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Chapter 1

Introduction

Biological activity in both terrestrial and marine environments represent a major source of volatile organic compounds (VOC) in the atmosphere [Guenther et al., 1995]. VOC is the collective name given to all the atmospheric hydrocarbons other than methane (CH_4) . Gases emitted from natural sources are often called biogenic volatile organic compounds (BVOC) as opposed to anthropogenic VOCs (AVOC). In the presence of oxides of nitrogen (NO_x) , VOCs enter complicated chemical reaction chains that yield to the formation of other carbonyls, radicals, ozone, particulate matter and finally carbon dioxide (CO_2) [Jacob, 1999; Seinfeld and Pandis, 1998]. Thus VOCs play a key role in controlling the so-called oxidizing power or self-cleansing capacity of the atmosphere [Jacob, 1999], that ultimately accounts for the impact of chemical emissions on air quality and climate. Tropospheric ozone has major adverse effects on human health and vegetation [EMEP Assessment, 2004] and it is usually regarded as "bad" ozone compared to the "good" stratospheric ozone that act as UV radiation shield for life. Also the BVOCs are more reactive than typical AVOCs [Atkinson and Arey, 2003], and they are released preferentially under fair and hot weather conditions, that are also

the best conditions for photochemical ozone production.

1.1 Overview of global biogenic emissions

In Table 1.1 the estimated emission fluxes of hydrocarbons on the global scale is reported [Seinfeld and Pandis, 1998]. A few things can be pointed out from these numbers. First of all, the biogenic contribution to global VOC emissions is more than double than the anthropogenic. Among the BVOCs, isoprene plays a major role, because its emissions almost equal methane emissions. Total anthropogenic VOC emissions contribute much less to the global carbon budget with a share that is comparable to monoterpenes. We must bear in mind that these numbers represent a global integral of the emissions and the contribution of these sources to ozone formation may greatly vary from place to place. For example, anthropogenic VOCs usually have a predominant role in urban and industrialized regions.

Taking a closer look to BVOC emission sources listed in Table 1.2, we see that woodlands are the major source of isoprene, monoterpenes and other BVOCs in the atmosphere, accounting for $\sim 70\%$ of total emissions. Shrublands represent also an important contribution to isoprene emissions. Crops are important for BVOCs other than isoprene and monoterpenes, while ocean and other sources are negligible.

In Figure 1.1 we can have a feeling of global and seasonal distribution of biogenic emissions. The values plotted are monthly emission factors for total BVOCs from the Model of Emissions of Gases and Aerosol from Nature (MEGAN) [Guenther et al., in review 2005] in January (top) and July (bottom). As expected, the major emission hot spots are co-located with the major forests worldwide. Dominant BVOC sources are equatorial woodlands

Table 1.1: Global emission estimates of hydrocarbons of both anthropogenic and biogenic origin (Tg y⁻¹, 1 Tg = 10^{12} g). ORVOC and OVOC are BVOCs other than isoprene and monoterpenes with chemical lifetime less and greater than 1 day respectively. [from Seinfeld and Pandis, 1998].

Species	Anthropogenic	Biogenic	Total
Methane	375	160	535
Anthropogenic VOC	142	-	142
Biogenic VOC			
Isoprene	-	503	
Monoterpenes	-	127	
ORVOC	-	260	
OVOC	-	260	
Total BVOC		1150	1150
Total	517	1310	1827

in South America and Africa. An important emission region in the Northern Hemisphere is the South East of United States. The amplitude of the seasonal variation is especially visible in the Northern Hemisphere, where there is a sharp increase from January to July of the emissions. Indeed, biogenic emissions are primarily driven by solar light intensity and temperature, which both increase in the summer season. Typically, at mid-latitudes, BVOC emission have a clear seasonal signature with null emissions in winter and maximum emissions in summer, with shoulder seasons being May and September. Another remarkable feature of most BVOC emitters is that they exponentially increase the emission flux with temperature. We shall better review these concepts in chapter 3. Figure 1.1: Global emission factors of total BVOCs (isoprene + monoterpenes + other) from the MEGAN [Guenther et al., in review 2005] emission inventory in January and July.



Source	Isoprene	Monoterpene	ORVOC	OVOC	Total VOC
Woods	372	95	177	177	821
Crops	24	6	45	45	120
Shrub	103	25	33	33	194
Ocean	0	0	2.5	2.5	5
Other	4	1	2	2	9
All	503	127	260	260	1150

Table 1.2: Global BVOC emission rate estimates by source and class of compound [from Guenther et al., 1995].

1.2 Overview of European biogenic emissions

While biogenic emissions outweigh anthropogenic globally, in Europe most carbon-containing emissions come from the combustion and processing of fossil fuels [Simpson et al., 1999]. Europe covers <7% of the world's land area and is inhabited by 13% of the world's population. Total European hydrocarbon emissions are summarized in Table 1.3. Europe accounts for ~15% of CH_4 emissions and ~20% of VOC emissions. Of the latter 20% natural sources account for only a small part, about 5% or 13 Tg y⁻¹. However, even in Europe, biogenic emissions can still be important for certain countries. For example, VOC emissions in the Mediterranean area are dominated by vegetation during summertime and methane emissions are dominated by wetlands in Scandinavia.

We have to notice that not all biogenic sources are purely "natural". Humans have been modifying the environment for thousand years, for example with agricultural practices and tree farming, causing deep changes to

Species	Anthropogenic	Biogenic	Total
Methane	72	8	80
Anthropogenic VOC	24	-	24
Biogenic VOC			
Isoprene	-	4.6	
Monoterpenes	-	3.9	
ORVOC	-	4.5	
Total BVOC			13
Total	96	21	117

Table 1.3: European emission estimates of hydrocarbons of both anthropogenic and biogenic origin (Tg y^{-1}) [from Simpson et al., 1999].

the landuse. These processes have altered the mix of trees and vegetation, thus masking with seemingly natural the ultimately anthropogenic changes [Purves et al., 2004; Zhang et al., 2004].

1.3 Overview of modelling and outline of the thesis

Modelling of biogenic emissions is a difficult task due to a number of reasons: need for (1) an accurate estimate of source types and densities, (2) accurate emission factors for each source type, (3) an understanding of how changes in meteorological variables such as temperature, light intensity and moisture affect the BVOC emissions, (4) estimate of the meteorological driving variables themselves. Emission modelling typically follows a "bottom-up" approach. One starts from a landuse map, that provides information about the composition of the terrain in a given area (kind of vegetation and soil, presence of manmade works, etc.), and then one applies estimated emission factors to each kind of entity of interest. For example, if we are to model biogenic emissions, we apply to each kind of tree a typical emission factor to estimate the emission flux of a certain gas. These base emissions are then modulated with other time-dependent correction factors to mimic the observed variability. This procedure involves a number of uncertainties connected to the issues listed above.

Current biogenic emission inventories in Europe has been reviewed by Simpson et al. [1995, 1999]. They found that uncertainties are as high as a factor of 5, mainly because there are only few data to constrain the emission factors and these data are heterogeneous in quantity and quality because they derive from many different countries with different scientific resources. In addition, many of the emission factors used to build European inventories are imported from North American ones, which are not necessarily generalizable to other places of the world.

Another way for building an emission inventory is the "top-down" approach. In this kind of approach one tries to constrain the emission flux of a certain species using the observed concentration of the same species of another species related to the one of interest.

In this thesis we use satellite observations of formaldehyde (HCHO) to constrain biogenic isoprene emissions. Formaldehyde is a high yield product of the oxidation of many VOCs of both biogenic and anthropogenic origin. Its atmospheric abundance is controlled by the balance among direct emissions from combustion processes, production from VOCs oxidation and losses by reaction with hydroxyl radical (OH) and photolysis. HCHO measurements can therefore provide constraints on the underlying reactive VOC emissions. Satellite-based observations of HCHO column abundance have shown the potential for estimating isoprene emissions over North America in previous work [Palmer et al., 2001; Abbot et al., 2003; Palmer et al., 2003]. Here we apply the same kind of approach to constrain biogenic isoprene emissions over the European continent in the attempt of reducing the high uncertainty in the current inventories.

Chapter 2

Isoprene and formaldehyde chemistry

In this chapter we summarize the main features of VOCs oxidation in the troposphere, with special attention to chemical mechanisms of isoprene and other BVOCs. Among the products of BVOCs degradation, formaldehyde is of particular importance, because it's an high-yield product and because its column abundance observed from space is used here as a proxy to constrain BVOCs emissions.

2.1 VOCs degradation in the troposphere

The Earth's troposphere, which is the lowest 10 to 17 km (depending on latitude and season) of the atmosphere, is an oxidizing medium [e.g. Jacob, 1999] and can be viewed as a chemical reactor where species emitted by biogenic and anthropogenic sources are processed. VOCs are lost both through transformation by the chemical processes of photolysis, reaction with hydroxyl radicals (OH), reaction with nitrate radicals (NO₃) and reaction with ozone Figure 2.1: General VOCs degradation/transformation pathway [from Atkinson, 2000]



 (O_3) and through the physical processes of wet and dry deposition [Seinfeld and Pandis, 1998]. In general, the degradation/transformation reactions of VOCs which occur in the troposphere can be represented by the scheme of Figure 2.1 [Atkinson, 2000], with the important intermediate radicals being alkyl radicals (\dot{R}), alkyl peroxy radicals (\dot{RO}_2), and alkoxy radicals (\dot{RO}). These radicals, in combination with oxides of nitrogen ($NO_x = NO + NO_2$) emitted from combustion sources (mainly anthropogenic), lead to a complex series of chemical and physical transformations which result in ozone formation in the troposphere [Kley, 1997; Chameides et al., 1992; Logan, 1985] and the formation of secondary organic aerosol (SOA) through gas-toparticle conversion [Claeys et al., 2004; Kanakidou et al., 2005; Andreae and Crutzen, 1997].

The simplest VOC oxidation scheme is that for methane [e.g. Jacobson, 1999]:

$$OH + CH_4 \rightarrow H_2O + CH_3$$
 (2.1)

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2$$
 (2.2)

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
 (2.3)

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$
 (2.4)

$$HO_2 + NO \rightarrow OH + NO_2$$
 (2.5)

$$NET: OH + CH_4 + 2NO + 2O_2 \rightarrow OH + HCHO + H_2O + 2NO_2$$

where M is a generic molecule of ambient air. An important intermediate product of methane, as well as most VOCs, oxidation is formaldehyde (HCHO). Formaldehyde is a carcinogen and an important ozone precursor. It decomposes primarily by photolysis and reaction with OH, producing carbon monoxide (CO):

$$\text{HCHO} + \text{h}\nu \rightarrow \text{CHO} + \text{H} \quad (\lambda < 334 \text{ nm})$$
 (2.6)

$$\text{HCHO} + \text{h}\nu \rightarrow \text{CO} + \text{H}_2 \quad (\lambda < 370 \text{ nm})$$
 (2.7)

$$HCHO + OH \rightarrow H_2O + CHO$$
 (2.8)

$$H + O_2 \xrightarrow{M} HO_2$$
 (2.9)

$$CHO + O_2 \rightarrow HO_2 + CO$$
 (2.10)

CO undergoes further degradation through reaction with OH:

$$\rm CO + OH \rightarrow \rm CO_2 + H$$
 (2.11)

At the end of the oxidation of both CO and HCHO an hydrogen atom (H) is produced which immediately forms an hydroperoxy radical (HO₂) through reaction 2.9. The latter can react with nitric oxide (NO) to form nitrogen

dioxide (NO_2) :

$$HO_2 + NO \rightarrow OH + NO_2$$
 (2.12)

Reaction 2.12 is extremely important, because it is the base for the photochemical production of ozone in the troposphere through photolysis of NO_2 :

$$NO_2 + h\nu \rightarrow NO + O(^{3}P) \quad (\lambda < 420 \text{ nm})$$
 (2.13)

$$O(^{3}P) + O_{2} \xrightarrow{M} O_{3}$$
 (2.14)

and because O_3 reacts rapidly with NO:

$$\mathrm{NO} + \mathrm{O}_3 \to \mathrm{NO}_2 + \mathrm{O}_2 \tag{2.15}$$

reactions 2.13, 2.14 and 2.15 result in a photostationary-state relationship between NO, NO₂ and O₃, with no net formation or loss of O₃, that usually holds in the free background troposphere. A schematic of this NO-to-NO₂ conversion cycle involving O₃ is shown in Figure 2.2A.

The presence of ozone in the troposphere [Lelieveld and Dentener, 2000] is of key importance, because its photolysis in the waveband $290 < \lambda < 335$ nm form excited oxygen (O(¹D)) atoms. O(¹D) can either decay to groundstate oxygen (O(³P)) that reform ozone through reaction 2.14 or react with water vapor to generate OH radicals:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (290 < \lambda < 335 \text{ nm}) \quad (2.16)$$

$$O(^{1}D) + H_{2}O \rightarrow 2OH$$

$$(2.17)$$

At 298 K and 50% relative humidity, ~ 0.2 OH radicals per O(¹D) atom are produced. OH is the most important radical in the atmosphere and it's responsible for the degradation of most species including CO, methane and most VOCs. Indeed, OH is often regarded as the scavenger of the atmosphere. Photolysis of ozone is a major source of OH in the troposphere, especially Figure 2.2: Schematics of the reactions involved in NO-to-NO₂ conversion and O_3 formation in (A) the absence of VOCs, and (B) in the presence of VOCs [from Atkinson, 2000]



in the lower troposphere where water vapor mixing ratios are high. Other sources of OH include the photolysis of nitrous acid (HONO), HCHO and other carbonyls. Among carbonyls, acetone is a major contributor to the OH budget in the upper troposphere [Jacob et al., 2002]. It has also been suggested that an important daytime and nighttime source of OH could be the reaction of alkenes with O_3 [Paulson and Orlando, 1996]. Because of its extreme reactivity OH lifetime is ~ 1 s and its concentration is extremely low and variable. A diurnally, seasonally and annually averaged global tropospheric OH concentration of 1.0×10^6 molecules cm⁻³ has been deduced from emission data and concentration measurement of methyl chloroform [Prinn et al., 2001, 1995].

The presence of VOCs, and in particular the presence of radical species

produced during their oxidation (Figure 2.1), affects the budget of ozone through modification of the NO-to-NO₂ cycle of Figure 2.2A as illustrated in Figure 2.2B. The intermediate formation of HO₂ and RO₂ radicals react with NO to form NO₂ in reaction 2.12 and in a similar reaction for peroxy radicals:

$$\mathrm{RO}_2 + \mathrm{NO} \to \mathrm{RO} + \mathrm{NO}_2$$
 (2.18)

As evident from Figure 2.2B, this process results in net formation of O_3 by 2.13 and 2.14.

To some extent atmospheric oxidation by radicals can be viewed as a combustion process for which hydrocarbons and CO supply the fuel and solar photons provide the necessary energy input for reaction activation [Johnstone and Kinnison, 1998]. It must be emphasized that NO_x play a key role as catalysts. Without NO_x the peroxy radicals formed during VOC degradation would destroy ozone:

$$HO_2 + O_3 \rightarrow OH + 2O_2$$
 (2.19)

$$OH + O_3 \rightarrow HO_2 + O_2$$
 (2.20)

or recombine in less reactive species:

$$\mathrm{HO}_2 + \mathrm{HO}_2 \quad \rightarrow \quad \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \tag{2.21}$$

$$\mathrm{RO}_2 + \mathrm{HO}_2 \rightarrow \mathrm{ROOH} + \mathrm{O}_2$$
 (2.22)

The oxidation of gases, and hence their residence time in the atmosphere, would depend only on the ozone influx from the stratosphere [e.g. Stohl et al., 2003; Lamarque et al., 1999].

2.1.1 Role of NO_x in VOCs oxidation

We can better understand how the ozone production nonlinearly depends on the interaction of NO_x and VOCs looking at Figure 2.3. It shows results from simulations with a regional photochemical model. The isopleths are concentrations of ozone calculated with various emission rates of NO_x and VOCs. The thick line divides the plane in two regions that mark two different chemical regimes: the $\mathrm{NO}_{\mathrm{x}}\text{-limited}$ regime (top-left) and the VOC-limited or NO_{x} -saturated regime (bottom-right) [Sillman, 1999]. In the NO_x-limited regime O_3 concentrations increase linearly with NO_x emissions. NO_x concentration are low and the ozone production is limited by the supply of NO_x and is independent of VOCs. Moving rightward on the plane of Figure 2.3 the O_3 production slows down reaching a local maximum, and then decreases with increasing NO_x . We entered the VOC-limited regime, because the O_3 production is linearly dependent on the supply of VOCs. Notably, the thick line separating the two chemical regimes generally follows a line of constant $\rm VOC/NO_x$ ratio, with low ratios corresponding to the VOC-limited regime and high ratios corresponding to the NO_x -limited regime.

The figure can also help us in understanding what happens into a plume as it moves downwind a source region following the grey arrow. Let's consider a plume near a polluted source that is characterized by high NO_x concentrations and low VOC/NO_x ratio. The air mass inside the plume is in the VOC-limited regime (beginning of the arrow) and undergoes oxidation as the time pass. The supply of NO_x gradually decrease, the VOC/NO_x ratio increases, and a certain point the transition to the NO_x -limited regime take place (the arrow cut the thick line). This explains why usually the urban areas affected by direct emissions of pollutants are in the NO_x -saturated regime and remote areas, advected by aged air masses from source regions, are in the Figure 2.3: Isopleths of ozone concentration in a model simulation as a function of NO_x and VOCs emissions. The thick line separates the NO_x -limited (top-left) and the VOC-limited (bottom-right) regimes. The grey arrow shows the hypothetical chemical path of an air plume oxidized from the emissions source as it is advected downwind [adapted from Jacob, 1999].



 NO_x -limited regime. This also explains why the VOC/NO_x ratio can be used as a "rule of thumb" to distinguish between polluted and remote regions, as applied later in this work.

Although VOC/NO_x ratio is certainly an important indicator of VOC impact on ozone formation it could be misleading because of the very different reactivities of the various VOCs. Very reactive VOCs, such as anthropogenic xylenes and biogenic isoprene, more likely to shift the environment toward a NO_x-limited regime than less reactive VOCs with similar total concentrations. For example, the transfer from a VOC-limited to a NO_x-limited regime in the plume of the above example could be accelerated by the higher rate Figure 2.4: Reactivity weighted VOC concentrations observed at Glendora, CA. Units are propylene equivalents (ppbC) [from Chameides et al., 1992].



of biogenic emissions in downwind regions. The impact of VOC reactivity is emphasized in Figure 2.4. The reactivity-weighted concentrations against OH of VOCs from various sources is shown at different local time periods. During early morning, anthropogenic VOCs from mobile and stationary sources contribute to most of the reactivity. During midday hours, biogenic emissions reach the maximum strength (they're null at night for isoprene), and the BVOCs contribute to 25% of total reactivity although the concentration does not exceed 1% of total VOCs. This point out how an accurate constrain on biogenic emissions is important in evaluating atmospheric chemical regime and hence the variability of its oxidizing power.

2.2 Isoprene oxidation mechanism

As we have seen in the introduction, isoprene (2-methyl-1,3-butadiene, chemical formula C_5H_8) is largely the most important BVOC on the global scale [Guenther et al., 1995]. It has long been recognized that isoprene emissions have a delicate role in controlling photochemistry in urbanized areas of the South-Eastern United States [e.g. Sillman et al., 1995]. The role of isoprene on the European territory has in general been less clear [Simpson, 1995], although a significant contribution to ozone formation in populated areas has recently been reported [e.g. Cortinovis et al., 2005; Derognat et al., 2003].

Isoprene undergoes oxidation by OH, O_3 and nitrate radical (NO₃), with the dominant loss being reaction with OH [Guenther et al., 1995]. For a full account on isoprene oxidation please refer to Atkinson and Arey [2003]; Sprengnether et al. [2002]; Poschl et al. [2000]; Paulson and Seinfeld [1992]. As many BVOCs, it is extremely reactive and hence have a relatively short lifetime with respect to most AVOCs. In Table 2.1 we show an "hit-list" of selected VOCs with their lifetime against photolysis and reaction with OH, NO₃ and O₃, that make itself the point (BVOCs are highlighted in boldface). The highly reactive nature of many of the BVOCs explains some of the difficulties encountered in reconciling BVOC emission inventories calculated from measured emission rates with observed ambient concentrations of these compounds. Note that the ambient concentrations of oxidizing species OH and NO₃ are highly variable and have pronounced diurnal profiles. Basically, OH is present only during day while NO₃ is present only at night, hence the lifetime of BVOCs also depends also on the time of the day.

Isoprene has a quite complicated oxidation mechanism that still present some uncertainty in the determination and yields of product species [e.g. Sprengnether et al., 2002]. The most important species with respect to this

Table 2.1: Calculated lifetimes for selected biogenic (highlighted in boldface) and anthropogenic VOCs with respect to photolysis, reaction with OH, NO_3 and O_3 [from Atkinson, 2000].

	Lifetime due to			
Compound	ОН	NO ₃	O ₃	Photolysis
Limonene	50 m	3 m	2 h	-
Isoprene	1.4 h	$50 \mathrm{m}$	1.3 d	-
2-Methyl-2-buten-3-ol	2.1 h	3.8 d	$1.7 { m d}$	-
trans-2-Butene	$2.2 \ h$	1.4 h	2.1 h	-
α -Pinene	2.6 h	$5 \mathrm{m}$	4.6 h	-
Pinoaldehyde	2.9 h	2.3 d	>2.2 y	-
Methacrolein	4.1 h	11 d	$15 \mathrm{d}$	$\sim 1~{\rm d}$
Propene	$5.3 \mathrm{h}$	4.9 d	1.6 d	-
<i>m</i> -Xylene	$5.9~\mathrm{h}$	200 d	>4.5 y	-
Methyl Vynil Ketone	6.8 h	$> 385 {\rm d}$	3.6 d	$\sim 2 \mathrm{d}$
Acetaldehyde	8.8 h	17 d	>4.5 y	6 d
Glyoxal	1.1 d	-	-	5 h
Formaldehyde	1.2 d	80 d	$> 4.5 { m y}$	4 h
Ethene	1.4 d	$225~\mathrm{d}$	10 d	-
Toluene	1.9 d	1.9 y	>4.5 y	-
Ethanol	$3.5 \mathrm{d}$	26 d	-	-
<i>n</i> -Butane	4.7 d	2.8 y	$>4500 { m y}$	-
Benzene	9.4 d	>4 y	>4.5 y	-
Propane	10 d	${\sim}7~{\rm y}$	$>4500 { m y}$	-
Methanol	12 d	1 y	-	-
Acetone	53 d	>11 y	-	${\sim}60~{\rm d}$

thesis are methyl vinyl ketone (MVK), methacrolein (MACR) and formaldehyde (HCHO). Over 95% of isoprene reaction with OH occurs via OH radical addition to one of isoprene C=C double bonds, and the other 5% via abstraction of an hydrogen atom [Sprengnether et al., 2002]. The second step is addition of an O_2 molecule to form eight possible peroxy radicals (ISO₂). In the presence of high NO, the first stage of products are thought to include eight hydroxycarbonyl species, eight alkyl nitrates, MVK, MACR, HCHO and 2-methyl furan (3MF). A sample oxidation pathway of the isoprene-OH system for two out of eight peroxy radicals formed at the beginning is shown in Figure 2.5.

2.2.1 Fate of Isoprene nitrates

Among the byproducts of the oxidation of ISO_2 , alkyl nitrates (ISON) have special importance, because their fate represent one of the major uncertainty in present isoprene modelling [Poschl et al., 2000; von Kuhlmann et al., 2004; Fiore et al., 2004]. ISON are formed from reaction of peroxy radicals with NO, and then react with OH:

$$ISO_2 + NO \rightarrow ISON$$
 (2.23)

$$ISON + OH \rightarrow products \qquad (2.24)$$

The key here is to understand the fate of products in reaction 2.24. Some authors [e.g. Chen et al., 1998] suggest that these products are directly converted to nitric acid, hence permanently remove NO_x from the atmosphere, because nitric acid is lost by wet deposition. Other authors [e.g. Shepson et al., 1996] suggest that ISON can recycle back NO_x via the products in reaction 2.24, based upon the assumption that OH reaction is a more important loss mechanism than deposition.

Figure 2.5: (a) First step of isoprene oxidation pathway by OH and production of formaldehyde, (b) MACR and (c) MVK. [from Jacobson, 1999].



2.2.2 Formaldehyde Yield from VOCs

A relevant quantity for this work is HCHO yield from VOC oxidation, i.e. the fraction of HCHO formed per unit carbon by a given VOC. From previous study is comes out that HCHO yield per unit carbon is 1 for methane, and typically 0.3-1 for $C_2 - C_6$ VOCs [Altshuller, 1991]. Sprengnether et al. [2002] report a first stage HCHO yield from isoprene of 0.11-0.13. Subsequent oxidation of short-lived by-products such as MVK and MACR form further HCHO for an ultimate yield around 0.4 [Palmer et al., 2005]. MVK and MACR reaction with OH and O_3 form also additional radicals that convert NO to NO₂ (see section 2.1.1). For larger VOCs, including in particular terpenes, HCHO yields are expected to be lower due to the formation of organic aerosols from low-volatility oxidation intermediates [Orlando et al., 2000]. A summary of HCHO yields from the oxidation of a number of VOCs is given in Table 2.2.

As we shall see in the following, the HCHO yield have a role when estimating the local relationship between isoprene emissions and HCHO column abundance. Since we use a global chemistry transport model (GEOS-Chem, section 3.1) to derive this relationship, we include here an analysis of the HCHO yield from BVOCs oxidation resulting from the model chemical mechanism. Palmer et al. [2005] used a box model to evaluate the time dependent production of formaldehyde from the oxidation of isoprene in the GEOS-Chem mechanism in comparison with the reference Master Chemical Mechanism (MCM, v3.1, http://mcm.leeds.ac.uk/MCM/) [Saunders et al., 2003; Jenkin et al., 2003]. The model keep constant mixing ratios for O₃ (40 ppb), CO (100 ppb), and NO_x (either 0.1 or 1.0 ppb), while 1 ppb considered VOC is allowed to decay. Under high NO_x conditions MCM predicts that 96% of the ultimate HCHO yield from isoprene (0.50 C⁻¹, Figure 2.6a) is reached within the first day. GEOS-Chem mechanism give similar results, but a slightly less final yield of 0.43 C⁻¹. Under low NO_x conditions peroxy recombination reactions limit HCHO production: MCM predict a final yield of 0.47 C⁻¹ 68% of which is reached within the first day, while GEOS-Chem has a final yield of only 0.27 C⁻¹ 66% of which is reached within the first day. The estimated error on modelled isoprene oxidation can hence be estimated in 20-40% [Palmer et al., 2005]. Figure 2.6b-d shows similar calculation for α -pinene, β -pinene and methylbutenol (MBO). Ultimate HCHO yield from these BVOCs range from 0.2 to 0.3 C⁻¹ and also the HCHO production is slower. In the best case (high NO_x conditions) only up to 60% of the final yield is reached within the first day.

2.3 Summary of BVOCs and formaldehyde chemistry

For the sake of clarity we summarize here the main concepts of the chemistry that involve volatile organic compounds and formaldehyde. The oxidation of VOCs usually begins with reaction with the OH radical, followed by NO-to- NO_2 conversion by peroxy radicals and subsequent production of ozone (the main proxy for OH production) by NO_2 photolysis:

- $VOC + OH \xrightarrow{O_2,M} RO_2 + H_2O$ (2.25)
- $\mathrm{RO}_2 + \mathrm{NO} \rightarrow \mathrm{RO} + \mathrm{NO}_2$ (2.26)
- $NO_2 + h\nu \rightarrow NO + O$ (2.27)
 - $O + O_2 \xrightarrow{M} O_3$ (2.28)

Compound	HCHO Yield	Reference
Methane	1.0	estimate
Ethene	1.8	estimate
Propene	1.0	Lee et al. [1998]
2-Methylpropene	1.0	estimate
1-Butene	1.0	Lee et al. [1998]
3-Methyl-1-Butene	0.7	Atkinson et al. [1998]
1-Pentene	1.0	estimate
2-Methyl-1-Butene	1.0	estimate
Isoprene	0.4	Palmer et al. [2005]
3-Methyl-1-Pentene	1.0	estimate
4-Methyl-1-Pentene	1.0	estimate
β -Pinene	0.57	Hatakeyama et al. [1991]
Limonene	0.5	estimate
Toluene	0.07	Dumdei et al. $[1988]$
Methacrolein	0.5	Tuazon and Atkinson [1990]
Methyl Vinyl Ketone	0.57	Tuazon and Atkinson [1989]

Table 2.2: Estimated HCHO yields from the oxidation of VOCs by hydroxyl radical [from Sumner et al., 2001].

Figure 2.6: Computation of HCHO yield from the oxidation of representative BVOCs in a box model with the GEOS-Chem (dashed lines) and the Master Chemical Mechanism (solid lines). Low-NO_x (red) and high-NO_x conditions are considered. (a) Time dependent HCHO yield from isoprene during the first 24 hours, (b) same, but for α -pinene, (c) same, but for β -pinene, and (d) same, but for methylbutenol [from Palmer et al., 2005].



The alkoxy radical RO forms an aldehyde or ketone (RCHO) and an H_2O molecule that produce a second NO_2 molecule:

$$\mathrm{RO} + \mathrm{O}_2 \rightarrow \mathrm{RCHO} + \mathrm{HO}_2$$
 (2.29)

$$HO_2 + NO \rightarrow OH + NO_2$$
 (2.30)

hence the net of reactions 2.25-2.30 is:

$$VOC + 4O_2 \rightarrow RCHO + 2O_3 + H_2O \tag{2.31}$$

In most cases RCHO continue to be oxidized in the same manner yielding more than the two ozone molecules formed by the net reaction 2.31 per VOC emitted. In particular, the net oxidation of formaldehyde, an high yield product of VOCs oxidation, follows:

$$\text{HCHO} + \text{h}\nu + 2\text{NO} \xrightarrow{\text{O}_2} 2\text{OH} + 2\text{NO}_2 + \text{CO}$$
 (2.32)

The rate-limiting step is usually the NO-to-NO₂ conversion by HO_2 and RO_2 . In condition of low NO_x and high peroxy radicals the latter react with each other and terminate the chain producing water vapor, molecular oxygen and organic hydroperoxy:

$$OH + HO_2 \rightarrow H_2O + O_2$$
 (2.33)

$$\mathrm{HO}_2 + \mathrm{HO}_2 \xrightarrow{\mathrm{M}} \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$$
 (2.34)

$$HO_2 + RO_2 \rightarrow ROOH + O_2$$
 (2.35)

In this case we are in a NO_x -limited regime and the O_3 production is approximately linear with NO_x supply. Reaction of peroxy radicals and NO_x lead to chain termination through formation of nitric acid and alkyl nitrate:

$$OH + NO_2 \xrightarrow{M} HNO_3$$
 (2.36)

$$\mathrm{RO}_2 + \mathrm{NO} \xrightarrow{\mathrm{M}} \mathrm{RONO}_2$$
 (2.37)

At this point, as NO_x increases, the latter chain terminations become faster than the above peroxy radical-peroxy radical terminations. We are in a NO_x -saturated of VOC – limited regime and O_3 production decreases with increasing NO_x and increases approximately linearly with VOC supply. In the case of isoprene oxidation, as we pointed out in section 2.2.1, the fate of $RONO_2$ (whether it is lost by wet deposition or recycle NO_x) is a factor of major uncertainty in assessing the impact of isoprene on global chemistry.

Chapter 3

Biogenic emissions in global chemistry transport models

In the introduction (section 1.3) we summarized the main difficulties in modelling biogenic emissions of VOCs from vegetation. The science related to emission of gases from nature is called phenology, which is the study of connections among climatic conditions and the cycles of the biosphere. This means that phenology is related to the highly nonlinear and uncertain meteorology, which hence introduce a great variability in the emission strength also on a day-to-day time scale. Further, as we have seen in chapter 2, the high reactivity of most BVOCs complicates their detection and the analysis of their oxidation pathways, with obvious recoils on the reliability of the observational constraints when estimating emissions.

We shall see in this chapter how to model biogenic emissions with a "bottom-up" approach and try to assess some of the uncertainties related to it. The common way of studying the impact of emissions on atmospheric chemistry is the use of global chemistry transport models (CTMs). We begin with introducing such kind of tool.

3.1 The GEOS-Chem chemistry and transport model

Chemistry and transport models (CTMs) are a class of models that exploit meteorology coming from general circulation models (GCMs) to drive the processes that are believed to control the concentrations of chemical compounds in the atmosphere. These models do not calculate the meteorology themselves for computational efficiency and do not generally allow for feedback between chemistry and climate. The main processes reproduced in a CTM are:

- Emissions: fluxes of species freshly introduced in the atmosphere both from surface and above surface sources (e.g. lightning, aircrafts)
- Advection: transport of species by winds far from the emission or production region
- **Convection**: fast vertical transport of species by convective motion in the troposphere. More generally, all the turbulent processes that happens on a sub-grid scale that are parameterized (see below)
- Chemistry: photochemical production and destruction of species
- Aerosol: microphysical transformation and multi-phase chemistry on atmospheric particulate matter
- **Deposition**: loss of species due to sticking onto surfaces and scavenging by precipitation

These processes are schematically represented in Figure 3.1. All these terms enter the mass continuity equation [e.g. Jacob, 1999; Jacobson, 1999], which

solution is calculated in the CTM at discrete grid points of the atmosphere. The continuity equation solves for the local tendency of a certain chemical species given the advection, loss and production terms:

$$\frac{\partial \chi_i}{\partial t} = -\nabla \cdot (V \cdot \chi_i) + P_i - L_i \tag{3.1}$$

being χ_i the mixing ratio of species *i* and *V* the three-dimensional wind vector. The first term on the right-hand side of equation 3.1 contains all the transport processes (advection, convection, turbulence, etc.), the second and third terms are the production and destruction processes respectively (photochemistry, emission, deposition, absorption to aerosol, etc). We have to point out here that the numerical solution of the system of partial differential equations 3.1 is generally carried out solving separately for each major process. This technique is called operator splitting [Jacobson, 1999] and it's a computational expedient to solve approximately the continuity equation 3.1 in five dimensions (three spatial coordinates, time and species). A simple schematic example of the technique is illustrated in Figure 3.2.

Meteorological fields, grids and transport. The global CTM we use in this work is the GEOS-Chem (Global Earth Observing System-Chemistry) model developed by the Atmospheric Chemistry Modeling Group at Harvard University (v.7-02-04; http://www-as.harvard.edu/chemistry/trop/geos/). GEOS-Chem is a three-dimensional tropospheric NO_x - O_3 -hydrocarbon CTM coupled to aerosol chemistry [Bey et al., 2001b; Park et al., 2004]. The model uses GEOS meteorological input with assimilated winds from the NASA Global Modeling and Assimilation Office (GMAO). Assimilated winds are output simulation of the GMAO GCM driven and corrected by heterogeneous observations from satellites, aircrafts and ground-based stations. Meteorological fields from such a system are realistically representative of the meteorological conditions of the specific period under analysis. GMAO-GEOS



Figure 3.1: Schematic of processes represented in a Chemistry and Transport Model (CTM)

met fields are provided every 6 hours (3 hours for surface fields) at $1^{\circ} \times 1^{\circ}$ horizontal resolution and a vertical resolution that depends on the GEOS data version (see Figure 3.3). The vertical coordinates uses the common σ pressure formulation:

$$\sigma = \frac{P - P_{top}}{P_{surf} - P_{top}} \tag{3.2}$$

where P is the pressure at a given altitude layer, and P_{top} and P_{surf} are pressures at the top and the surface of the model respectively. With this definition, the vertical σ coordinate goes from 1 at the surface to 0 at the top of the model. In this work we use versions GEOS-STRAT for simulation years 1996-1997 and GEOS-3 and GEOS-4 for 2001. The bottom 2.5 km of the model contains 6 levels in GEOS-STRAT and GEOS-4 and 9 levels in GEOS-3. Grid spacing in the free troposphere is roughly 1 km. For computational expediency original GEOS fields are degraded in model simulations to $4^{\circ} \times 5^{\circ}$ Figure 3.2: Example of operator splitting in a CTM. Three main processes are considered in the model: dynamics, transport and chemistry. During the first time interval each process is solved separately with the appropriate internal time step. Values at the end of time interval 1 are used to initialize the first process at beginning of time interval 2 and so on [from Jacobson, 1999]



or $2^{\circ} \times 2.5^{\circ}$ (latitude × longitude). For a full list of meteorological variables used in the model, please refer to the user's guide available on the web site (http://www-as.harvard.edu/chemistry/trop/geos/doc/man/).

Advection is computed every 15 minutes $(2^{\circ} \times 2.5^{\circ} \text{ resolution})$ or 30 minutes $(4^{\circ} \times 5^{\circ})$ with a flux-form semi-lagrangian algorithm described by Lin and Rood [1996]. Moist convection is computed using the GEOS convective, entrainment, and detrainment mass fluxes as described by Allen et al. [1996b,a]. Full mixing is assumed within the GEOS-diagnosed atmospheric mixed layer generated by surface instability.

The GEOS-Chem Chemistry solver. chemical mecha-Bey nism originally described al. [2001b], was by et the version is available the web (http://wwwmost recent on as.harvard.edu/chemistry/trop/geos/geos_mech.html). The chemistry solver is the SMVGEAR II package by Jacobson [1995], while photolysis frequencies are computed using the Fast-J radiative transfer algorithm [Wild et al., 2000]. It contains a quite detailed NO_x - O_3 -hydrocarbon mechanism.

Figure 3.3: Vertical σ -levels in the bottom 10 km of GEOS (NASA GMAO) meteorological field input to GEOS-Chem CTM (source: http://www-as.harvard.edu/chemitry/trop/geos/doc/man/)



The isoprene oxidation mechanism [Horowitz et al., 1998; Palmer et al., 2003] is based mostly on the work by Paulson and Seinfeld [1992] and a full description has been given in . The model does not include an explicit treatment of higher-carbon BVOCs such as monoterpenes. Regarding the fate of isoprene organic nitrates (see section 2.2.1), a yield of 12% of ISON from reaction 2.23 is assumed [Sprengnether et al., 2002], and ISON is directly converted to nitric acid, hence isoprene nitrates are treated as NO_x sink.

Anthropogenic emissions. As described in Bey et al. [2001b], GEOS-Chem uses base emissions for 1985 described by Wang et al. [1998] that in-
cludes NO_x emissions from the Global Emission Inventory Activity (GEIA), AVOCs emissions from Picott et al. [1992] and CO emissions developed at Harvard. Emissions are scaled to other years using trends in CO_2 emissions for unregulated countries, and trends of other specific regions using detailed available inventories (e.g. Environmental Protection Agency (EPA) for United States, and European Monitoring and Evaluation Program (EMEP) for Europe).

Biomass burning emissions. Biomass burning and wood fuel emissions are from a seasonal climatology described by Wang et al. [1998]. This inventory includes CO emissions from different categories of burning: forest wildfires, tropical deforestation, slash-and-burn agriculture, savanna burning, and burning of agriculture waste. Emissions of NO_x and VOCs are derived from CO emissions using scaling ratios.

Deposition. Dry deposition of oxidants and water soluble species is calculated with a resistance-in-series method derived from Wesely [1989]. Wet deposition for HNO_3 and H_2O_2 includes scavenging by convective updrafts and anvils and by large-scale precipitation [Liu et al., 2001].

Cross tropopause flux of ozone. The cross-tropopause transport of ozone is parameterized with the Synoz algorithm by McLinden et al. [2000]. In this method, stratospheric ozone is a passive tracer that is released uniformly in the lowermost tropical stratosphere at a rate constrained by the observed global mean cross-tropopause ozone flux.

3.1.1 Biogenic emissions

Isoprene emissions in the GEOS-Chem model rely on the GEIA inventory [Guenther et al., 1995]. Monoterpene emissions are not directly included into the model, but are used to distribute the biogenic source of acetone. CO emissions from the oxidation of methanol is scaled to isoprene, while CO from monoterpene oxidation is scaled from monoterpene emissions with the assumption that the production of CO is instantaneous.

We expand here on the modelling of biogenic emissions in CTMs, because of the relevance to this thesis. Isoprene emissions are generally modelled as a function of vegetation type, leaf area index (LAI, defined as cm^2 of leaf area per cm^2 of surface), leaf age, temperature and solar radiation.

The most recent inventory of biogenic emissions is the Model of Emissions of Gases and Aerosol from Nature (MEGAN) [Guenther et al., in review 2005]. We explain how does it works, but its principles are applicable basically to any process-based biogenic emission algorithm. Isoprene emissions E in MEGAN is described as:

$$E = E_0 * \text{MEA} * \text{DEA} * \text{HEA} = E_0 \gamma_{LAI} \gamma_T \gamma_{AGE} \gamma_{PAR}$$
(3.3)

where E_0 is the annual emission factor (μ g C m⁻² h⁻¹) weighted among six plant functional types. The flux E_0 is modulated in time with monthly, daily and hourly emission activities (MEA, DEA, and HEA respectively) that mimic the observed dependence and variability of isoprene emissions against phenological variables.

Monthly emission activity (MEA) is estimated as:

$$MEA = \gamma_{LAI} \ \gamma_{AGE} \tag{3.4}$$

where γ_{LAI} is the correction for leaf area index and γ_{AGE} is the correction for leaf age. γ_{LAI} adjusts for variation relative to a standard LAI=5:

$$\gamma_{LAI} = 0.49 \frac{LAI}{\sqrt{1 + 0.2LAI^2}} \tag{3.5}$$

and it is a rapidly growing function from LAI=0–5 and an almost logarithmic function for LAI>5 (see Figure 3.4a). Young leaves begin to photosynthetize

soon after budbreak, but isoprene is not emitted in substantial quantities for several weeks after the onset of photosynthesis. Old leaves gradually lose their ability to photosynthesis and to produce isoprene. This is modelled in MEGAN in the following way:

$$\gamma_{AGE} = F_{new}A_{new} + F_{gro}A_{gro} + F_{mat}A_{mat} + F_{sen}A_{sen}$$
(3.6)

where F's are the fractions of new, growing, mature and senile foliage respectively and A's are relative emission factors ($A_{new} = 0.01$, $A_{gro} = 0.5$, $A_{mat} = 1$, $A_{sen} = 0.33$). The F's are estimated from the variation of the LAI with time. Let's consider the GEOS-Chem model, where the LAI is updated daily. If we were to implement MEGAN into the GEOS-Chem, being LAI_c and LAI_p the leaf area index of current and previous day respectively, we would have:

1. if $LAI_c = LAI_p$ (no variation)

$$F_{new} = 0$$

$$F_{gro} = 0$$

$$F_{mat} = 1$$

$$F_{sen} = 0$$

$$(3.7)$$

2. if $LAI_c > LAI_p$ (increasing LAI)

$$\begin{split} F_{new} &= 1 - \frac{LAI_p}{LAI_c} \\ F_{gro} &= 0 \end{split} \tag{3.8} \\ F_{mat} &= 1 - F_{new} \\ F_{sen} &= 0 \end{split}$$

Figure 3.4: Variation of MEGAN correction factors. (a) LAI correction γ_{LAI} (eq. 3.5), (b) PAR correction γ_{PAR} (eq. 3.12), (c) Temperature correction γ_T (eq. 3.11). Values for which the γ 's are unity are highlighted. Optimal emission point E_{opt} at T_{opt} is also highlighted in (c).



3. if $LAI_c < LAI_p$ (decreasing LAI)

$$\begin{split} F_{new} &= 0 \\ F_{gro} &= 0 \\ F_{mat} &= 1 - F_{sen} \\ F_{sen} &= \frac{LAI_p - LAI_c}{LAI_p} \end{split} \tag{3.9}$$

This is actually how MEA has been implemented into the GEOS-Chem (see section 3.2).

Daily emission activity (DEA) in MEGAN is set to unity in the current version.

Hourly emission activity (HEA) is modelled as a function of temperature T and photosynthetic active radiation (PAR):

$$\text{HEA} = \gamma_T \ \gamma_{PAR} \tag{3.10}$$

The correction for temperature γ_T express the observed tendency of isoprene emitters to increase their isoprene output exponentially with temperature. It is modelled using the following formula:

$$\gamma_T = E_{opt} \frac{C_{T_2} \exp(C_{T_1} x)}{C_{T_2} - C_{T_1} (1 - \exp(C_{T_2} x))}$$
(3.11)
where $x = \left(\frac{1}{T_{opt}} - \frac{1}{T}\right) / 0.00831$

where $E_{opt} = 2.26$, $C_{T_1} = 70$, $C_{T_2} = 200$, $T_{opt} = 317$ and $\gamma_T = 1$ if T = 30. In this way, as also illustrated in Figure 3.4c, isoprene emission increase exponentially up to an optimal maximum at T_{opt} and then decreases. The correction for photosynthetically active radiation PAR is estimated with:

$$\gamma_{PAR} = 1.21 \frac{\alpha \ PAR}{\sqrt{1 + (\alpha \ PAR)^2}} \tag{3.12}$$

where $\alpha = 0.001$ and PAR has units μ mol m⁻² s⁻¹. $\gamma_{PAR} = 1$ if PAR=1500. The variation of γ_{PAR} with PAR is similar to the variation of γ_{LAI} with LAI (see Figure 3.4). If PAR is not available from the meteorological input it can be estimated from incoming short wave solar radiation assuming 4.766 (μ mol m⁻² s⁻¹) per (W m⁻² and assuming that half of the short wave radiation is in the 400 to 700 waveband. For example, if RADSW is the short wave solar radiation in W m⁻², PAR is approximated simply by:

$$PAR = RADSW * 4.766 * 0.5 \quad (\mu mol m^{-2} s^{-1})$$
(3.13)

The two main take-away messages from this detailed description of biogenic emission modelling are: (1) biogenic emissions have a marked seasonal cycle with usually null emissions in the winter season and maximum emissions in summer, and (2) BVOCs emission depends exponentially on temperature.

In the current version of GEOS-Chem isoprene emissions are implemented as described in Wang et al. [1998] using the algorithm of Guenther et al. [1995] with minor modifications. The basic features of the model are the same as the MEGAN model just explained. The main difference is that the PAR attenuation at canopy level is modelled with a one dimensional radiative transfer code that should improve the estimate of γ_{PAR} . In the GEOS-Chem, a global surface-type map from Olson [1992] that distinguishes among 72 ecosystems is used to calculate base emission factors (E_0) at 30° and for a photosynthetically active radiation (PAR) flux of 1000 μ mol m⁻² s⁻¹:

$$E = E_0 * LAI_{eff} * f(T) \tag{3.14}$$

$$LAI_{eff} = \int_0^{LAI} g(PAR) dL \qquad (3.15)$$

where f(T) is a correction function for surface air temperature T, g(PAR) is a correction function for the local PAR incident on the leaf of the canopy, and LAI_{eff} is the effective leaf area index corrected for light attenuation inside the canopy. The functions f(T) and g(PAR) are taken from Guenther et al. [1995], and mimic the features of γ_T and γ_{PAR} in MEGAN. The vertical profile of PAR inside the canopy is calculated using the one dimensional algorithm by Norman [1982]. In this algorithm LAI_{eff} is a polynomial function of LAI, solar zenith angle θ , and cloud cover fraction C. A sample plot showing the dependence of LAI_{eff} against LAI is given in Figure 3.5. As can be seen LAI_{eff} decreases with increasing solar zenith angle (angle of the sun with respect to the local zenith) because of the decreasing direct radiation, and obviously increase with increasing LAI.

In section 3.2 we shall see a comparison of emissions from Guenther et al. [1995] already implemented into GEOS-Chem, and emissions from MEGAN Figure 3.5: Effective leaf area index LAI_{eff} for canopy emission of isoprene as a function of LAI for different solar zenith angle and clear sky [from Wang et al., 1998].



[Guenther et al., in review 2005] newly implemented into the model during this thesis work.

3.1.2 Evaluation of Isoprene and HCHO fields

GEOS-Chem model output has been extensively validated in several papers [e.g. Bey et al., 2001a; Fiore et al., 2002; Jacob et al., 2002; Martin et al., 2004b; Park et al., 2004]. It usually reproduce ozone from worldwide ozonesonde network within 10 ppb. It reproduce seasonal phase and amplitude of ozone, except at Northern Midlatitudes where underestimates the seasonal amplitude. Concentrations of NO_x , PAN and HNO_3 are usually reproduced within a factor of 2 or much better. CO is often underestimated by 10-30 ppb.

We report here for completeness some validation for isoprene and

Figure 3.6: Comparison of observed (triangles and solid lines) and modelled (circles and dashed lines) concentrations of isoprene [from Bey et al., 2001b].



formaldehyde. Figure 3.6 shows comparison of monthly mean isoprene profiles compared to aircraft campaign average profiles. Observed values show a strong gradient in the boundary layer, decreasing from about 1 ppb near the surface to less than 0.05 ppb at 3 km at most of the sites. The vertical structure as well as the overall magnitudes of concentrations are captured by the model. The C-shaped profiles over South Eastern United States are due to convective pumping to the middle troposphere, but no observations are available to test this model feature. We have to point out here that isoprene total annual flux is forced to 397 Tg C yr⁻¹ on the basis of estimates of total emissions from tropical vegetation [Bey et al., 2001b, and references therein].

GEOS-Chem formaldehyde has been previously validated by Palmer et al. [2001] and Martin et al. [2004b]. The validation of HCHO profiles has been made through comparison with aircraft campaigns over the United States and North Atlantic region. A specific validation over Europe has not been carried out during this thesis work, because of the lack of data. We assume here that previous validation could be extended to Europe (D. Jacob, personal communication). Palmer et al. [2001] compared GEOS-Chem HCHO profiles from in-situ aircraft measurements during SOS 1995 campaign (Southern Oxidants Study [Lee et al., 1998]) and NARE97 campaign (North Atlantic Regional Experiment [Fried et al., 2002]) and are reported here in Figure 3.7. The SOS campaign, to which refer Figure 3.7a,b, was located in a region where isoprene is the dominant precursor of HCHO [Lee et al., 1998]. Much of the HCHO is confined to the boundary layer below 2 km. The model is able to reproduce HCHO in the boundary layer but the decrease toward free troposphere is steeper with respect to measurements. Figure 3.7c show comparison with NARE97 measurements of the marine environment of North Atlantic east of Canada, where HCHO production is dominated by long lived methane. The HCHO profile show a much less pronounced gradient from surface to free troposphere in both observations and model, but the model tends to underestimate HCHO levels in lower free troposphere (2-5 km). High values below 2 km on September 16 (Figure 3.7d) is due to an episode of continental outflow, that is captured by the model.

In Figure 3.8 we report the comparison of HCHO profiles from TexAQS 2000 (Texas Air Quality Study [Wert et al., 2003]) campaign and GEOS-Chem. The profile over polluted area of Houston show a very good agreement between observations and model, that is capable of reproducing both the magnitude and the distribution of HCHO (3.8a). The profile on the coast of Texas (3.8b) show substantial differences between measurements and model. The model has too low values in the boundary layer and too high values in the free troposphere, and it does not capture the steep vertical gradient of

Figure 3.7: Comparison of observed (open circles) and modelled (solid lines) concentrations of formaldehyde [from Palmer et al., 2001]. Model values at $2^{\circ} \times 2.5^{\circ}$ horizontal resolution are sampled along flight tracks.



HCHO profile.

3.2 Comparison of GEIA and MEGAN biogenic emissions

In this section, we compare GEOS-Chem output from several runs that use two different biogenic emission inventories (GEIA and MEGAN, see section 3.1.1), two different leaf area index databases, and two different meteorological fields. The aim of the exercise is to test for the sensitivity of GEOS-Chem to changes to driving variables of isoprene biogenic emissions.

Current GEOS-Chem version implements GEIA emission inventory [Guenther et al., 1995] for isoprene. As mentioned in section 3.1.1, the total annual flux of isoprene is forced to 397 Tg C yr⁻¹.

A total of seven simulations for July 2001 has been carried out. In Table 3.1 we resume the characteristics of this sensitivity runs. In the first colFigure 3.8: Comparison of observed (solid lines) and modelled (dashed lines) mixing ratios (upper abscissa) of formaldehyde [from Martin et al., 2004b]. Model values at $2^{\circ} \times 2.5^{\circ}$ horizontal resolution are sampled along flight tracks. Numbers on the right are number of measurements at each vertical level.



umn of the table the meteorological fields (see section 3.1) used are reported. In the second column, we report 'old' when using the LAI described in Wang et al. [1998] that follows the implementation of Guenther et al. [1995], and 'new' when using the improved satellite-derived LAI from the work of Buermann et al. [2002]. The third column indicates whether we are using GEIA or MEGAN biogenic emissions. The fourth column indicates other specific features of the run that will be explained below.

Let's start to look at Figure 3.9. It shows isoprene global emissions from the first run listed in Table 3.1. It is basically the benchmark run against which the other will be compared. A few hot spots are visible, corresponding to major woodlands (see Table 1.2): Southeastern United States, tropical forests in Amazonian and African areas, Siberia and Southeastern Asia. The total amount of carbon from isoprene is calculated by the model in 38.3 Tg $(1 \text{ Tg} = 10^{12} \text{ g}).$

N°	Met Fields	LAI	MEGAN	Other
1	GEOS-4	old	no	-
2	GEOS-4	new	no	-
3	GEOS-4	old	yes	-
4	GEOS-4	new	yes	fixed γ_{AGE}
5	GEOS-4	new	yes	-
6	GEOS-4	new	yes	PAR parametrization
7	GEOS-3	new	yes	PAR parametrization

Table 3.1: List and features of simulations performed to test for GEOS-Chem sensitivity to biogenic emission modelling.

The impact of the use of a different leaf area index database can be estimated from Figure 3.10. LAI data used for this run (2 in Table 3.1) is derived from satellite observations of normalized difference vegetation index (NDVI) measured by the Advanced Very High Resolution Radiometer (AVHRR) instrument onboard several platforms. The 'old' LAI database implemented into the GEOS-Chem uses landuse map and a climatology of temperature and precipitation to estimate the net primary productivity (NPP) of vegetation to estimate the LAI map. This can be seen as a "bottom-up" approach. The 'new' AVHRR-LAI database uses satellite observation as a "top-down" constraint on LAI map. The AVHRR-LAI has greater variability than the 'old' LAI database and its values are usually within \pm 20% of 'old' LAI [Fu, 2005]. As can be seen, the AVHRR-LAI induces a slightly increased isoprene emissions from Brazil, Russia and East Asia, decreased emissions from Central America, Central Africa and Australia and a sharp decrease of emissions from Middle East. Globally the isoprene emissions increase by 0.3 Tg with respect to run 1. The distribution of isoprene emissions is also not very affected by the change in LAI map. The correlation between plot in Figure 3.10 and 3.9 is 0.96.

In Figure 3.11 we show GEOS-Chem isoprene emissions using MEGAN inventory extensively described in section 3.1.1 and using the 'old' LAI archive (run 3 in Table 3.1). The picture we get is quite different with respect to GEIA. Emissions from the Southern Hemisphere are generally much higher, although the distribution is similar. In the Northern Hemisphere we observe increased emissions from North America and decreased emissions from other continents. The distribution over North America is also different with much higher emissions in the Western part of the continent. The hot spot over Russia is not there anymore. The substantial change with respect to GEIA are to be found in revised emissions factor from vegetation types estimated from new sets of measurements [Guenther et al., in review 2005]. The model predicts an increased global isoprene emission strength to 54.2 Tg. The correlation between Figure 3.11 and Figure 3.9 is 0.80.

Figure 3.12 shows the same as the figure just described, but using the AVHRR-LAI database (run 5 in Table 3.1). Isoprene emissions differs from the previous figure especially in Australia and Northern Eurasia, where we observe a decrease and an increase respectively. The overall emissions decrease to 50.3 Tg globally. The distribution is very similar to that seen with 'old' LAI, and the correlation between the two figures is 0.95, very similar to the 0.96 found with the GEIA inventory using the two LAI databases. The correlation with reference run 1 of Figure 3.9 is 0.79, again indicating that the updated LAI database does not affect much the distribution of isoprene emissions.

Figure 3.13 is the same as Figure 3.11, but uses a fixed γ_{AGE} set to

unity (see equation 3.6) (run 4 in Table 3.1). This is to test the sensitivity of MEGAN to the daily variation of LAI. The two pictures do not present major differences and their correlation is close to 1.

Figure 3.14 show emissions using MEGAN with AVHRR-LAI and the photosynthetically active radiation estimate of equation 3.13 (run 6 in Table 3.1). This is to test the use of the parametrization necessary to simulate the year 1997 with GEOS-Chem model, because the GEOS-STRAT met fields available for that time frame do not contain diffuse and direct PAR as GEOS-4, but shortwave radiation fields only. Comparing this figure with Figure 3.12 we don't see much difference and the overall emissions are decreased just by 3.8 Tg globally. The correlation between the two is very close to 1. The lack of direct and diffuse PAR fields in GEOS-STRAT data hence are not a shortcoming and do not prevent us from using them with MEGAN.

Figure 3.15 is the same as the previous figure, but uses GEOS-3 meteorological fields to drive the model (run 7 in Table 3.1). At a first glance there seem not to be great differences between the two figures, indeed their correlation is 0.98. However, looking carefully at their differences in Figure 3.16, we realize that regional discrepancy for example on the Amazonian forest can be up to 1×10^{12} molec cm⁻², which is more than 30% total emissions. This give an estimate of the importance of the choice of the driving meteorological fields and the uncertainty related to this choice.

The large differences found in model emissions when using GEIA or MEGAN have direct consequences on the formaldehyde column of the model, as illustrated in Figure 3.17. The correlation between plots in 3.17a and 3.17b is high (0.94), that is much higher than the correlation between the two underlying emission inventories (0.79). A possible explanation is that globally the distribution of formaldehyde column is not influenced by isoprene emissions only. The magnitude of the HCHO column increase up to a factor of two in North America, Southern Hemisphere and Northern Asia and decrease in Southeastern United States, Europe and South East Asia.

The global mean uncertainty on model HCHO column introduced by the use of a different biogenic emission inventory is only 5%, but varies locally from -60% to +50%. Recently, other authors have tried to asses the uncertainty related to isoprene modelling. von Kuhlmann et al. [2004] found a spread of $\pm 35\%$ of the overall effect of isoprene in their eleven model sensitivity scenarios. The same authors and Fiore et al. [2004] both report that the two major uncertainties in isoprene modelling are emission inventory and the fate of isoprene nitrates. These two factors suggest that isoprene modelling can only be seen as a first order estimate at present.

Figure 3.9: GEOS-Chem global isoprene emissions for July 2001 using GEIA inventory (run 1 of Table 3.1). Total carbon emissions from isoprene is shown inset (units: $1 \text{ Tg} = 10^{12} \text{ g}$)



Figure 3.10: Same as Figure 3.9, but using new AVHRR LAI (run 2 of Table 3.1).



Figure 3.11: Same as Figure 3.9, but using MEGAN emissions (run 3 of Table 3.1).



Figure 3.12: Same as Figure 3.9, but using MEGAN emissions and new AVHRR leaf area index database (run 5 of Table 3.1).



Figure 3.13: Same as Figure 3.9, but using MEGAN emissions, new AVHRR leaf area index database and a fixed γ_{AGE} (run 4 of Table 3.1).



Figure 3.14: Same as Figure 3.9, but using MEGAN emissions with PAR estimate using formula 3.13 (run 6 of Table 3.1).



Figure 3.15: Same as Figure 3.14, but using GEOS-3 meteorology (run 7 of Table 3.1).



Figure 3.16: Difference between isoprene emissions in Figure 3.14 (GEOS-4 met fields) and Figure 3.15 (GEOS-3).



Figure 3.17: GEOS-Chem formaldehyde column for July 2001. Comparison of runs using GEIA and MEGAN biogenic emissions. (a) HCHO column using GEIA emissions (Figure 3.9, run 1 of Table 3.1), (b) HCHO column using MEGAN emissions (Figure 3.12, run 5 of Table 3.1), (c) difference b-a, (d) ratio b/a. Units in a, b, c read 10^{16} molecules cm⁻².













Chapter 4

Observations of formaldehyde from GOME

As we have seen in chapter 2, formaldehyde is an high-yield intermediate product of hydrocarbons oxidation. Its column abundance has been measured for the first time from a satellite platform by the Global Ozone Monitoring Experiment (GOME) instrument onboard the ESA ERS-2 satellite since 1995. In this chapter we shall briefly review the steps to retrieve the column abundance, and we shall look at the HCHO column retrieved from GOME with particular attention to Europe. GOME HCHO column will be used as a proxy to estimate biogenic emissions over Europe in the last chapter.

4.1 Formaldehyde retrieval from GOME

The GOME instrument [European Space Agency, 1995] points at his nadir with respect to Earth surface and measures the solar radiation backscattered from the surface-atmosphere system (see picture in Figure 4.1a). The ERS- Figure 4.1: (a) Artist's view of GOME measurements from ESA ERS-2 satellite, (b) sample swath of slant HCHO column over Europe.



2 satellite is on a polar sun-synchronous orbit with an equatorial overpass time of 10:30 local time and global coverage completed in three days. The instrument has a field of view of 40×320 km² and collect data in three adjacent scans (center and sideways). A sample swath of the instrument is shown in Figure 4.1b.

The retrieval of formaldehyde vertical column is performed in three steps. In the first step, GOME radiance spectra are fitted in the 337-356 nm UVwaveband to determine the so-called "slant" column that minimize the differences between observed and calculated radiances [Chance et al., 2000]. In the second step, slant columns from the first step are corrected to remove a known solar diffuser plate artifact that introduce a bias in the measurements [Richter and Wagner, 2001; Richter et al., 2002]. In the last step, slant debiased column are converted to vertical columns through an air mass factor formulation described by Palmer et al. [2001] and improved by Martin et al. [2002]. The first step is extensively illustrated by Chance et al. [2000] and we got fitted slant column data from the same authors, hence our work began from step two. We remind here that estimated uncertainty on slant column fitting is about 4×10^{15} molec cm⁻².

4.1.1 Diffuser plate artifact correction

The solar irradiance measurements used for spectral fitting are taken by GOME every three days or less, a period denoted as solarday. The diffuser plate of the GOME instrument introduces an artifact in the solar irradiance measurements that results in a global bias in the retrieved columns varying from solarday to solarday [Richter and Wagner, 2001; Richter et al., 2002]. The bias is removed subtracting GOME slant column with GEOS-Chem slant column over remote Pacific [Martin et al., 2002]. The bias is modelled here as a function of latitude and scan angle of the measurement.

The debias procedure includes several steps. First of all, we identify "bad" solardays by computing the global mean slant HCHO column for each solarday and comparing it with the solarday means from the rest of the month. Solarday means that are outside the mean ± 1 standard deviation for that month are removed from the analysis. As an example, in Figure 4.2 we show the results of "bad" solarday filtering for July 1997. A total of 6 bad solardays are identified out of a total of 29. Generally, a few bad solardays are found for each month.

The second step for debias is removal of cloudy scenes. Clouds heavily affect the backscattered solar radiance, yielding generally unrealistically high HCHO column abundances. The GOME cloud product come from the GOME Cloud AlgoriThm (GOMECAT) [Kurosu et al., 1999]. A sample orbit showing effect of cloud filtering is reported in Figure 4.3. Removing GOME Figure 4.2: Identification of "bad" GOME solardays (see text) for July 1997. The black solid line is solarday HCHO global column means, red dashed line is this month HCHO mean column and red solid lines are $\pm 1\sigma$. Solarday not labelled as "good" (identified by a G in the row of letter at the bottom) are excluded from further analysis.



scans with cloud fraction >40% removes the artificial hot spot over Central Europe. Cloud filtering removes usually 40-60% of good solarday data per month.

The third step consist in estimating the bias introduced by the GOME diffuser plate artifact [Richter and Wagner, 2001; Richter et al., 2002] and remove it from data. GOME bias is estimated from the differences between GOME slant column and GEOS-Chem slant column over the remote Pacific. Over the Pacific HCHO column is controlled by methane and other long-lived VOCs. The model is assumed to reproduce with reasonable accuracy the column abundance in this background region. The region considered to estimate the bias is highlighted in red in Figure 4.4. For each solarday we



Figure 4.3: Effect of removing GOME pixels with cloud fraction >40%, for a sample orbit on July 17, 1997.

compute the difference between GOME and GEOS-Chem slant column for every single pixel sampling the model along satellite track. The differences are then averaged along 5 degrees wide latitude bands for each scan angle over all the solardays in a month. Hence, the bias is a function of latitude, scan angle and month. As can be seen from Figure 4.5a, there are 30-70 pixels available to estimate the bias for each latitude band per month. The bias varies from 4 to 14 molec cm⁻² with the minimum at southernmost latitude and the maximum at the equator (Figure 4.5b). The scan position 0 is the most affected by the diffuser plate artifact. If the bias is not calculated independently for each scan angle this feature would be cancelled and pixels in scan position 0 would not be debiased properly (black line in Figure 4.5b). The values of the bias shown here for July 1997 are very similar also in other months.

The impact of the debias procedure can be appreciated looking at Figure 4.6. The original GOME formaldehyde slant column (4.6a) has very high



Figure 4.4: Region of remote Pacific used to estimate the bias introduced by the GOME diffuser plate.

values over the oceans and adjacent strips with very different column concentrations are clearly visible. This is due to the bias dependence on the scan position, as seen in Figure 4.5b. Slant columns over continents are also unrealistically high. The debias procedure removes all these features as shown in Figure 4.6b. The strips are removed and column values are lower.

The estimated uncertainty introduced by the debias procedure, considering also the GEOS-Chem HCHO validation illustrated in section 3.1.2, is of the same order of magnitude of the column fitting error $(4 \times 10^{15} \text{ molec cm}^{-2} \text{ [Palmer et al., 2005]}.$

4.1.2 Calculation of vertical column

Air Mass Factor calculation

The third step for vertical column retrieval from GOME data is the conversion of slant column to vertical column through application of air mass factor (AMF). The AMF is defined as the ratio of the slant column (Ω_s) to Figure 4.5: Sample of estimated bias due to GOME diffuser plate artifact over the remote Pacific for July 1997. (a) pixel count used for debias as a function of latitude, (b) estimated bias as a function of latitude. Black: scan independent debias; Blue, Green, Red: debias for scan position 0, 1, 2 respectively. Scan positions go from East to West.



the vertical column (Ω_v) , and depends on the radiative transfer properties of the atmosphere:

$$AMF = \frac{\Omega_s}{\Omega_v} \tag{4.1}$$

The AMF is composed by a geometric component, which is a function of the viewing angles of the satellite instrument, and a scattering component, which account for scattering in the UV-visible spectral region by gases, clouds and aerosols in the atmosphere. Introducing scattering, AMF becomes sensitive to the vertical distribution of the atmospheric species being analyzed. Although the GOME instrument has different sensitivity to different atmospheric layers it cannot alone provide information on the vertical distribution of atmospheric constituents. One possible way to overcome this difficulty is to use information from global CTMs. In the approach illustrated by Palmer et al. [2001], which is also applied here, the AMF is formulated as to deFigure 4.6: (a) Monthly mean GOME HCHO slant column for July 1997,(b) same as a, but after the debiasing procedure. Bad solarday and cloud filtering applied to both plots.



couple the contribution from GOME vertical sensitivity from the shape of the vertical profile of formal dehyde taken from the GEOS-Chem model. The geometrical AMF (AMF_G) is defined as:

$$AMF_{G} = \sec \theta_{sun} + \sec \theta_{sat} \tag{4.2}$$

where θ_{sun} is the solar zenith angle and θ_{sat} is the satellite viewing angle. In the formulation by Palmer et al. [2001] the AMF is defined as:

$$AMF = AMF_{G} \int_{\sigma_{trop}}^{1} \underbrace{w(\sigma)}_{RTM} \underbrace{S(\sigma)}_{CTM} d\sigma$$
(4.3)

where σ is the vertical coordinate (eq. 3.2) and the integral goes from the model tropopause (σ_{trop}) to the surface ($\sigma = 1$). Scattering weights $w(\sigma)$ describe the sensitivity of the solar backscattered radiance I measured by GOME to the abundance of HCHO at each σ -level:

$$w(\sigma) = -\frac{1}{\text{AMF}_{G}} \frac{\alpha(\sigma)}{\alpha_{e}} \frac{\partial(\ln I)}{\partial\tau}$$
(4.4)

where $\alpha(\sigma)$ is the temperature-dependent absorption cross-section (m² molec⁻¹), α_e is the effective absorption cross-section (m² molec⁻¹), representing a weighted average over the tropospheric column [Palmer et al., 2001], and $\partial \tau$ is the incremental HCHO optical depth as a function of σ . AMF_G normalizes the scattering weight such that $w(\sigma) = 1$ in a nonscattering atmosphere. Scattering weight are determined from a radiative transfer model (RTM). The dimensionless shape factor $S(\sigma)$ are determined from the GEOS-Chem model for each individual observation scene:

$$S(\sigma) = \chi(\sigma) \frac{\Omega_{air}}{\Omega_v}$$
(4.5)

where Ω_{air} and Ω_v are tropospheric vertical columns of air and formaldehyde respectively, and $\chi(\sigma)$ is the HCHO mixing ratio. It is basically a normalized vertical profile of model HCHO. The profiles of calculated scattering weights and shape factors are shown for two illustrative cases in Figure 4.7 over the ocean (North Pacific, 4.7a) and over United States (Tennessee, 4.7b). We see from the vertical profiles of the scattering weights $w(\sigma)$ that observations are about an order of magnitude more sensitive to a given mixing ratio increment in the upper troposphere than near the surface, because penetration of UV radiation to the lower atmosphere is inhibited by scattering. Similarly to what we have seen in Figure 3.7, shape factor $S(\sigma)$ is almost flat over the ocean, because HCHO is produced mostly by methane oxidation, and has a steep vertical gradient over land, where more reactive VOCs contribute to HCHO production. The product $S(\sigma)w(\sigma)$, that is the argument of the integral in equation 4.3, shows altitude where HCHO seen by GOME reside. Indeed it is peaked in the mid-troposphere over the ocean and in the lower troposphere over land. In both cases, the AMF is much less that the AMF_G, pointing out the importance of accounting for atmospheric scattering in air mass factor calculation.

The AMF formulation has then been improved to account for scattering by clouds [Martin et al., 2002] and aerosols [Palmer et al., 2003]. Increasing the aerosol optical depth from 0.1 to 1.0 increase the GOME sensitivity to the HCHO column by approximately 30% relative to an aerosol-free atmosphere [Palmer et al., 2001]. In practice, the presence of aerosols artificially diminishes the HCHO vertical column, because of the AMF increase. The presence of clouds can either increase or decrease the AMF, depending on the height of clouds. This is exemplified in Figure 4.8, used by Martin et al. [2002] in their work on GOME NO₂ retrieval, but that can be applied to HCHO too. The profiles we see there are similar to those of Figure 4.7, but they are distinguished in cloud-free (subscript a) and cloudy (subscript c) Figure 4.7: Scattering weights $w(\sigma)$ (dashed line) and vertical shape factors $S(\sigma)$ (solid line) for HCHO as a function of altitude σ for two sample GOME scenes over (a) North Pacific, and (b) Tennessee. The product $S(\sigma)w(\sigma)$, which provides a measure of the HCHO signal seen by GOME, is shown as a dotted line. Values of AMF and AMF_G are shown inset [from Palmer et al., 2001].



scenes. The contribution to AMF from clouds is taken into account calculating scattering weights (and hence AMFs) separately for clear-sky and cloudy fraction for each GOME scene as described in Martin et al. [2002]. Again we have a scene over land (upper plots) and one over the ocean (bottom plots). The hypothetical cloud layer shown as a shaded net has an optical thickness of 10, and his located at an height typical of the two regions. The scattering weights (left plots) are strongly modified by the presence of clouds, because the satellite becomes almost blind to the portion of the atmosphere below the cloud layer. Further, the GOME instrument becomes more sensitive above the cloud top, because of the radiation reflected back by the clouds. These facts have direct consequences on the AMF calculation. In the land scene, where most HCHO is in the boundary layer and hence below the cloud layer, the product $S(\sigma)w(\sigma)$ is strongly reduced with with respect to cloud free atmosphere, and the AMF decrease from 1.0 to 0.3. If cloud calculation were not included, we would have retrieved a much lower vertical GOME column, because of a too high AMF. In the ocean scene, we have an opposite effect. Since most of the HCHO is in the mid-troposphere, and GOME sensitivity is enhanced there by clouds, the cloud-free AMF_a is too low with respect to the more realistic AMF_c. We would have a positive bias if not accounting for clouds.

Treating clouds properly is also more important if we consider the amplitude of GOME footprint ($40 \times 320 \text{ km}^2$): with such a wide view there are virtually no cloud-free scenes on Earth!

An illustrative picture of air mass factor calculation is given in Figure 4.9. The AMF in 4.9a is a monthly mean for July 1997 averaged using the debiased pixels of GOME with cloud fraction <40%. This the AMF that we use in practice to convert GOME slant to vertical column. The values of the AMF range from 0.5-1 over land and 1-1.5 over the ocean. The land-ocean difference is mostly due to the low albedo of the ocean. The AMF is a weighted sum of the clear-sky AMF (Figure 4.9b) and cloudy AMF (4.9c). The weighting factors of the sum are cloud fraction and fraction of backscattered radiance from clouds (4.9d). In practice, the correction for clouds is more important where the values in Figure 4.9d are higher. For July 1997, the most relevant correction to AMF are over Europe, South East Asia, Central America and Central Africa.

AMF validation

The first validation of GEOS-Chem derived air mass factors has been carried out by Millet et al. [2005]. They uses aircraft observations of atmospheric constituents during 2004 ICARTT campaign to estimate AMFs. GEOS-Chem AMFs and ICARTT observed AMFs are shown in Figure 4.10. The model tends to underestimate AMFs over land and overestimate them over the ocean. Model AMF bias over land has a mean value of -5%, but varies from -57% to 70% locally. Over the ocean model AMF mean bias is +13%, with a range from -14% to 72%. The variability of AMF bias is driven prevalently by clouds, because they introduce the greatest uncertainty and the error increases linearly with cloud fraction. The error of GEOS-Chem AMF is estimated in 25% for a single scene when filtering out pixel with cloud fraction >40%. Figure 4.8: Illustration of the effect of clouds in AMF calculations. Top plots are relative to an over land scene, bottom plots over the ocean. Subscript a and c are for cloud-free and cloudy calculations respectively. The shaded layer indicate an hypothetical cloud layer with an optical thickness of 10. [from Martin et al., 2002].



Figure 4.9: (a) Calculated Air Mass Factor for July 1997 using formulation of Palmer et al. [2001]; Martin et al. [2002] accounting for clouds, (b) AMF calculated assuming clear sky, (c) AMF contribution from clouds, (d) fraction of backscattered solar irradiance from clouds.



Figure 4.10: Validation of GEOS-Chem AMF against ICARTT aircraft data. (a) ICARTT flighttracks, (b) measured and modelled AMFs, (c) Cloud optical thickness, (d) model AMF bias [from Millet et al., 2005].


4.1.3 Global picture of formaldehyde

In Figure 4.11 we compare GOME HCHO slant versus vertical column for July 1997. The values are monthly mean averages over GEOS-Chem $2^{\circ} \times 2.5^{\circ}$ grid, which is the model resolution used to compute shape factors in AMF calculations. GOME artifact debias and cloud filtering are both applied (see above). The emerging global picture of formaldehyde does not change drastically when converting slant to vertical columns. Indeed, the correlation between the two pictures is 0.93. The main differences are found in regions where the AMF is affected by clouds the most, the same we have seen in Figure 4.9. Differences up to 1×10^{16} molec cm⁻², which is 30-50% of total column, are found over North and South America, Southern Europe, Central Africa and East Asia.

Figure 4.11 also gives a feeling of how appears the global picture of formaldehyde column observed from satellite. It is interesting to notice that the hot spots are usually co-located with the strongest biogenic emission regions seen in chapter 3. In particular, we see high column values over the Southeastern United States, over Amazonia, over Central Africa, and over Indonesia. In the South East of United States the HCHO column is know to be controlled by isoprene emissions, while in the tropical forest the contribution from biomass burning emissions is also important. European formaldehyde column is relatively lower with respect to these areas. HCHO column in Europe is likely controlled by both biogenic and anthropogenic VOC emissions. Another interesting region is South East Asia, where the chemistry of HCHO is even more complicated, because is controlled by biogenic and anthropogenic VOC emissions and also by biomass burning emissions. The noisy data over South America are due to geomagnetic disturbances that alter GOME signal.

It is also interesting to compare formaldehyde column observed by GOME with the one simulated into the GEOS-Chem model. As we have seen, the GOME data retrieval procedure includes some important contributions from the GEOS-Chem model, and one have to be careful when looking at these data if he doesn't want to be fooled by model contamination. On the other hand, mixing information of satellite and model is the only way we have to compare them, because the instrument sensitivity varies in the vertical direction. Grabbing shape factors from the model, for example, make the "eyes" through which model and instrument look at the atmosphere more similar. In Figure 4.12 we compare monthly mean HCHO column on July 1997 from GOME and from GEOS-Chem. Model values are sampled along satellite track at roughly the same overpass hours. The two picture are similar, but present significant differences (correlation coefficient 0.59). Over the United States the model predicts an higher column over the Southeastern region and a lower column over the Northeastern region. The hot spot over Amazonia is predicted at southern latitudes. The hot spot over Central Africa is underestimated and there is a band of high HCHO column near 10°N not present in the observations. The column over Europe is generally higher in the model than measurements. The column is underestimated in East Asia. GOME HCHO column over the ocean is generally a bit higher than in GEOS-Chem, but the values are within column fitting uncertainty $(4 \times 10^{15} \text{ molec})$ $\rm cm^{-2}$). The large positive bias of the model over Sahara is most likely due to a problem in the retrieval.

Figure 4.11: Comparison of GOME HCHO slant and vertical column in July 1997. Slant columns are converted to vertical using AMF formulation by Palmer et al. [2001]; Martin et al. [2002] and removing scenes with cloud fractions >40%.



Figure 4.12: Comparison of HCHO vertical column (July 1997) as seen by GOME and GEOS-Chem model.



4.2 GOME HCHO column over Europe

Let's now look in more detail to the European formaldehyde column seen by GOME. In Figure 4.13 we show monthly mean HCHO column seen by GOME over Europe in the time frame from September 1996 to August 1997. It is clear that the highest values of the column are measured in summer (JJA). During the other season HCHO column is barely above the column fitting uncertainty. The seasonal cycle seen by the satellite suggests that HCHO column variability over Europe is driven by biogenic VOC emissions. Indeed, as we have seen in section 3, one of the distinctive features of BVOC emissions is the annual cycle with null emissions in winter and maximum emissions in summer, with shoulder seasons being May and September. The AVOC emissions are actually flat during the year, so that they can contribute to the background HCHO abundance, but don't introduce much variability in its annual cycle. In Figure 4.14 we show monthly mean ground-based measurement of three major AVOCs and total VOCs in the urban environment of Pescara, a medium-sized city in middle Italy. We see that the AVOCs have a flat seasonal cycle, while total VOCs have a cycle typical of biogenic VOCs. This is probably due to BVOCs coming from the rural surroundings of the city.

It is useful also to compare GEOS-Chem model results to GOME observations, as we are going to use the model as the tool to estimate the local relationship between isoprene emissions and HCHO column in the following chapter. In Figure 4.15 we show the comparison of monthly mean HCHO column for July and August 1997 from GOME and GEOS-Chem. Model values at $2^{\circ} \times 2.5^{\circ}$ horizontal resolution are sampled at selected GOME pixels and are averaged values at typical GOME overpass time (10–12 am local time). We see that some important discrepancies between observations and model

Figure 4.13: Monthly mean HCHO column observed by GOME over Europe. Timeseries is relative to months from September 1996 to August 1997.



arise. While we found good agreement in certain regions (Greece, Balcanes, Italy and Southern France), we got a significant overestimate of the model in many other regions. The correlation coefficient between model and observations is indeed quite low, in the range 0.46–0.5. Possible reasons are a bias in GEOS-Chem emission inventory and errors in GOME formaldehyde retrieval. However, we have to point out that GOME HCHO data seem generally quite noisy, also when we calculate monthly mean. This is for example illustrated in Figure 4.16 where we see high values of the standard deviation of the HCHO column for July 1997. This yields a patchy picture of the column that prevent us from distinguishing clear patterns of the European

Figure 4.14: Monthly mean AVOC (benzene, toluene and *m*-xylene) and total VOCs surface concentrations measured in the urban environment of Pescara (middle Italy, 14.22 E, 42.47 N) in 2003. Units read μ g C m⁻³.



HCHO column. For example, the large differences between the two 1997 summer months shown in Figure 4.15 could be due to eccessive noise in the data and might not be a real feature of the column variability.

We then use the available long-term timeseries of GOME HCHO measurements from 1996 to 2000 in the attempt to have a clearer picture of HCHO column over Europe. The debias procedure for these multi-year dataset is performed using GEOS-Chem vertical column and AMFs calculated for the year 1997 to avoid lengthly multi-annual model simulations. In practice, this is of little importance since the interannual variability of formaldehyde over the remote Pacific is expected to be quite low. In Figure 4.17 we show monthly mean HCHO slant column in summer over Europe averaged over the 1996-2000 period. We obtain a much clear picture. Formaldehyde column generally increases from June to August and we observe the highest values over the Figure 4.15: Monthly mean HCHO column as seen by GOME (left) and GEOS-Chem model (right). Displayed month are July (top) and August (bottom) 1997. Correlation coefficient between GOME and GEOS-Chem column is shown inset.



Mediterranean sea, especially in the Southeastern part. These features are quite interesting, because the increase of the HCHO column is in phase with the growing season of vegetation. The processes that can contribute to the production of HCHO are hence most likely biogenic VOC emissions and direct emission from biomass burning. We will expand the argument further in the next chapter, where we shall discuss what controls the HCHO column variability (section 5.2).

Figure 4.16: Standard deviation of GOME HCHO column over Europe in July 1997.



Figure 4.17: GOME HCHO slant column in summer over Europe averaged over the 1996-2000 period.



Chapter 5

European isoprene emissions constrained by GOME observations

5.1 Relating HCHO column to VOC emissions

Consider an atmospheric HCHO column Ω (molec cm⁻²) produced by the oxidation of a number of VOC_i (i = 1...n), each one with an emissions flux E_i (C cm⁻² s⁻¹), a loss rate constant k_i (s⁻¹) and an HCHO yield Y_i (C⁻¹). Let k_{HCHO} (s⁻¹) represent the loss rate constant for HCHO in the column from oxidation and photolysis. In the limit case of null horizontal wind, Ω at steady state would be simply given by the ratio of its production rate and its loss rate:

$$\Omega = \frac{\sum_{i} Y_i E_i}{k_{\rm HCHO}} \tag{5.1}$$

In this case a measurement of Ω would also provide an estimate of the sum of local VOC emissions weighted by their HCHO yields, because the HCHO signal is independent of chemical lifetime of each VOC_i.

In the real case, horizontal transport displaces VOCs from their emissions source and the production of HCHO is smeared within a certain range that depends on the k_i 's. Let's consider an air column (for all practical purposes the boundary layer) with a mean column wind speed U in which a single VOC_i is injected. By solving the mass balance equations for VOC_i and HCHO in the air column one finds that the peak of HCHO produced from the VOC_i is located at a displacement length from the source:

$$L_{d,i} = \frac{U}{k_i - k_{\rm HCHO}} \ln\left(\frac{k_i}{k_{\rm HCHO}}\right)$$
(5.2)

One can further define a smearing length scale $L_{s,i}$ as the distance where the integral of Ω downwind of the point of emission, $\int_0^{L_{s,i}} \Omega dx$ reaches a fraction (1 - 1/e) of its asymptotic value $\int_0^\infty \Omega dx = [\text{VOC}]_0 / k_{\text{HCHO}}$, where $[\text{VOC}]_0$ is the initial VOC column concentration at the point of emission. Solving for mass balance one finds that $L_{s,i}$ is the solution of the following equation:

$$\frac{1}{k_{\rm HCHO} - k_i} \left[k_{\rm HCHO} \exp\left(\frac{-k_i L_{s,i}}{U}\right) - k_i \exp\left(\frac{-k_{\rm HCHO} L_{s,i}}{U}\right) \right] - \frac{1}{e} = 0 \quad (5.3)$$

with limiting values:

$$L_{s,i} \to U/k_i$$
 when $k_i \ll k_{\text{HCHO}}$
 $L_{s,i} \to U/k_{\text{HCHO}}$ when $k_{\text{HCHO}} \ll k_i$

We can use these two length measures to estimate the spatial resolution needed to detect the HCHO signal from the oxidation of a certain VOC_i. For isoprene, a typical lifetime in late morning summertime conditions against OH attack is roughly 0.5 hour, i.e. $k_i = 2 \text{ h}^{-1}$. Assuming typical values $k_{\text{HCHO}} = 0.5 \text{ h}^{-1}$ and $U = 20 \text{ km h}^{-1}$ we obtain $L_{d,i} = 20 \text{ km}$ and $L_{s,i} = 50$ km. For other BVOCs with reactivity similar to isoprene (see Table 2.1) the length scale is of the same order of magnitude. For methane and methanol (lifetimes of several years and several days respectively) $L_{s,i}$ values are sufficiently large that there is no spatial resolution to the HCHO signal. We conclude that the spatial resolution needed to map reactive VOC emissions from their HCHO signal is O(100 km). This is the same order of magnitude of the GOME pixel $(320 \times 40 \text{ km}^{-2})$, and hence we can view the variability in the observed HCHO column as reflecting local reactive VOC emissions. If reactive VOCs make a major contribution to Ω , then we can neglect transport and we can use the relationship 5.1 to estimate VOC emissions from HCHO column measurements. This is the principle used by Palmer et al. [2003] to derive isoprene emissions from GOME formaldehyde observations over North America, where isoprene is known to control the variability of HCHO column. In case only less reactive VOCs contribute to the HCHO column, as would expected for example in winter, then the smearing length scale is O(1000 km) or more. Relating GOME HCHO observations to VOC emissions would require a complicated inversion that account for transport. Before applying the inversion method by Palmer et al. [2003] to the European case, we have to assess what controls HCHO column over there.

5.2 What controls HCHO column over Europe?

Our first attempt to answer that question rely on previous work of several authors. In Table 5.1 we summarize the total European emissions of biogenic and anthropogenic VOCs in summer, together with their potential contribution to HCHO production. Most of the data are taken from the GEIA inventory of the GEOS-Chem model (see chapter 3) and from the work of Simpson et al. [1999]. We see that HCHO production over Europe in summer is dominated by methane, isoprene and methanol. A minor contribution come from alkanes, acetone, monoterpenes and propene. Since, as we have discussed above, methane and methanol have too long lifetime to give a localized HCHO signal near their source, isoprene only is expected to dominate the formaldehyde variability over Europe in summer. Further, since the 1-day HCHO yields from oxidation of monoterpenes are much lower than that of isoprene it is likely that monoterpenes make little contribution to the HCHO column variability over Europe. We have to point out here that some authors reporting on recent measurements warn that the role of monoterpenes in Europe could have been undervalued so far.

5.2.1 Biogenic vs anthropogenic control

Assuming that the overall control at continental scale on HCHO production is driven by isoprene emissions, we have to account for possible regional discrepancies. We do that using the GEOS-Chem model. We run two simulations at $2^{\circ} \times 2.5^{\circ}$ horizontal resolution in July 1997, one switching off isoprene emissions and the other switching off anthropogenic emissions. We then compute the gridded ratio of HCHO column obtained from the first simulation to the HCHO column from the second one. The result is shown in Figure 5.1. The model predicts that HCHO column over Northern and Eastern Europe, Turkey and the Iberian Peninsula is largely controlled by biogenic VOCs. In Central Europe and Italy there is no prevalence of biogenic nor anthropogenic emissions. It is interesting to notice that in remote ocean regions the HCHO column is largely controlled by the oxidation of anthropogenic VOCs, which is completely consistent with the fact that AVOCs have generally longer lifetimes than BVOCs.

Information from current knowledge hence suggests that the HCHO column is controlled by isoprene emissions over most of Europe. However, in chapter 4 we have seen that the agreement between model and GOME HCHO column is quite low. We then try to understand what controls HCHO column directly from the data. We do that using the information deriving from the $\rm HCHO/NO_2$ column ratio. $\rm NO_2$ column is another product of the GOME instrument. The retrieval procedure is very similar to that illustrated for HCHO and is explained in details by Martin et al. [2002]. In a recent paper Martin et al. [2004a] used HCHO/NO₂ column ratio from GOME to assess the chemical regimes driving ozone production over various polluted areas of the world. The argument is very similar to that we have reviewed in chapter 2 about the NO_x-limited and VOC-limited chemical regimes. The procedure described by Martin et al. [2004a] is basically an extension of local concentration measurements to column measurements. They found that the $HCHO/NO_2$ column ratio can discriminate between the two chemical regimes: we are in a VOC-limited regime when the ratio is below 1 and in a NO_x -limited regime when the ratio is above 1. We apply this criterium here to locate European regions that are under NO_x-limited regions, and compare these regions to those we have found to be under biogenic control with model simulation. In Figure 5.2 we see that in the Eastern part of Europe the GOME $HCHO/NO_2$ column ratio (top panel of the figure) is well above 1, while in the Western part the ratio has much lower values. Looking at GEOS-Chem column ratio we see that we get very high values in the Eastern part of the domain, and lower values, though well above 1, in the Western part. From this analysis we can conclude that GOME and GEOS-Chem agree that HCHO column is controlled by biogenic emissions over Eastern Europe,

while there is not a clear answer for the Western part. This is likely due to the much higher anthropogenic NO_x emissions in the more industrialized countries of Western Europe.

Table 5.1: Emissions of VOCs and production of HCHO over Europe in summer. Emission data are estimated from the GEOS-Chem model unless otherwise stated. Lifetimes and yields estimated from GEOS-Chem model and other sources by Palmer et al. [2003, Table 2 and references therein]. Notes: ^{*a*} Methane emissions from Simpson et al. [1999]; ^{*b*} estimated from Simpson et al. [1999] assuming that a summer month contributes 25% of the annual emissions; ^{*c*} Estimated upper bound average yield for monoterpenes after 1 day; ^{*c*} Estimated scaling isoprene emissions ($\sim 30\%$ of isoprene emissions).

Species	Emission E_i	Lifetime	HCHO Yield Y_i	Potential HCHO
VOC_i	(Tg C)	$1/k_i$	(reacted C^{-1})	Production $(\%)$
Methane	4.7^{a}	1 y	1.0	68.2
Propane	0.15	2 d	0.2	0.4
$\geq C_4$ alkanes	0.45	1 d	0.5	3.3
Propene	0.19	1.5 h	0.65	1.8
Isoprene	1.2^{b}	$35 \mathrm{m}$	0.45	7.8
Monoterpenes	0.7^{b}	1 h	0.1^c	1.0
НСНО	0.02	2 h	1.0	0.3
Acetone	0.27	10 d	0.67	2.6
Methanol	1.0^d	2 d	1.0	14.6

Figure 5.1: Ratio of HCHO column calculated in the GEOS-Chem without isoprene emissions to HCHO column without anthropogenic emissions. Values below 1 indicate isoprene control on the HCHO column (blue), and values above 1 indicate anthropogenic control (red).



GEOS-CHEM HCHO Column Ratio NO EM. ISOP / NO EM. ANTHRO - Jul 1997

Figure 5.2: Ratio of $HCHO/NO_2$ column from GOME (top) and GEOS-Chem model (bottom). Values below 1 indicate regions in VOC-limited regime and values above 1 indicate regions in NO_x -limited regime.



5.2.2 Contribution form biomass burning

As mentioned at the end of the last chapter, another possible contribution to HCHO column production over Europe is direct emission from biomass burning. The 1996-2000 year averaged monthly mean picture in Figure 4.17, show a clear stable pattern of high HCHO column in the Southeastern Mediterranean. The accumulation of the column is in phase with the vegetation growing season. To test for possible contribution of biomass burning to the column we combine GOME data with ATSR derived fire counts (freely available through ESA web site of the Ionia project, http://dup.esrin.esa.it/ionia/wfa/index.asp). We compute a new multiyear monthly average of the column excluding those GOME pixels that are collocated with an ATSR fire spot, and exclude also any other pixel at the same location measured within one day before and two days after the detection of the fire spot. The result is shown in Figure 5.3. The picture we get is very similar to one seen in Figure 4.17, indeed the difference between the two (shown in the right panel) is of the order of a few 10^{15} molec cm⁻² in the grid boxes where many fires are detected. We can conclude from this figure that the contribution of biomass burning to HCHO column production over Europe is quite limited and basically undetectable by GOME (fitting uncertainty of 4×10^{15} molec cm⁻²). The hot spot over Southeastern Mediterranean is hence likely to be due to the oxidation of AVOCs and BVOCs transported by winds from the continent. The little contribution from biomass burning also reinforces our statement about the isoprene control on HCHO column over the continent.

Figure 5.3: Left figure: monthly mean of GOME HCHO column over Europe in summer averaged over the years 1996-2000 and filtering out pixels where ATSR fire spots are detected (see text). The fire spots detected by the ATSR instrument are shown as red dots. The total number of fires per month is shown inset each subplot. Right figure: difference between column average without (Figure 4.17) and with fire filtering (left figure).



5.3 Inverting HCHO column for isoprene emissions in Eastern Europe

From the analysis of current emission inventories and of space diagnosed chemical regimes illustrated in the previous section, we have found that the only region where there is clear biogenic emission control on the HCHO column in Europe is the Eastern domain. We then apply the method by Palmer et al. [2003] described above to this region, because the anthropogenic influence on the HCHO production in the rest of Europe would require a more complicated bivariate inversion.

5.3.1 Relationship between isoprene emissions and HCHO column

Following the discussion of section 5.1, we find a local relationship between isoprene emission and HCHO column using the GEOS-Chem model, sampled at same selected GOME pixels used to produce the figures of section 4.2. HCHO column Ω can be linearly related to isoprene emissions:

$$\Omega = SE_{\rm isop} + B \tag{5.4}$$

where S denotes the linear slope, E_{isop} is the local isoprene emission and B is the HCHO background determined by the other, generally, long-lived VOCs. The slope S depends on the model yield of HCHO from isoprene oxidation and the loss rate constant for column HCHO. As we have seen in section 2.2.2 the GEOS-Chem model has an HCHO yield close to that of the reference Master Chemical Mechanism under high-NO_x conditions, while underestimates the yield under low-NO_x conditions. Since we have found that the region we have chosen (Eastern Europe) is under NO_x-limited regime, it is likely that low-NO_x conditions hold. In this case, the underestimate of HCHO yield by GEOS-Chem would reflect in an underestimate of the slope S.

In Figure 5.4 we find the relationship of equation 5.4 in the domain highlighted in the small frame on the right. GEOS-Chem values are sampled along GOME track as usual. The correlation between isoprene emissions and HCHO column (0.44) in the region is not as high as one would expected from previous discussion. However, using data from a simulation with zero isoprene emissions (red dots in the figure) we found a lower background and a less steep slope, indicating that isoprene emissions still drive the HCHO column production. We found a background B = 0.87 molec cm⁻² and a slope $S = 0.27 \times 10^4$ (molec cm⁻²) of HCHO per (C cm⁻² s⁻¹) of emitted isoprene. 94

Figure 5.4: Linear relationship between local isoprene emission and HCHO column over Eastern Europe (region highlighted in the frame) in July 1997 using the GEOS-Chem model sampled along GOME flighttrack. Number of data, correlation coefficient and estimated parameters of equation 5.4 are shown inset. Red dots are relative to a simulation without isoprene emissions.



Figure 5.5: Isoprene emissions estimated from regressions of GOME HCHO column (left) and calculated in the GEOS-Chem using GEIA inventory (right).



5.3.2 Inversion of GOME HCHO for isoprene emissions over Eastern Europe

We use the relationship between isoprene emission and HCHO column estimated in the previous section to invert GOME HCHO column for isoprene emissions over Eastern Europe. In Figure 5.5 we show the result of the inversion (left panel) compared to isoprene emissions in the GEIA inventory as computed in the GEOS-Chem (right) for July 1997. GOME and GEIA have similar fluxes in the left half of the selected domain, while in the right half GOME emissions are much lower than GEIA. The total emission estimated by GOME in the domain is halved with respect to GEIA.

Error analysis

The formula to invert HCHO column for isoprene emissions (from equation 5.4) is:

$$E_{\rm isop} = \frac{\Omega - B}{S} \tag{5.5}$$

so that the uncertainties implied in the estimate of E_{isop} are related directly to the model through parameters S and B, and to both GOME retrieval and model through Ω . To the uncertainty on the vertical column Ω contribute (1) column fitting error, (2) instrument artifact debias, and (3) air mass factor calculation. If we write the procedure to obtain Ω (see chapter 4) in mathematical form:

$$\Omega = \frac{\Omega_{slant} - D}{\text{AMF}} \tag{5.6}$$

where Ω_{slant} is the raw slant column, D is the debias applied to remove the diffuser plate artifact and AMF is the air mass factor. Using the error propagation formula we get:

$$\Delta\Omega = \left| \frac{\mathrm{d}\Omega}{\mathrm{d}\Omega_{slant}} \right| \Delta\Omega_{slant} + \left| \frac{\mathrm{d}\Omega}{\mathrm{d}D} \right| \Delta D + \left| \frac{\mathrm{d}\Omega}{\mathrm{dAMF}} \right| \Delta \mathrm{AMF} \qquad (5.7)$$
$$= \frac{\Delta\Omega_{slant}}{\mathrm{AMF}} + \frac{\Delta D}{\mathrm{AMF}} + \frac{\Omega_{slant} - D}{\mathrm{AMF}^2} \Delta \mathrm{AMF}$$

considering typical values $\Omega_{slant} = 2.5 \pm 0.4 \times 10^{16}$ molec cm⁻², $D = 0.8 \pm 0.15 \times 10^{16}$ molec cm⁻², AMF = 0.7 ± 0.2 we get and error on the vertical column $\Delta \Omega \simeq 1 \times 10^{16}$ molec cm⁻². The error ΔD is estimated considering a pessimistic model error of 20% and the error Δ AMF has been estimated in 30% by Palmer et al. [2005]. This means that error on the HCHO vertical column from GOME over Europe are of the order of 60–70%.

The propagation error applied to equation 5.5 gives an expression similar to equation 5.7, so that assuming an error on B and S of $\sim 30\%$ and considering typical values $\Omega = 1.7 \pm 1 \times 10^{16}$ molec cm⁻², $B = 0.9 \pm 0.3 \times 10^{16}$ molec cm⁻², and $S = 0.3 \pm 0.1 \times 10^4$ (molec cm⁻²) per (C cm⁻² s⁻¹), we get an error on the estimate of isoprene emission $\Delta E_{isop} = 4 \times 10^{12}$ C cm⁻² s⁻¹. Considering a typical European isoprene flux in summer of 0.4×10^{12} C cm⁻² s⁻¹ we see that the error on the inversion is really huge, an order of magnitude larger than the estimate itself. Uncertainty on the estimate of formaldehyde vertical column contribute 70% of this error. We conclude that the inversion of formaldehyde column for isoprene emission over Europe is subjected to too large errors to add significant information to previous knowledge on the emissions.

Chapter 6

Conclusions and Outlook

In this thesis we applied a top-down approach to estimate isoprene emissions over Europe. The observations used as a proxy for emissions are formaldehyde column measured by the GOME instrument onboard the ESA ERS-2 satellite. The method has previously successfully applied to North America by Palmer et al. [2003], where HCHO column variability is known to be controlled by isoprene emissions. A check on possible contribution to HCHO column production over Europe from AVOCs, BVOCs and biomass burning emissions has shown that (1) over Eastern Europe HCHO column is controlled by isoprene emissions, (2) over the rest of the continent both AVOCs and BVOCs contribute to HCHO column formation, (3) direct emission of HCHO from biomass burning make little contribution to the column. Extension of the method of Palmer et al. [2003] to Europe has shown to have limited use mainly for two reasons: (1) the HCHO column over Europe is controlled by both biogenic and anthropogenic VOC oxidation, apart from remote Eastern Europe, and (2) the column abundance is generally much lower over Europe with respect to North America, so that errors in GOME HCHO retrieval have a much higher weight. The method has been quantitatively applied to a selected region in Eastern Europe only, suggesting a reduction of isoprene emissions of about 50%. However, the error on the estimated flux constrained by satellite data is of an order of magnitude larger than the estimate itself, suggesting that the inversion of GOME HCHO over Europe cannot provide useful quantitative information as applied here. The main reason is that the retrieval of the vertical column contains a too large error, that contributes 70% of the total estimated error on isoprene emission.

A promising way to improve the study of formaldehyde column detected by GOME over Europe is to use multiyear average data, that give a much clear and stable picture of the column. For example, there is an interesting hot spot over the Southeastern Mediterranean that seem to receive contribution from the oxidation of both AVOCs and BVOCs. The formation of the hot spot is in phase with the vegetation growing season, hence lending support to the contribution of BVOCs longer-lived than isoprene. As mentioned above, a check on biomass burning suggests a little contribution to the column from this source. However, these points surely deserve further investigation.

Future work on the inversion would imply tackling several issues: (1) use of the long available time series of GOME HCHO data from 1996 to 2001 in the attempt of reducing the retrieval errors, (2) need for bivariate regression against anthropogenic and biogenic VOC emissions to extend the inversion to parts of Europe other than the Eastern domain, (3) implementation of the top-down inventory into the GEOS-Chem model and comparison of the impact on simulated HCHO column against independent data from European ground-based and aircraft campaigns. The latter point could benefit from data coming from the two recent campaigns FORMAT (North Italy) and MINOS (Southeastern Mediterranean). Data from this latter campaign could also help in understanding the formation of the summer hot spot in that Chapter 6. Conclusions and Outlook

region of the Mediterranean.

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