air temperature (Celsius) , and the flux is expressed in ng N/m<sup>2</sup>/s.

The measurements from this site averaged about 3 ng N/m<sup>2</sup>/s, which is roughly the order of magnitude of the mean NO emissions measured at other sites in non-tropical ecosystems. This temperature relationship was used to derive the NO emission in all environments except the desert and the tropical forests. The role of rainfall on emissions is more complex. Desiccation as well as excessive inundation is expected to inhibit the emissions, as demonstrated by field studies [e.g., Johansson and Sanhueza, 1988; Williams and Fehsenfeld, 1991; Bakwin et al., 1990a]. The ABLE 2A and ABLE 2B missions in the Amazon rain forest show that NO emissions are about 6 times higher during the dry season than during the wet season [Bakwin et al., 1990a]. Maximum dry season fluxes amount to about 12 ng/m<sup>2</sup>/s, or  $5.2 \times 10^{10}$  molec./cm<sup>2</sup>/s [Kaplan et al., 1988]. Rainfall in the region of the ABLE 2A and 2B measurements is about 5 times lower in the dry season than during the wet season [Harris et al., 1990]. This feature is also found in the climatology of Shea [1986]. We assume that the emissions vary with time as the inverse of precipitation in tropical forests. The annual mean fluxes were assumed proportional to the NPP, scaled to reproduce the flux estimated by Kaplan et al., during the dry season in the Amazon rain forest. In contrast, the NO emissions measured at a tropical savanna site in Venezuela [Johansson et al., 1988; Johansson and Sanhueza, 1988] show the opposite pattern, with the highest fluxes (3–60 ng N/m<sup>2</sup>/s) occurring during the rainy season. However, another field study conducted in a savanna site in Venezuela during the rainy season [Sanhueza et al., 1990] found NO fluxes about 100 times lower than during the previous study. The possible reasons for this difference are complex (e.g., lack of nitrifying bacteria in the soil of the latter study), as discussed by Sanheza et al. [1990]. We

assumed therefore that the NO emissions in non-forest tropical ecosystems are approximated by (6).

Monthly mean NO fluxes were derived, and distributed on a  $5^\circ \times 5^\circ$  grid (Figure 5). The global emissions are estimated to be 20 Tg(NO<sub>2</sub>), or 6 Tg NO<sub>x</sub>-N annually, in good agreement with previous studies, e.g., of Lipschultz et al. [1981] and Slemr and Seiler [1984]. About 2.4 Tg(N) are produced by tropical forests. The highest and lowest global emissions occur in July (0.7 Tg(N)) and in November (0.4 Tg(N)), respectively.

A substantial fraction (about 60–80% during the wet season) of the NO emitted by the tropical forest soils is believed to be oxidized to NO<sub>2</sub> by reaction with O<sub>3</sub> and other oxidants below the forest canopy [Jacob and Wofsy, 1990; Bakwin et al., 1990a]. As NO<sub>2</sub> and probably NO are subject to deposition to leaves, only a little fraction of the NO<sub>x</sub> emitted by soils eventually escapes to the atmosphere. The consequence of this on the atmospheric budget of NO<sub>x</sub> is difficult to assess, due to the large uncertainties in the measurements. However, a second source map was realized, where the NO flux was reduced to account for the NO<sub>x</sub> deposited within the canopy. Forest fluxes were multiplied by 0.3 in tropical forests, and by 0.6 in other forests. The global source of NO<sub>x</sub> escaping to the atmosphere is now evaluated to 4.1 Tg(N)/yr, or 13.6 Tg(NO<sub>2</sub>)/yr. Tropical forests contribute only 0.7 Tg(N), or 17% of the global flux.

A simple method to distribute the continental natural emissions of other species is to rely on the NPP's model described in the previous section. The justification is that NPP is a good measure of the intensity of the biological processes which produce the emissions. Knowing the world annual NPP predicted by our simple model (about 130 Pg of dry matter), it is easy to produce the geographical distribution of biogenic emissions once the



Fig. 5a.- Nitric oxide emissions from the soils for the month of January (molec/cm<sup>2</sup>/s).



Fig. 5b.- Nitric oxide emissions from the soils for the month of July (molec/cm<sup>2</sup>/s).

total emission is known. In the case of methane, the total biogenic source could be for example 310 Tg/yr [Cicerone and Oremland, 1988]. It is however certain that a better description of these sources is required for more detailed studies. This is particularly true in the case of methane whose emissions are mostly biogenic in nature. The global distribution and seasonal variation of the emissions from wetlands and rice paddies [Aselman and Crutzen, 1989; Matthews and Fung, 1987; Matthews et al., 1990], from animals [Crutzen et al., 1987; Lerner et al., 1988; Reuss et al., 1990], from solid wastes [Bingemer and Crutzen, 1987], and from termites [Khalil et al., 1990] have been investigated in recent studies and emission rates have been suggested for each of these sources. The uncertainties associated with these estimates are still very large, perhaps a factor of two for most individual sources. Taylor et al. [1990], who used a three-dimensional transport model to test the recently reported methane sources distributions, noted that using NPP as a source function for biological emissions appears not convincingly worse than using more detailed source distributions. Information can be provided by models, to quantify, for example, the total tropical source strength. But it appears difficult to further discriminate between source functions whose tropical emissions have the same total strength but different distributions. See, for example, Cicerone and Oremland [1988] or Fung et al. [1990] for a more complete discussion of the methane budget.

Carbon monoxide is produced biologically, by soils and probably by vegetation and termites [see e.g., Logan et al., 1981; Kirchhoff and Marinho, 1990; Zimmerman et al., 1982]. Observations in the Amazonian rain forest show that direct biogenic emissions account for about 80% of the total wet season CO source. Emissions proportional to NPP were assumed; the scaling was chosen to reproduce the global estimate of Logan et al., except for the tropics where it was estimated from the data of Kirchhoff and Marinho (flux

of  $4 \times 10^{11}$  molec./cm<sup>2</sup>/s for an NPP of 0.22 g/m<sup>2</sup>/month). The resulting global emissions are 165 Tg(CO)/yr.

The oceans are a source of various trace gases, but these emissions are poorly documented. Erickson [1989] produced seasonally-varying distribution maps of the carbon monoxide oceanic source. The emissions were derived by using global data fields from an atmospheric general circulation model, such as cloud and radiation fields (to compute the solar energy at the surface) and surface winds and temperature (used to derive the transfer velocity field of CO). His estimate for the contribution of the oceans to the global budget of CO is  $165 \pm 80$  Tg/yr, at the upper bound of previous estimates. Oceanic emissions of CH<sub>4</sub> and NO<sub>x</sub> are probably very small: about 10 Tg/yr for methane, or about 2% of total CH<sub>4</sub> emissions [e.g., Cicerone and Oremland, 1988], and less than 0.05 Tg for NO<sub>x</sub> (estimate based on Zafiriou and McFarland [1981]). The case of the non-methane hydrocarbons is more controversial. A recent study [Donahue and Prinn, 1990] suggests a possible important oceanic source of non-methane hydrocarbons, particularly the heavier alkenes. The fluxes were deduced from balance requirements between surface source and chemical atmospheric sink. However, the data are not sufficient to derive any reliable global estimate. The uncertainties estimated by Donahue and Prinn are of a factor of 4 for C<sub>2</sub>-C<sub>3</sub> NMHC, and 25 for heavier hydrocarbons. But even the lower bound of their estimates is higher than the fluxes derived from diffusive microlayer models. Previous estimates of the global oceanic source of NMHC are 21 Tg/yr [Ehhalt and Rudolph, 1984] and 52 Tg/yr [Bonsang et al., 1988]. We assume a range from 30 to more than 300 Tg NMHC/yr on the global scale. Relying on the fact that oceanic emissions of hydrocarbons are biogenic, as for CO, a first approximation for the geographical distribution of the NMHC emissions is to assume that it is identical to the distribution of CO emissions determined by Erickson [1989].

## 6. Dry Deposition

Several trace gases undergo irreversible absorption at the earth's surface. The downward flux associated with this deposition is usually expressed as

$$F = v_d \times n \times X \quad (7)$$

Here  $n$  is the air number density,  $X$  is the mixing ratio of the trace gas and  $v_d$  is the deposition velocity.  $v_d$  is usually determined at a height of a few meters above the ground or the plants canopy. The choice of the reference height does not significantly affect the value of the deposition velocity since  $n$  and  $X$  in (7) vary slowly with altitude.  $v_d$  is determined by the aerodynamic resistance ( $r_a$ ) to the trace gas absorption, and by the resistance occurring at the surface itself ( $r_s$ ):

$$v_d = \frac{1}{r_a + r_s} \quad (8)$$

For some trace gases, e.g.,  $\text{HNO}_3$ , the surface resistance is negligible and their surface deposition is determined by aerodynamic parameters only (vertical mixing above the surface). A detailed discussion of the aerodynamic resistance determination can be found e.g., in Hicks and Liss [1976], Warnek [1987] or Chang et al. [1987]. We adopted for simplicity a unique value of  $r_a$  for all species of 50 s/m. At the opposite, the deposition of compounds such as CO or  $\text{CH}_4$  is controlled by the surface resistance only ( $r_s \gg r_a$ ).

For ozone, the surface resistance is very high on water, ice and snow (more than 1000 s/m), while generally much lower on grasslands, soils and forest canopy [Galbally and Roy, 1980; Lenschow et al., 1982]. Deposition of ozone appears to be particularly efficient in tropical forests during daytime,  $v_d(\text{O}_3)$  being of the order of 1.5–2 cm/s [Kaplan et al., 1988; Gregory et al., 1988]. Nighttime deposition velocities are generally

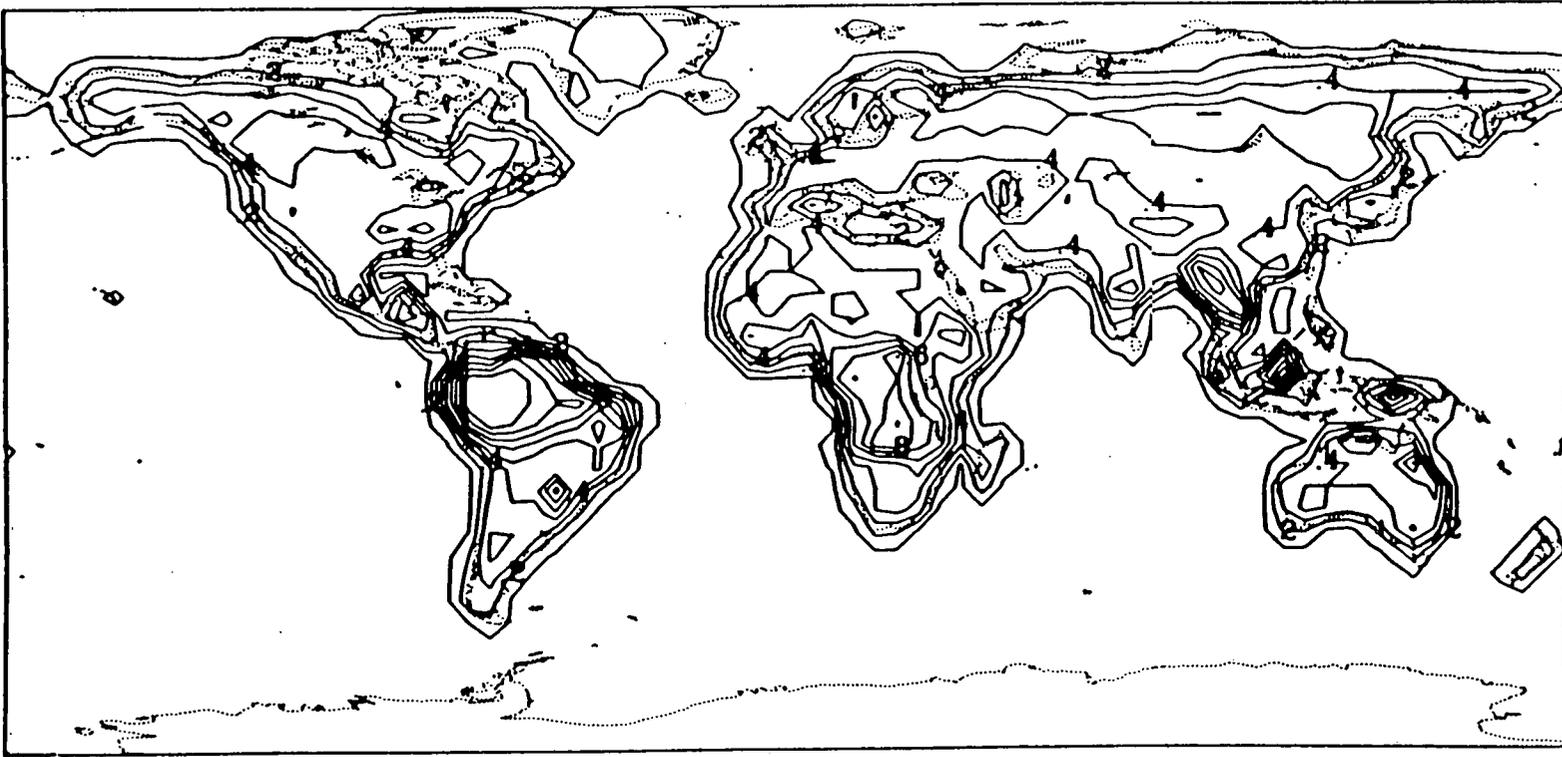


Fig. 6.- Ozone deposition velocity (cm/s) (July).

lower, by a factor of about two or three for grasslands, soils and temperate forests, and more than six for the tropical forests [Fan, 1990; Galbally and Roy, 1980]. A map of the ozone deposition velocity was constructed, based on these results and on the Olson Ecosystem Database (Figure 6). The adopted  $v_d$  values are 0.075 cm/s on water and snow, 0.4 cm/s on bare soils and grasslands, 0.5 cm/s on the savannah, 1 and 0.6 cm/s on tropical and other forests, respectively.

Deposition of nitrogen are much more poorly known, and probably highly variable. Deposition on vegetation is possibly controlled by stomatal opening, resulting in a strong diurnal cycle, with lower velocities at night than during the day [Bakwin et al., 1990b]. Relying on Chang et al. [1987] and Thompson and Cicerone [1982], we estimated  $v_d(\text{NO}_x)$  to be  $0.6 \times v_d(\text{O}_3)$  on land and 0.1 cm/s on sea.

Born et al. [1990] reported methane consumption in several terrestrial environments. They noted a slow increase of the deposition flux with temperature in temperate forest soils, resulting in a 50% difference between winter and summer fluxes. The data of Born et al. [1990], Goreau and de Mello [1988] and Keller et al. [1983] were used to estimate the methane deposition velocity for each of the Olson ecosystems. A seasonal variation of the fluxes based on temperature data was assigned in the non-tropical regions, to reproduce the seasonality observed by Born et al. The global deposition flux is estimated to be about 10 Tg(CH<sub>4</sub>)/yr.

Jacob and Wofsy [1988] formulated the hypothesis that isoprene could be deposited on surface, in order to explain its observed sink during the night in the Amazon forest boundary layer. They proposed a deposition velocity as large as 2 cm/s in this environment. However, there is no data corroborating such value, and the physical,

chemical or biologic processes governing this deposition are not known. Further studies, however, are needed to investigate this possibility.

Finally, the carbon monoxide deposition velocity was supposed proportional to the NPP ( $v_d(\text{CO}) = 5 \times \text{NPP}$  (g/m<sup>2</sup>/month), in cm/s). Typical values are 0.02–0.07 cm/s [Liebl and Seiler, 1976; Scharffe et al., 1990].

## 7. Conclusions

The ground sources and deposition velocities of various trace gases were studied, and 5° × 5° resolution maps of the emissions were produced. These maps will be used as surface boundary conditions in a three-dimensional chemical model of the troposphere. A general summary of the surface emissions of CO, NO<sub>x</sub>, SO<sub>x</sub>, CH<sub>4</sub> and NMHC is given in Table 9. Technological activities represent the largest source only for NO<sub>x</sub> and SO<sub>x</sub>. But if all processes directly or indirectly controlled by man are taken into account, i.e. also biomass burning and methane production by paddy fields and ruminants, anthropogenic sources contribute to about 75% or more of the global ground sources of CO, NO<sub>x</sub>, SO<sub>x</sub> and CH<sub>4</sub>, and around 20% of the source of NMHCs. Furthermore, as biogenic NMHC are mostly emitted in remote areas such as the tropical forests and the oceans, where physical and photochemical conditions (low NO levels, high rainout and deposition rates) cause very low CO yields per hydrocarbon molecule oxidized (e.g., Jacob and Wofsy [1990], Hatakeyama et al. [1991]), the contribution of biogenic NMHC to the global budget of CO is probably much lower than the contribution suggested by previous authors (e.g., Zimmerman et al. [1978]). Assuming CO yields to be one fifth and two thirds in low NO and high NO environments, respectively, and assuming that only 100 Tg/yr of biogenic NMHC are produced in high NO environments, we estimate that about 300 Tg(CO)/yr are produced by the oxidation of (continental and oceanic) biogenic NMHC.

Considering that fossil fuel burning and biomass burning emit large quantities of  $\text{NO}_x$  together with the NMHC, it is estimated that an additional 180 Tg(CO)/yr is produced by the oxidation of anthropogenic NMHC. Methane oxidation by OH also produces large amounts of CO, about 800 Tg/yr; its CO yield is probably close to 80–90% [Logan et al., 1981]. We estimate from these considerations that about 2500–3000 Tg(CO) are produced each year on the global scale, in good agreement with other estimations by Logan et al. [1981] and Khalil and Rasmussen [1990]; about 1800 Tg or two thirds of this source is provided by technological activities or human-controlled sources. These numbers cannot be considered as a definitive assessments of the global budget of CO; atmospheric models, accounting for photochemistry, transport, cloud and surface processes are required to refine these estimates, and also to assess the importance of CO deposition at the Earth's surface. The uncertainties of the flux estimates of Table 9 are very large: about a factor of three or more for biomass burning, the ocean emissions and most biogenic emissions. As most biogenic emissions may take place in the tropics, much future experimental work should be performed in environments such as tropical forests, savannah and tropical wetlands; the improvement of the source estimates also requires to parameterize the various factors influencing the emissions, such as water and mineral content in soils, ecosystem composition with respect to individual species, surface wind, soil type, agricultural practices, etc. The technological source also needs to be further investigated; emission factors are probably more variable than assumed in this study. Little or no information is available from Eastern Europe, USSR, China and the Third World. Natural gas losses, appearing as a possible important source of methane and some other light alkanes, are still poorly documented.

TABLE 9. Global emission estimates for CO, NO<sub>x</sub>, SO<sub>x</sub>, CH<sub>4</sub> and NMHC (in Tg/yr), by source category

	Technological Sources	Biomass Burning	Biogenic Sources*		Total
			(contin.)	Oceans	
CO	383 <sup>1</sup>	730 <sup>2</sup>	165 <sup>1</sup>	165 <sup>4</sup>	1440
NO <sub>2</sub>	72 <sup>1</sup>	18 <sup>2</sup>	20 <sup>1</sup>	0.01 <sup>5</sup>	120
SO <sub>2</sub>	184 <sup>1</sup>				184
CH <sub>4</sub>	132 <sup>1</sup>	54 <sup>2</sup>	310 <sup>3</sup>	10 <sup>3</sup>	506
NMHC	103 <sup>1</sup>	51 <sup>2</sup>	500 <sup>1</sup>	30-300 <sup>6</sup>	750

\*includes animal, microbial and foliage emissions

<sup>1</sup> this study

<sup>2</sup> this study, adapted from Crutzen et al. [1989]

<sup>3</sup> Cicerone and Oremland [1988]

<sup>4</sup> Erickson [1989]

<sup>5</sup> estimate derived from Zafiriou and McFarland [1981]

<sup>6</sup> estimate derived from Donahue and Prinn [1990]

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