Review

Sources and reactivity of NMHCs and VOCs in the atmosphere: A review

Ankur Kansal *

Uttarakhand Environment Protection and Pollution Control Board, E-115 Nehru Colony, Dehradun, Uttarakhand, India

ARTICLE INFO

ABSTRACT

Nonmethane hydrocarbons (NMHCs) and volatile organic compounds (VOCs) are important species present in the environment, which results in alteration of the chemistry of atmosphere. On the global scale natural emissions of NMHCs and VOCs exceed anthropogenic emissions, although anthropogenic sources usually dominate within urban areas. Among the natural sources, vegetation is the dominant source. Oceanic and microbial production of these species is minimal as compared to other sources of input. Isoprene and terpenes are main species of NMHCs which are emitted from plants as a protective mechanism against temperature stress tolerance and protection from ravages of insects and pests. The major anthropogenic sources for NMHCs emissions are biomass burning and transportation. NMHCs play a significant role in ozone (O_3) production in the presence of adequate concentration of oxides of nitrogen in the atmosphere. The production of O_3 is based on Maximum Incremental Reactivity (MIR) of NMHCS and VOCs. The compound's MIR multiplied by molecular weight gives Relative Ozone Productivity (ROPi). To check the reliability of current methods of measuring the NMHCs the Nonmethane Hydrocarbon Inter-comparison Experiment (NMHICE) had been designed. The sample of known composition and unknown concentration of different hydrocarbons was supplied to different laboratories worldwide and less than 50% laboratories correctly separated the unknown mixture. Atmospheric scientists throughout the world are evaluating current analytical methods being employed and are trying to correct the problems to ensure quality control in hydrocarbon analysis.

© 2008 Elsevier B.V. All rights reserved.

Contents

1. Introduction

A large variety of hydrocarbons is found in the atmosphere. The atmospheric abundance of these species is found at mixing ratio ranging from parts per billion by volume (ppbv) to parts per trillion by volume (pptv). These species are found in significant amount over remote oceans, rural areas as also in urban environments. Nonmethane hydrocarbons (NMHCs) are introduced into atmosphere by fossil fuel burning, emission from vegetation and sea, biomass burning, transportation and geochemical processes. These compounds when oxidized produce a wide variety of oxygenated products including aldehydes, ketones, alcohols, phenols, etc. most of which have proven toxicity. Atmospheric OH radicals combine with the hydrocarbons. Atmosphere therefore, acts as a sink for these hydrocarbons. This reaction in the presence of oxides of nitrogen leads to the production of tropospheric ozone [1,2].

* Tel.: +91 9412992375.
  E-mail address: kansal2manj@yahoo.com.

Table 1
Global estimation of hydrocarbons [4].

Source	Emission (tg-C/yr)
Anthropogenic	
(1) Transportation	22
(2) Stationary sources	04
(3) Industrial processing including natural gas production	17
(4) Biomass burning, forest fires	45
(5) Organic solvents	15
Total	103
Natural	
Oceanic	
(1) Light	5–10
(2) C9–C28 hydrocarbons	1–26
Terrestrial	
(1) Microbial production	6
(2) Emission from vegetation	1140
Total	1170
Total emission	1273

2. Sources

NHHCs can be categorized into two broad categories: natural and anthropogenic. Natural sources contribute 69% of the total NMHCs emission while rest 31% is contributed by anthropogenic sources [3]. An attempt was made to find the sources of emission of hydrocarbons at global level in 1992 [4]. The findings are given in Table 1.

2.1. Natural sources

The broad leaf trees and conifer plants are responsible for the emission of terpenes, semiterpenes, and diterpenes, etc. which provide major emission among the natural sources [5]. Monoterpenes such as alpha and beta pinene, camphor and limonene, which are photochemically reactive hydrocarbons, are also released in significant quantities by plant species. These compounds generally serve as a defense mechanism against ravages of insects and pests [6,7]. Two of the most typical Mediterranean species *Pinus pinea* and *Quercus ilex* were screened for emission of monoterpenes during the period of 1997–1998 in the field at semirural location in Spain [8]. Monoterpenes have physical and chemical properties that make them attractive alternatives to chlorofluorocarbons in many industrial applications [9]. Isoprene is another reactive hydrocarbon emitted by a large variety of plant species [10,11] as a by-product of photosynthesis [12,13]. Most of the plant species emit isoprene as a protective mechanism against high temperature stress in a range of conditions even in darkness [14]. Isoprene emission is closely linked to the activity of the enzyme isoprene synthatase [15,16]. Isoprene emission is maximum during daytime and minimum at night. Since there is no storage of isoprene within plant's tissues and production requires substrate from photosynthesis, isoprene emission, therefore, cease in darkness [17].

Vegetation is thought to be the dominant source of hydrocarbon emission [18]. Annual global volatile organic compounds (VOCs) flux from plants was estimated to be 1150 tg-C, which consisted of 44% isoprene, 11% monoterpenes, 22.5% other reactive hydrocarbons and 22.5% other non-reactive hydrocarbons. As per study in North America the flux of NMHCs as 8.4×10^{12} g of carbon in which isoprene was 35%, 19 terpenoids contributed to 25% and 17 terpenoids 40% of the total emission was observed [19].

Guenther et al. [19] proposed the following emission model for NMHCs:

$$\text{Emission} \rightarrow [E]\,[Dp\,Df]\,[Rp\,Rt\,Ra][P]$$

where E is the landscape average emission capacity; Dp is the annual peak foliar density; Df is the fraction of foliage present at particular time of the year; Rp is the photosynthesis photon flux density; Rt is the temperature of the leaf; Ra is the leaf age; P is the escape efficiency.

In 1985, a study at Amazon tropical forest [20] showed that biogenic isoprene flux was $25{,}000\,\mu g/m^2$/day and it was calculated that isoprene emission was equal to the 2% of net primary productivity of the tropical forests. Tropical woodlands (rain forests, secondary drought deciduous and savannas) contribute about half of all global natural VOCs emission. Crop lands and other woodlands contribute 10–20% of VOCs emission [21], while it was very little from agricultural fields at Southwest British Columbia [22].

Various nonmethane volatile organic compounds (NMVOCs) such as propane, isoprene, methanol, etc. are also produced by the variety of soil microbes [23,24]. Microorganisms can also metabolize these compounds and in many cases soils are the sinks for such NMVOCs [25,26]. Isoprene emission activity directly depends upon leaf temperature (Fig. 1) As the leaf temperature and photosynthetic photon flux density (PPDF) increases isoprene emission activity also increases.

The emissions of VOC from freshly cut and shredded *Grevillea robusta* (Australian Silky Oak) leaves and wood have been mea-
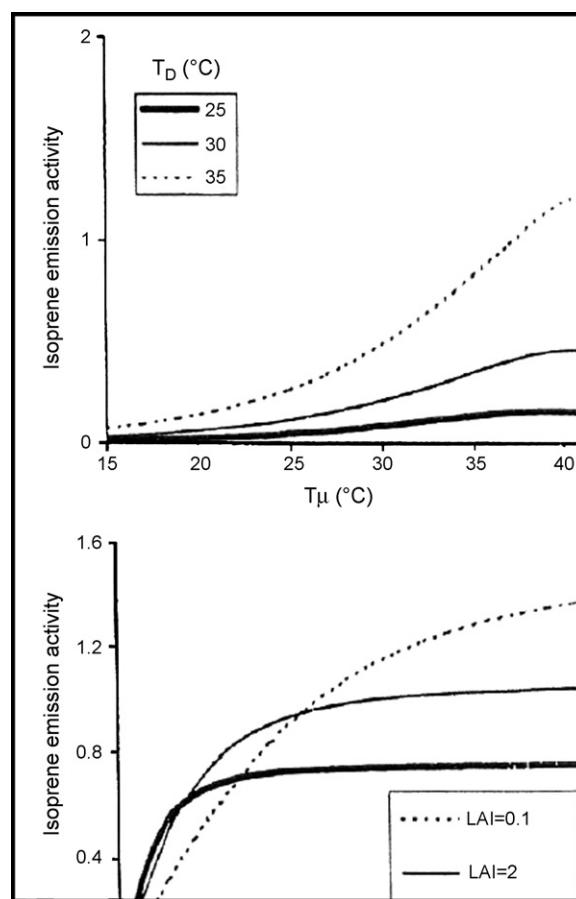

Fig. 1. Predicted influence of temperature (top) and photosynthetic photon flux density (PPDF) (bottom) on isoprene emission activity factors. T_D is the mean leaf temperature of the past 15 days. T_M is the leaf temperature of last few minutes. LAI is the leaf area index. Source: [19].

sured to study the VOC emissions from fresh leaf mulch and wood chips lasted typically for 30 and 20 h respectively, and consisted primarily of ethanol, (E)-2-hexenal, (Z)-3-hexen-1-ol and acetaldehyde. The integrated emissions of the VOCs were 0.38 ± 0.04 g kg^{-1} from leaf mulch, and 0.022 ± 0.003 g kg^{-1} from wood chips. These emissions represented a source of VOCs in urban and rural air that had previously been unquantified and is currently unaccounted for. These VOCs from leaf mulch and wood chips will contribute to both urban photochemistry and secondary organic aerosol formation [95].

Oceanic sources of NMHCs are minimal compared to the terrestrial inputs which are dominated by natural, biogenically derived isoprene, terpenes, etc. [27]. Ocean is supersaturated with the VOCs with respect to atmosphere. Because of this imbalance, ocean is considered as a source of these highly reactive compounds to the atmosphere. Calculation of flux from the air sea exchange [28] can be calculated as:

$$K = Kw[Cso - Ceq]$$

where: Kw is the transfer velocity; Cso is the surface ocean VOCs concentration; Ceq is the equilibrium surface ocean VOCs concentration with atmospheric concentrations.

Photochemical transformation of dissolved organic matter in the surface sea water results in the production of the C2–C4 alkenes in the surface ocean with UV portion (295–340 nm) of the solar spectrum controlling the bulk of this production. During a study under summer sunlight intensities in Miami, FL, net production rate for ethene, the dominant photoproduced of NMHC in surface sea water, varied from 0.220 pmol^{-1} min^{-1} for transparent oligotrophic waters to 6.11 pmol^{-1} min^{-1} for highly coloured estuarine waters [96].

Laboratory measurements of marine phytoplanktons indicate oceans as a potential source of isoprene to the atmosphere [29]. Surface concentrations of oceanic NMHCs result from both direct biological production and by-product of photochemical transformation of dissolved organic matter [30–32]. Emission of isoprene and other NMHCs from macroalgae (sea weed) were observed at temperate coastal site (Macae head, Ireland). Emission from all the algae investigated were dominated by alkenes and the production is algae dependent and temperature dependent and related to light availability [97]. Marine sources of ethylene and propylene and island sources of isoprene were also reported at Mauna Loa observatory [33].

At the Stordalen Mire in the Subarctic, variability in growing season hydrocarbon flux dynamics during 2002–2006 was observed. Accordingly NMHCs contribution to Total Hydrocarbons was estimated and it was found that the NMHCs contribute 15–25% in Total Hydrocarbons [98].

2.2. Anthropogenic sources

In the urban areas a wide variety of anthropogenic sources lead to the enhancement of hydrocarbon level in the atmosphere [34]. Among the anthropogenic sources primary source of NMHCs was found due to combustion and gasoline evaporation as per the studies in 43 Chinese cities, conducted in 2001 [99].

The largest source of organic gases including NMHCs and VOCs from anthropogenic sources are related to emission from mobile sources [35–39]. Ethene, acetylene, 1-butene, isobutene, propane, propene, isopentane, n-pentane, toluene, ethylbenzene, m and p-xylene, etc. are the most abundant compounds in these emissions. Mixing ratio of NMHCs in Happo, Japan showed winter maximum for ethane, propane, C4–C5 alkanes, n-hexane and acetylene consistent with seasonal variation of OH radical. Comparison of seasonal variation revealed that higher the latitude, higher is the concentration of C2–C5 hydrocarbons [40]. Vehicle exhaust is invariably the major contributor (more than 50%) to NMHCs in urban and suburban areas. Global impact of road traffic emission on chemical composition and climate was studied with particular emphasis on emission of NMHCs. It was observed that the concentration of ozone in the atmosphere increases due to road traffic emission (NO$_x$, CO, NMHCs) result in an annula and global mean adjusted radiative forcing of 0.058 W/m^2. Further it is concluded that the road traffic increases and decreases the concentration of hydroxyl radicals depending on geographical region and season. The global and annula indirect forcing due to road traffic-induced changes in the lifetime of methane amounts to 0.006 W/m^2. Results of the study show that NMHCs emission considerably contributes to the global impact of road traffic emissions [100]. The gasoline exhaust contribution is typically four times more than the diesel exhaust. Evaporated gasoline and liquid gasoline are the next most abundant contributors in most of the areas. Refineries, forest fires and other industrial sources are area specific [41]. In NO$_x$ rich environment dominating anthropogenic sources of NMHCs include automobile exhaust, gasoline evaporation and emission from commercial and industrial use of solvents [42]. Walter et al. [43] worked on the emission from automobiles powered by 2.5-L indirect diesel engine and outfitted with production oxidation catalyst for exhaust after treatment, showed the presence of 80% light hydrocarbons and 20% semivolatile fraction up to C15 hydrocarbons. Global emission of the anthropogenic VOCs was 98 tg/yr out of total 750 tg/yr [44]. A good correlation between total NMHCs, CO and other pollutants associated with motor vehicle emission was observed indicating vehicular traffic as a main source of total NMHCs [45]. Tai-Yih et al. [46] concluded that LPG especially propane contributes as much as 50% of the excess O$_3$ level in Santiago's air even under the heavy traffic conditions. It is also studied that the CMB (Chemical Mass Balance) discrimination between diesel and gasoline exhaust is distinctive when heavy hydrocarbons are included [38]. Most of these compounds are highly enriched in diesel exhaust but have negligible abundance in normal running gasoline vehicle exhaust.

Petrochemical production, especially the refining of gasoline and other fuel oils [47,48] can be a large contributor in some areas [49] in which ethane, propane, propene, n-pentane, benzene, n-heptane, toluene and n-octane are abundant species. Although solvents from the paints and industrial uses are large component of all VOCs inventories, their reported profiles are however, few [50–52]. Printing ink solvents from offset [53] and rotogravures are commonly identified in emission inventories. Most of these emissions are captured, condensed and reused by modern printing facilities, especially the toluene used for thinning rotogravure inks.

In addition to these common emission sources, landfills are sometimes identified as large total organic gas emitters owing to their prodigious production of methane that may be accompanied by reactive organic gases, depending on the nature of landfill wastes and disposal practices. Acetone, alpha terpinene, benzene, butyl alcohol, ethyl mercaptan, limonene, furans, terpenes, etc. are found to be among the most abundant components of landfill [54]. Aerobic decomposition of organic waste material also produces the light or small hydrocarbons. Several VOCs are used to be outgassed by plastics when they are heated [55].

Coal-fired power stations are also the source of VOCs. Small quantities of VOCs are emitted by several French coal-fired power stations, with benzene, toluene, ethylbenzene, xylenes, tetrachloroethane, benzaldehyde and phenol being the most abundant compounds [56]. Some data has also been obtained from petroleum fires [57], food and beverage production [58] household products and indoor building materials [59]. Summary of NMHCs source apportionment studies and the concentrations of various hydrocarbons from major U.S. cities are given in Tables 2 and 3

Table 2
Summary of NMHCs source apportionment studies [41].

Study, Location and Period Measurement	Findings		
San Joaquin Valley and San Francisco Bay Area, CA (7/90-8/90) [83] 2-h C2–C11 canister and carbonyl DNPH[a] samples at 34 sites in Central California representing urban and non urban, oilfield background and forested areas.	Average Contribution (%)		
	Vehicle exhaust	35–70	
	Gasoline evaporation	10–40	
	Coating and solvents	1–20	
	Oil production	30–50 (near oil fields), 5–15 (other sites)	
	Biogenic	0–15 (based on measured isoprene)	
	Others	2–20 (morning), 20–60 (afternoon)	
Los Angeles, CA (8/86) [84] Hourly 4-, 8-h C2–C10 canister samples collected at 9 sites between 8/10/86 and 8/21/86	Average Contribution (%)		
	Gasoline engine exhaust	31–37	
	Whole liquid gasoline	32–38	
	Headspace gasoline vapors	5–13	
	Waste and natural gas	10–15	
	Dry cleaning	0–14	
	Degreasing solvents	5–12	
Los Angeles, CA (7/95 to 10/95) [85] 3-hour C2–C11 canister samples for six 7 day periods at CARB[b] sites and for 3 day periods at 8 Coordinating Research Council (CRC) sites.	Average Contribution (%)		
		3CARB sites	8 CRC sites
	Diesel vehicle exhaust	11–15	10–15
	Liquid duty vehicle exhaust	38–50	42–54
	Liquid gasoline	0.6–11	1–14
	Gasoline vapors	15–29	10–20
	Gas (CNG[c])	3.1–3.7	2.2–2.7
	Gas (CNG[d])	5.2–8.8	6.6–8.6
	Gas (LPG[e])	2.6–3.7	1.9–3.0
	Biogenic	0.2–0.3	0.1–0.2
	Coating (architectural)	3.2–5	0.3–1.1
	Coating (industrial)	1.7–9.3	4.1–6.9
	Coating (others)	1.7–10	1.1–8.9
	Unexplained	3.5–11	0.9–7.8
Phoenix Ozone Study, Phoenix, AZ (Summer, 1996) [86] 4-hour C2–C11 canister samples at three sites	Average Contribution (%)		
	Diesel exhaust	5.4–11.7	Gas (LPG) 0.5–1.0
	Gasoline exhaust	51.5–59.0	Biogenic 0.2–2.6
	Liquid gasoline	6.6–8.9	Coatings (architectural) 0.4–2.2
	Gasoline vapors	2.8–7.3	Coatings (industrial) 2.2–3.1
	Gas (CNG)	1.2–3.2	Unexplained 7–8
	Gas (GNG)	5.6–8.0	
Coastal Oxidant Assessment for Southeast texas (COAST) study, Huston,TX (7/93-8/93) Hourly canister C2–C10 and DNPH cartridge C1–C7 carbonyl compounds from 6 surface sites, 6 time per day during 1993	Average Contribution (%)		
	Vehicle exhaust	19–36	
	Liquid gasoline	7–15	
	Gasoline vapors	7–20	
	CNG	3.5–6.4	
	Industrial	22–50	
	Biogenic	0.5–1.8	
	Unexplained	1–2	
Chicago, IL (7/87-9/87) [87] 4-hour C2–C7 and Tenax trap (aromatic and chlorinated compounds) at 3 down sites	Average Contribution (%)		
		CMB[f] Calculated	Emission inventory
	Vehicle exhaust	21	39
	Gasoline vapors	7.1	7.6
	Solvent (architectural)	3.1	5.5
	Solvent (graphic art)	1.0	9.8
	Vapor degreasing	3.4	3.1
	Dry-cleaning	0.3	0.1
	Industry (Refinery)	7.4	1.3
Beamount, TX, Detroit, MI, Chicago, IL, Washington, DC and Atlanta, GA (Summers of 1984–1988) [88] 1-hour and 3-hour samples at 18 sites	Average Contribution (%)		
	Vehicle exhaust	28–55	
	Gasoline vapors	9–20	
	Solvent (architectural)	2–6	
	Solvent (graphic art)	5–12	
	Industry (refinery)	9–17 (in cities with refineries)	
	Industry (coke oven)	4 (in Detroit and Washington)	

Table 2 (*Continued*)

Study, Location and Period Measurement	Findings		
Detroit, MI (7/88-8/8) [89] 1-hour canister samples at 18 cities	Average Contribution (%)		
		CMB calculated	Emission inventory
Vehicle exhaust		28	33
Gasoline vapors		9	7
Solvent (architectural)		2.5	3.8
Solvent (graphic art)		4.7	0.7
Industry (refinery)		17	0.7
Industry (coke oven)		3.7	2
Others		35	39

Study, Location and Period Measurement	Findings		
1995 NARSTO[g] Northeast Ozone study (6/95-8/95) [90] Four, 3-hour C2–C11 canister samples at five sites and three, 3-hour samples at three sites.	Average Contribution (%)		
	10 surface sites	6 surface sites	7 aloft sites
Diesel exhaust	3–44	6–8	6–9
Gasoline exhaust	17–62	7–23	9–25
Liquid gasoline	2–9	1–7	1.5–5.7
Gasoline vapors	12–31	2–6	0.8–5.9
CNG	7–12	3–34	7–11
LPG	1–30	0.6–3.2	0.7–2.4
Biogenic	1–12	2–10	0–5.8
Unidentified	–	46–72	59–75
Unexplained	8–17	4–8	6–11

[a] DNPH, 2,4-dinitrophenylhydrazide.
[b] CARB, California Air Resource Board, Sacramento, CA.
[c] CNG, Compressed Natural Gas.
[d] GNG, Geogenic Natural Gas.
[e] LPG, Liquefied Petroleum Gas.
[f] CMB, Chemical Mass Balance receptor model.
[g] NARSTO, North America Research Strategy for Tropospheric Ozone.

respectively. During ozone episode in Beijing (China) from August 16 to 19, 2006, carbonyl compounds and NMHCs were measured. Principal component analysis/absolute principal component scores (PCA/APCS) was used to identify the dominant emission sources and evaluate their contribution to NMHCs and carbonyls. It was found that the ratios of NMHCs/NO$_x$ and Carbonyls/NO$_x$ were 11.8 ± 3.9 and 2.7 ± 0.8. Based on the Maximum Incremental Reactivity (MIR) scale, the leading contributors to O$_3$ formation in Beijing are formaldehyde, xylenes, trimethylbenzenes, acetaldehyde and propene which account for 56% of the total ozone formation potential. However, ranking by Prop-Equiv, isoprene, xylenes, formaldehyde, trimethylbenzenes and propene are top 5 VOCs which account for 43% of the total Prop-Equiv concentration [101].

Table 3
Median concentrations of the 48 most abundant Ambient Air Hydrocarbons in 39 U.S. cities [94].

Rank	Compound	ppb	Rank	Compound	ppb
1.	i-Pentane	45.3	25.	n-Heptane	4.7
2.	n-Butane	40.3	26.	2,3-Dimethylbutane	3.8
3.	Toluene	33.8	27.	c-2-Pentene	3.6
4.	Propane	23.5	28.	1,2,3-Trimethylbenzene	3.4
5.	Ethane	23.3	29.	Methylcyclohexane	3.4
6.	n-Pentane	22.0	30.	n-Decane	3.3
7.	Ethene	21.4	31.	1,3,5-Trimethylbenzene	3.0
8.	m&p-Xylene	18.1	32.	C11 aromatic	3.0
9.	2-Methylpentane	14.9	33.	t2-Pentane	2.9
10.	i-Butane	14.8	34.	o-Ethyltoluene	2.9
11.	Acetylene	12.9	35.	p-Ethyltoluene	2.8
12.	Benzene	12.6	36.	C10 aromatic	2.8
13.	2-Ethyl-1-butene	11.0	37.	n-Octane	2.6
14.	3-Methylpentane	10.7	38.	2-Methyl-1-butene	2.6
15.	1,2,4-Trimethylbenzene	10.6	39.	1,2-Dimethyl-3-ethylbenzene 2.5	
16.	Propene	7.7	40.	t-2-Butene	2.5
17.	2-Methylhexane	7.3	41.	2,3,4-Trimethylpentane	2.5
18.	o-Xylene	7.2	42.	2-Methylpentane	2.5
19.	2,2,4-Trimethylpentane	6.8	43.	1,4-Dimethylbenzene	2.4
20.	Methylcyclopentane	6.4	44.	3-Methylpentane	2.2
21.	3-Methylhexane	5.9	45.	n-Nonane	2.2
22.	2-Methylpropene	5.9	46.	Cyclohexane	2.2
23.	Ethylbenzene	5.9	47.	2,4-Dimethylpentane	2.2
24.	m-Ethyltoluene	5.3	48.	Cyclopentene	2.1

Table 4
Sources of nitrogen oxides [91].

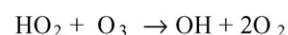| Source	% Emission
1. Motor vehicle traffic	64
2. Power plants	18
3. Industries	12
4. Household, minor consumer	06

3. NMHCs and tropospheric ozone production

Anthropogenic and natural NMHCs are a portion of the fuel for tropospheric photochemistry [60,61]. Natural NMHCs play a
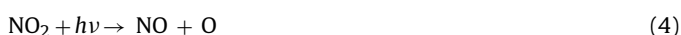
Isoprene is responsible for 31% of measured OH reactivity. Isoprene in conjunction with two of its primary oxidant products, Methcralein and Methylvinylketone [69] was responsible for 35% reactivity [70]. The reaction of isoprene is very fast with OH radical ($K_{OH} = 1.0 \times 10^{-10}$ cm^3/mol/s) [71]. High emissions as compared to other NMHCs [20] over remote areas imply that boundary layer photochemistry can be greatly influenced by its presence. Depending on the local NO_x concentration presence of isoprene can cause significant boundary layer O_3 production in rural [72] remote [73] and in urban areas [74,69].

NHMCs are also proposed as an important source of atmospheric CO, a fuel product in a multi-step decomposition of hydrocarbons in the atmosphere [75,76]. Carbon monoxide again produces O_3 in troposphere in NO_x rich environment:

$$CO + OH \rightarrow H + CO_2$$

$$H + O_2 \rightarrow HO_2 + M$$

In NOx rich air

$$HO_2 + NO \rightarrow HO + NO_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 \rightarrow O_3 + M$$

in NOx poor air

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$CO + 2O_2 \rightarrow CO_2 + O_3$$

(Production)
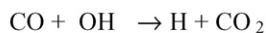
$$CO + O_3 \rightarrow CO_2 + O_2$$

(Loss)

significant role in the O_3 production [62]. In the rural areas where NO_x concentration is very small, O_3 production is also less. But in the urban areas due to the industrial and vehicular pollution the relative concentration of NO_x reaches up to a level so that it easily contributes to production of O_3 even in small concentration of NMHCs [63]. The importance of NMHCs as O_3 producing precursor through the OH radical initiated oxidation and subsequent reaction with NO_x has been well studied [64]. In polluted areas with relatively high concentration of NO_x, photochemical oxidants of NMHCs, initiate a complex series of photochemical reactions known as photochemical smog mechanism that leads to the production of O_3 and other secondary oxidant pollutants [65,66]. NO_x being important in the O_3 production, it is imperative to consider its sources (Table 4). Ground level O_3 is created in the reaction of excess concentration of NMHCs and NO_x in the presence of sunlight (Reaction (1)–(5)) where R is an alkyl group, $h\nu$ is photon, M is third body molecule.

$$RH + OH \rightarrow R + H_2O \tag{1}$$

$$R + O_2 \rightarrow RO_2 \tag{2}$$

$$RO_2 + NO \rightarrow NO_2 + RO \tag{3}$$

$$NO_2 + h\nu \rightarrow NO + O \tag{4}$$

$$O_2 + O + M \rightarrow O_3 + M \tag{5}$$

The contribution of each NMHC to local O_3 production can be approximately based on the Maximum Incremental Reactivity [67]. A compound's MIR multiplied by its molecular weight gives the Relative Ozone Productivity (ROPi) for that compound [68].

Production or loss depends on these two equation. From here we can calculate the minimum concentration of the NO for the production of O_3 as:

$$K_a[NO] = K_b[O_3]$$
$$[NO] = \left(\frac{K_b}{K_a}\right) \times [O_3] = \left(\frac{2.0 \times 10^{-15}}{8.3 \times 10^{-12}}\right) \times 10^{12} = 2.4 \times 10^8 \text{ mol/cm}^3$$

Thus the minimum of 2.4×10^8 mol/cm^3 NO is required for the production of O_3 in the troposphere. The values of the rate constant are taken from Atinkson [71].

Aromatic compounds are most effective in urban/rural transient zone, limit O_3 formation [77]. Under most conditions studied, natural NHMCs are predicted to contribute little daily O_3 formation despite their high reactivity and under low NO_x concentration may even lead to small reduction in O_3 formation. Only moderate NO_x level as observed above and favorable NMHC/NO_x ratio does the sizeable enhancement of O_3 production [78].

Some NMHCs have atmospheric lifetime less than one day in tropics and mid-latitudes; others have sufficient long lifetime measured in areas remote from sources such as Antarctica [79]. As number of carbon atoms increase in the hydrocarbon chain, the lifetime of the hydrocarbon decreases and their reactivity and O_3 producing capacity increases (Table 5). Lifetime v/s reactivity of different hydrocarbons is given in Fig. 2.

In the stratosphere, only ethane, acetylene and propane are found because most NMHCs are completely destroyed in troposphere by the oxidation reactions with OH, O_3, NO_3 and other oxidants [80] Presence of oxidants other than O_3 facilitates conversion of NO to NO_2 [81]. They indicate the photochemical origin of oxidants and their dependence on the peroxy radicals including RO_2, HO_2, $RCOO_2$; the other type was exemplified by iodine monoxide 'IO'.

Table 5
Relative reactivates of hydrocarbons and CO with OH radical [92].

Reactivity class	Reactivity range[a]	Approximate half time in the atmosphere	Compounds in increasing order of reactivity
I	<10	>10 days	Methane
II	10–100	24 h to 10 days	CO, acetylene, ethane
III	100–1000	2.4–24 h	Benzene, propane, n-butane, isopentane, methyl ethyl ketone, 2-methylpentane, toluene, n-propylbenzene, isopropylbenzene, ethene, n-hexane, 3-methylpentane, ethylbenzene
IV	1000–10000	15 min to 2.4 h	p-Xylene, p-ethyltoluene, o-ethyltoluene, o-xylene, methylisobutyl ketone, m-ethyltoluene, m-xylene, 1,2,3-trimethylbenzene, propene,1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, cis-2-butene, β-pinene, 1,3-butadiene
V	>10000	<15 min	2-Methyl-2-butene, 2,4-dimethyl-2-butene, d-limonene

[a] Based on an assigned reactivity of 1.0 for methane.
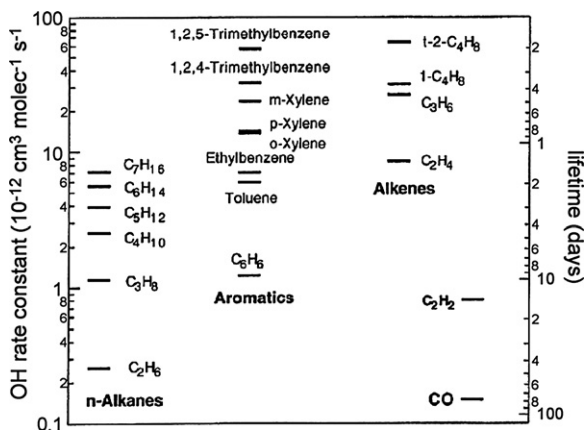

Fig. 2. Rate constant (left ordinate) and approximate tropospheric lifetime (right ordinate) for the less reactive NMHCs. CO includes for comparison. Rate constant data were taken from Atkinson [93]. To estimate lifetime a concentration of OH molecules equal to 10^6 molecules cm^{-3} and a temperature of 298 K were assumed. Source: [60].
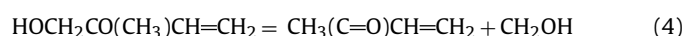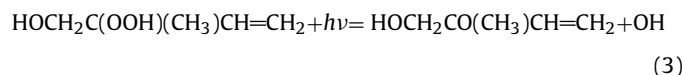
4. Isoprene and its oxidation products

With an estimated 44% of the total volatile organic compound (VOC) emissions by vegetation, isoprene (C_5H_8) constitutes the largest single NMHC source to the global atmosphere [102]. So, it is important to see the oxidation products of this species Oxidation of isoprene results in the production of CO and CO_2, accounting for about 16% of the global CO production [103]. The atmospheric oxidation of isoprene mostly starts with the addition of HO and O_2 (Fehsenfeld et al. [104] and references therein), producing 6 isomeric organic peroxy radicals. These peroxy radicals may react with NO, when present, to form alkoxy radicals and then carbonyl compounds. The first order carbonyl products with the highest yield are methacrolein ($CH_2C(CH_3)CHO$), MACR and methyl vinyl ketone ($CH_2CHCOCH_3$, MVK). In low NO_x (NO C NO_2) situations, which are more typical over the rainforest, the peroxy radicals may react with other peroxy radicals to form alkoxy radicals and then further to form the same carbonyl products as mentioned above. Alternatively the peroxy radicals may react with HO_2 to give the hydroperoxides, e.g., $HOCH_2COO(CH_3)CH=CH_2$.

$$CH_2=C(CH_3)CH=CH_2 + OH + O_2 = HOCH_2COO(CH_3)CH=CH_2 \quad (1)$$

$$HOCH_2COO(CH_3)CH=CH_2 + HO_2 = HOCH_2C(OOH)(CH_3)CH=CH_2 \quad (2)$$
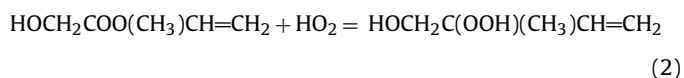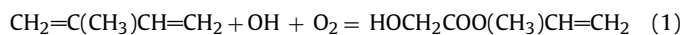
These organic hydroperoxides further photodecompose by absorption of solar radiation, or by reaction with HO to form the aforementioned carbonyl compounds, e.g., methyl vinyl ketone ($CH_2CHCOCH_3$, MVK) [105] through the following intermediates:

$$HOCH_2C(OOH)(CH_3)CH=CH_2 + h\nu = HOCH_2CO(CH_3)CH=CH_2 + OH \quad (3)$$

$$HOCH_2CO(CH_3)CH=CH_2 = CH_3(C=O)CH=CH_2 + CH_2OH \quad (4)$$

CH_2OH rapidly reacts with O_2 to produce CH_2O and HO_2:

$$CH_2OH + O_2 = CH_2O + HO_2 \quad (5)$$

Further oxidation of CH_2O gives rise to CO which, through the reaction with HO, is oxidized to CO_2. Only the reaction path leading to MVK is shown by Reactions (1)–(4). In similar ways, methacrolein ($H_2C=C(CH_3)CHO$; MACR) is formed. The 1,4-addition of HO leads to 3-ethylfuran by isomerisation and cyclization. The ozone addition mechanism (ozonolysis) is significantly slower, but gains importance during night, when HO concentrations are low. However, also ozonolysis leads to MVK and MACR. In this paper we present online airborne measurements of isoprene, its oxidation products MVK, MACR, and compounds likely identified as the Isoprene Hydroperoxide (ISOHP) isomers by means of a new aircraft-based PTR-MS instrument focussing on the boundary layer, but with data obtained also at higher altitudes up to 12 km.

5. Studies of NMHCs in India

A little references are available of studies of NMHCs in India. A study in the year 2006 presented that the NMHCs contribution to atmosphere is maximum due to combustion of bio-fuels [106]. Percentage of emission of NMHCs from different sources in India is presented in Fig. 3. Simultaneous surface level measurements of O_3, CO, methane, and light nonmethane hydrocarbons were made over the Bay of Bengal during a cruise campaign between 19 February and 28 February 2003. The mixing ratios of O_3, CO, methane, ethane and acetylene were observed in the ranges of 20–52 ppbv, 126–293 ppbv, 1.65–1.85 ppmv, 622–2088 pptv and 134–1388 pptv, respectively [107]. The annual mean mixing ratios of ethane, ethene, propane, propene, i-butane, acetylene, and n-butane are 1.22 ± 0.58, 0.34 ± 0.24, 0.46 ± 0.20, 0.17 ± 0.14, 0.21 ± 0.18, 0.41 ± 0.43, and 0.31 ± 0.35 ppbv, respectively at Mt Abu, Rajasthan, India, and the annual mean propylene (propene) equivalent concentrations of about 1.12 and 8.62 ppbC were calculated for Mt. Abu and Ahmedabad, respectively was observed [108]. In a study in India also presented that residue burning in rice–wheat cropping system results in the emission of CO_2, CO, CH_4, N_2O, NO_x, NMHCs and aerosols [109].
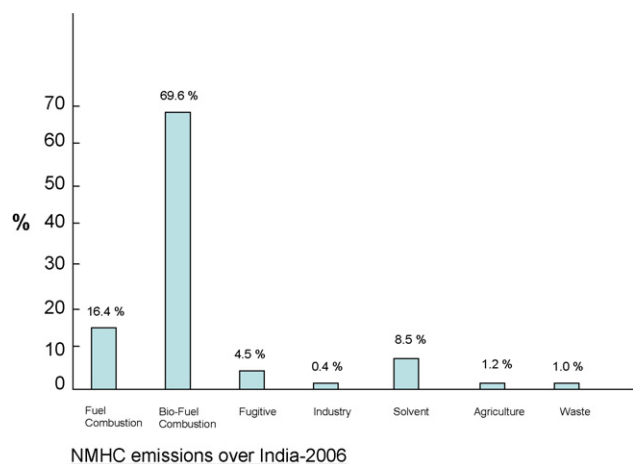
Fig. 3. NMHC emissions over India, 2006. Source: [106].

6. Various latest models used for flux/emission of NMHCs and VOCs

There are a few latest models which are developed in this decade for estimation of flux and emission of these species. Here some of the most popular studies in this regard are being referred.

Atmospheric Radon-222 (^{222}Rn) was used as a natural tracer for methane and other NMHCs from the specific area. The methane flux from urban areas in Nagoya, Japan, was estimated to be almost constant at $0.02\,gCH_4\,m^{-2}\,d^{-1}$ over a year [110].

A global three-dimensional chemical model for troposphere for study of Atmospheric environment and radiative forces (CHASER) was developed. This model simulates oxidation of NMHCs through 88 chemical reactions and 25 photolytic reactions with 47 chemical species. The model covers the emission sources, dry and wet deposits and chemical transformations. The main objective of this model is to study the global distribution of ozone and its precursors [111].

The potential role of isoprene and other naturally emitted hydrocarbons in biosphereclimate-chemistry feedbacks has been summarised recently [112,113]. Plants also emit a wide range of other VOCs, including many oxygenated species [114]. Met Office chemistry-transport model STOCHEM was used to estimate the emissions of isoprene, monoterpenes, ethene and propene from vegetation [115]. In this model ecosystems, specific leaf weights and emission factors used to calculate the flux of isoprene and monoterpenes. These factors are given in Table 6.

Most of the fast reactant and quickly decomposing products of NMHCs are localized near the emission sources. A series of reduced chemical models of decreasing complexity with increasing distance from source was presented recently in Proceedings of National

Table 6
Ecosystems, specific leaf weights and emission factors used in STOCHEM to calculate flux of isoprene and monoterpenes [115].

S. No.	Ecosystem	Leaf weight (w/g^{-2})	Emission factor, e ($\mu g\,Cg^{-1}\,h^{-1}$)	
			Isoprene	Monoterpenes
1.	Broadleaf forest	125	24	0.4, 0.8[a]
2.	Needleleaf forest	150	08	2.4
3.	C3 Grass	125	16	0.8
4.	C4 Grass	125	16	0.8
5.	Shrub	125	16	0.8

[a] Broadleaf forests have a base monoterpene emission factor of $0.4\,\mu g\,Cg^{-1}\,h^{-1}$ in the tropics, and $0.8\,\mu g\,Cg^{-1}\,h^{-1}$ in temperate zones.

Academy of Science, USA [116]. The algorithm diagnoses the chemical dynamics on-the-run, locally and separately for every species according to its characteristic reaction time.

7. Nonmethane Hydrocarbon Inter-comparison Experiment (NMHICE)

There are various methods used fro measure the NMHCs and VOCs in atmosphere. Most common method of the same is using Gas Chromatography. Here some of the studies are being referred regarding methods of measurement of NMHCs and VOCs. However, the details of the various monitoring/analysis methods and comparison thereof is the separate issue and is out of scope from the topic of this article.

GC-FID, GC-ECD, GC–MS analyses of NMHCs, together with applications of CIMS/PTR-MS, DOAS and LIF are described in a review of instrumentation and measurement techniques. In the said review article direct and indirect fluorimetric, chromatographic and spectroscopic detection techniques are also discussed for CH_2O, and higher carbonyls along with the observations of ROOH utilizing colorimetry, chemo-luminescence, fluorescence, HPLC and TDLAS [117].

A multi-bed, peltier cooled adsorption trap was developed for concurrent analyses of C2–C7 Hydrocarbons and C2–C5 oxygenated volatile organic compounds (o-VOCs). Analysis of the samples was made through FID. The system results NMHC detection limit between 1 and 10 pptv and o-VOCs detection limit between 10 and 40 pptv [118].

An innovative cryogen-free concentrator system for measurement of atmospheric trace gases at the parts per trillion level has been developed with detection by routinely used gas chromatographic methods. The first generation system was capable of reaching a trapping temperature of $-186\,°C$, while the current version can reach $-195\,°C$. This robust system quantified 98 ambient volatile organic compounds with precisions ranging from 0.3 to 15% [119].

The NMHICE programme has been designed to evaluate current methods being used to determine the ambient levels of various atmospheric nonmethane hydrocarbons, to identify existing problems in these analysis, to correct these problems and to help ensure quality control of hydrocarbon analysis made by atmospheric scientists throughout the world. The various tasks of the study have been scheduled in the order to increase complexity so that problem can be addressed as they rise. The first task of NMHICE involved the circulation of two-component gravimetrically prepared hydrocarbon mixture of known composition and unknown concentration to 36 participating scientific groups throughout world. Task two involved the circulation, to participant laboratories, of more complex, gravimetrically prepared 16 component mixture of unknown concentration. In task one, both of components were correctly separated but in task two only 28 laboratories had send their results out of which 12 laboratories correctly separated all the components [82].

8. Conclusion

(1) Globally natural emission of NMHCs and VOCs is always higher than the emission from the anthropogenic activities.

(2) Isoprene and monoterpenes emitted in large quantities by the plant species to protect themselves from high temperature stress and ravages of insects and pests.

(3) Emission varies with change in latitude. Emission is higher in the tropics and decreases while moving towards the higher latitude.

(4) Among the anthropogenic sources transportation and biomass burning are the major ones.

(5) NMHCs cause the production of tropospheric ozone in the presence of sufficient amount of NO in the atmosphere.

(6) Higher molecular weight of the hydrocarbon species results in more reactivity in ozone production.

Acknowledgement

References

[1] J.G. Calvert, Test of theory of ozone generation in Los Angeles atmosphere, Environ. Sci. Technol. 10 (1976) 248–256.

[2] J.H. Seinfeld, S.N. Pandis, Atmospheric Chemistry and Physics, Air Pollution to Climate Change', Wiley, New York, NY, 1997.

[3] P. Middelton, in: H.B. Singh, J. Nriager (Eds.), Sources of Air Pollutants in Composition, Chemistry and Climate of Atmosphere, John Wiley and Sons, New York, 1995.

[4] H.B. Singh, P. Zimmerman, Atmospheric distributions and sources of non methane hydrocarbons, in: J.O. Nriagu (Ed.), Gaseous Pollutants: Characterisation and Cycling, Wiley, New York, 1992, p. 235.

[5] R.P. Wayne, Chemistry of Atmosphere, Oxford University Press, London, 2000, p. 323.

[6] M. Lerdau, Plant function and biogenic terpene emission, in: Trace Gas Emission by Plants, Academic Press, San Diego, 1991, pp. 121–133.

[7] D.V. Banthorpe, Classification of terpenoids and general procedures: methods, in: Plant Biochemistry, Academic Press, London, 1991.

[8] D. Sabillon, L.V. Cremades, Diurnal and seasonal variation of monoterpene emission rates for two Mediterranean species (*Pinus pinea* and *Quercus ilex*) from field measurements—relationship with temperature and PAR, Atmos. Environ. 35 (26) (2001) 4419–4431.

[9] J. Li, E.M. Perdue, S.G. Pavlostathis, R. Araujo, Physicochemical properties of selected monoterpenes, Environ. Int. 24 (3) (1998) 353–358.

[10] D.T. Tingey, M. Manning, L.C. Grothaus, W.F. Burns, The influence of light and temperature on isoprene emission rates from live oak, Physiol. Plant 47 (1979) 112.

[11] A.B. Guenther, R.K. Monson, R. Fall, Isoprene and monoterpenes emission rate variability: observation with Eucalyptus and emission rate algorithm development, J. Geophys. Res. 96 (1991) 13033.

[12] B. Lamb, H. Westberg, G. Allwine, Biogenic hydrocarbon emissions from deciduous & Coniferous trees in United States, J. Geophys. Res. 90 (1985) 2380–2390.

[13] A.B. Guenther, P. Zimmerman, M. Wildermuth, Natural volatile organic compound emission rate estimates for U.S. woodland landscape, Atmos. Environ. 28 (1994) 1197–1210.

[14] T.D. Shankey, E.L. Singsaas, Why plants emit isoprene, Nature 374 (1995) 769.

[15] G.M. Silver, R. Fall, Enzymatic synthesis of isoprene from dimethyldiphosphate in aspen leaf extracts, Plant Physiol. 97 (1991) 1588–1591.

[16] G.M. Silver, R. Fall, Characterization of aspen isoprene synthatase, an enzyme responsible for leaf isoprene emission to the atmosphere, J. Biol. Chem. 270 (1995) 13010–13016.

[17] G. Sanadze, Isoprene effect—light dependent emission of isoprene by green parts of plants, in: Trace Gas Emission by Plants, Academic Press, San Diego, 1991, pp. 135–150.

[18] P.R. Zimmerman, Tampa Bay-Photochemical Oxidant Studies, Report EPA 904/9-77-028' Environment Protection Agency, Research triangle Par, N.C., 1979.

[19] A.B. Guenther, C. Geron, T. Pierce, B. Lamb, P. Harley, R. Fall, Natural emission of non-methane volatile organic compounds, carbon mono oxide and oxides of nitrogen from North America, Atmos. Environ. 34 (2000) 2205–2230.

[20] P.R. Zimmerman, J.P. Greenberg, C.E. Westberg, Measurement of atmospheric hydrocarbons and biogenic emission fluxes in the Amazon Boundary Layer, J. Geophys. Res. 93 (D2) (1998) 1407–1416.

[21] A.B. Guenther, C.H. Nichoolas, D. Ericson, R. Fall, C. Geron, T. Garedel, A global model of volatile organic compound emission, J. Geophys. Res. 100 (D5) (1995) 8873–8892.

[22] G.B. Drewitt, K. Current, D.G. Steyn, T.J. Gillespie, H. Niki, Measurement of biogenic hydrocarbon emission from vegetation in lower Fraser valley, British Columbia, Atmos. Environ. 32 (20) (1998) 3457–3466.

[23] V. Isidorov, Organic Chemistry of Earth's Atmosphere, Springer, Berlin, 1990.

[24] J. Kuzma, M. Nemecek-Marshall, W.H. Pollock, R. Fall, Bacteria produce the volatile hydrocarbon isoprene, Curr. Microbiol. 30 (1995) 97–103.

[25] C. Cleveland, J. Yavitt, Consumption of atmospheric isoprene in soil, Geophys. Res. Lett. 24 (1997) 2379–2382.

[26] G. Morsdorf, K. Franzke, D. Gandkari, O. Meyer, Microbial growth on carbon monoxide, Biodegradation 3 (1992) 61–82.

[27] F.C. Fehsnfeld, J.G. Calvert, R. Fall, P. Goldan, A. Guenther, C. Hewitt, Emission of volatile organic compounds from vegetation and implication for atmospheric chemistry, Global Biogeochem. Cycles 5 (1992) 389–430.

[28] P. Liss, L. Merlivat, Air sea gas exchange rates: introduction and synthesis, in: P. Buat-Menard, D. Reidel, M. Norwall (Eds.), The Role of Air-Sea Exchange in Geochemical Cycling, 1986.

[29] R.M. Moore, D.E. Oram, S.A. Penkett, Production of isoprene by marine phytoplanktons, Geophys. Res. Lett. 21 (1994) 2507–2510.

[30] M. Ratte, C. Plass-Dulmer, R. Koppmann, J. Rudolph, J. Denya, Production mechanism of C2–C4 hydrocarbons in sea water: field measurement and experiment, J. Global Bigeochem. Cycles 7 (1993) 369–378.

[31] M. Ratte, O. Bujok, A. Spitzy, J. Rudolph, Photochemical alkene formation in sea water from dissolve organic carbon, results from laboratory experiment, J. Geophys. Res. 103 (1998) 5707–5717.

[32] D. Reimer, P. Milne, R. Zika, W. Pos, Photo production of non-methane hydrocarbons (NMHCs) in sea waters, Mar. Chem. 71 (2000) 177–198.

[33] J.P. Greenberg, P.R. Zimmerman, W.F. Pollock, R.A. Lueb, L.E. Heidt, Diurnal variability of atmospheric methane, non-methane hydrocarbon and carbon monoxide at Mauna-Loa, J. Geophys. Res. 97 (D10) (1992) 10395–10413.

[34] R.A. Field, M.E. Goldstone, J.N. Lester, R. Perry, The source and behavior of tropospheric anthropogenic volatile hydrocarbons, Atmos. Environ. 26 (A) (1992) 2983–2996.

[35] F.M. Black, L.E. High, J.M. Lang, Composition of automobile evaporative and tailpipe hydrocarbon emissions, J. Air Pollut. Control Assoc. (1980) 1216–1221.

[36] J.C. Bailey, B. Schmidi, M. Williams, Speciated hydrocarbon emissions from vehicle operated over the normal speed range on the road, Atmos. Environ. 24 (A) (1990) 43–52.

[37] L. Haszpra, I. Szilagyi, Non-methane hydrocarbon composition of car exhausts in Hungary, Atmos. Environ. 28 (1994) 2609–2614.

[38] A.W. Gertler, E.M. Fujita, W.R. Pierson, D.N. Wittorf, Apportionment of NMHC tailpipe vs non tailpipe emission in the Fort McHenry and Tuscarora Mountain tunnels, Atmos. Environ. 30 (1996) 2297–2305.

[39] V. Mugica, E. Vega, J.L. Arriaga, M.E. Ruiz, Determination of motor vehicle profiles for non-methane organic compounds in the Mexico City metropolitan area, J. Air Waste Manage. Assoc. 48 (1998) 1060–1068.

[40] U.K. Sharma, Y. Kajii, H.A. Kimoto, Seasonal variation of C2–C6 NMHCs at Happo, a remote site in Japan, Atmos. Environ. 34 (2000) 4447–4458.

[41] J.G. Watson, J.C. Chow, E.M. Fujita, Review of volatile organic compound source apportionment by chemical mass balance, Atmos. Environ. 35 (2001) 1567–1584.

[42] P.F. Nelson, S.M. Quigley, M.Y. Smith, Sources of atmospheric hydrocarbons in Sydney: a quantitative determination using a source reconciliation technique, Atmos. Environ. 17 (1983) 434–449.

[43] O.S. Walter, H.H. Robert, M.H. Heiko, W.W. Bernd, B. Luers-Jonger, Organic emission profile for a light duty diesel vehicle, Atmos. Environ. 33 (1999) 797–805.

[44] J.F. Muller, Geographical distribution and seasonal variation of surface emission and deposition velocities of trace gases, J. Geophys. Res. 97 (1992) 3787–3804.

[45] B. Zielinsk, J. Sagebiel, G. Harshfield, R. Pasek, Volatile organic compound measurements in the California/Mexico border region during SCOS97, Sci. Total Environ. 276 (2001) 19–31.

[46] C. Tai-Yih, I.J. Simpson, D.R. Blake, F.S. Rowland, Impact of leakage of Liquefied Petroleum Gas (LPG) on Santiago Air Quality, Geophys. Res. Lett. 28 (11) (2001) 2193–2196.

[47] K. Sexton, H.H. Westberg, Ambient air measurements of petroleum refinery emissions, J. Air Pollut. Control Assoc. 29 (1979) 1149–1152.

[48] K. Sexton, H.H. Westberg, Photochemical ozone formation from petroleum refinery emissions, Atmos. Environ. 17 (1983) 467–475.

[49] E.M. Fujita, Z. Lu, J. Sagebiel, N.F. Robinson, J.G. Watson, VOC source apportionment for the Coastal Oxidant Assessment for Southeast Texas, Prepared for Texas Natural Resource Conservation Commission, Austin, TX, Desert Research Institute, Reno, NV, 1995.

[50] A.M. Kitto, M. Pirbazari, B.N. Badriyha, V. Ravindran, R. Tyner, C.E. Synolakis, Emissions of volatile and semi-volatile organic compounds and particulate matter from hot asphalts, Environ. Technol. 18 (1997) 121–138.

[51] Z. Guo, L.E. Sparks, B.A. Tichenor, J.C.S. Chang, Predicting the emissions of individual VOCs from petroleum-based indoor coatings, Atmos. Environ. 32 (1998) 231–238.

[52] Z. Guo, J.C.S. Chang, L.E. Sparks, R.C. Fortmann, Estimation of the rate of VOC emissions from solvent-based indoor coating materials based on product formulation, Atmos. Environ. 33 (1999) 1205–1216.

[53] R.A. Wadden, P.A. Scheff, J.E. Franke, L.M. Conroy, C.B. Keil, Determination of VOC emission rates and composition for offset printing, J. Air Waste Manage. Assoc. 45 (1995) 547–555.

[54] J. Brosseau, M. Heitz, Trace gas compound emissions from municipal landfill sanitary sites, Atmos. Environ. 28 (1994) 285–294.

[55] D. Kalman, Survey analysis of volatile organics released from plastic under thermal stress, Am. Ind. Hygiene Assoc. J. 47 (1986) 270–275.

[56] J.P. Gracia, M.S. Beyne, G. Mouvier, Emission of volatile organic compounds by coal fired power stations, Atmos. Environ. 26 (1992) 1589–1597.

[57] L.E. Booher, B. Janke, Air emission from petroleum hydrocarbon fires during controlled burning, Am. Ind. Hygiene Assoc. J. 58 (1997) 359–365.

[58] N.R. Passant, S.J. Richardson, R.P.J. Swannell, N. Gibson, M.J. Woodfield, J.P. Van der Lugt, Emission of volatile organic compounds (VOCs) from the food and drinking industries of the European community, Atmos. Environ. 27 (A) (1993) 2555–2566.

[59] T.M. Sack, D.H. Steele, K. Hammerstrom, J. Remmers, A survey of household products for volatile organic compounds, Atmos. Environ. 26 (A) (1992) 1063–1070.

[60] D.D. Parish, M. Trainee, V. Young, P.D. Golden, W.C. Kuster, B.J. Jabson, Internal consistency test for evaluation of measurements of anthropogenic hydrocarbons in the troposphere, J. Geophys. Res. 103 (D17) (1998) 22339–22359.

[61] D.R. Blake, D.F. Hurst, T.W. Smith Jr., W.J. Whipple, T.Y. Chen, N.J. Blake, F.S. Rowland, Summertime measurements of selected nonmethane hydrocarbons in Sub-Arctic during 1988 Arctic boundary layer expedition (ABLE 3A), J. Geophys. Res. 97 (D15) (1999) 16559–16588.

[62] F.C. Fehsnfeld, S.C. Liu, Impact of natural hydrocarbons on hydroxyl and peroxy radicals at remote site, J. Geophys. Res. 92 (1987) 11879.

[63] N.M. Donahue, R.G. Prinn, Nonmethane hydrocarbons chemistry in the remote marine boundary layer, J. Geophys. Res. 95 (1990) 18378–18411.

[64] P. Warnec, Chemistry of Natural Atmosphere, Academic Press Inc. (London) Ltd., 1988, pp. 223–277.

[65] A.J. Haggansmith, Chemistry and physiology of Los Angeles smog, Ind. Eng. Chem. Res. 44 (1952) 1342–1346.

[66] F.M. Bowman, J.H. Seinfeld, Ozone productivity of atmospheric organics, J. Geophys. Res. 99 (1994) 5309–5324.

[67] W.P.L. Carter, Development of ozone reactivity scale for volatile organic compounds, J. Air Waste Manage. Assoc. 44 (1994) 881–899.

[68] D.R. Blake, F.S. Rowland, Urban leakage of LPG and its impact on Mexico air quality, Science 269 (1995) 953–956.

[69] S.A. Montzka, M. Trainer, P.D. Goldan, W.C. Kuster, F.C. Fehsenfeld, Isoprene and its oxidation products, methyl vinyl ketone and methacrolein in the rural troposphere, J. Geophys. Res. 98 (1993) 1101–1111.

[70] D. Remier, W. Pos, P.J. Milne, C. Farmer, R. Zika, E. Apel, Observation of nonmethane hydrocarbons and oxygenated volatile organic compounds at rural site in Southeastern United State, J. Geophys. Res. 103 (D21) (1998) 28111–28128.

[71] R. Atkinson, Kinetics and mechanisms of the gas phase reaction of hydroxyl radical with organic compounds under atmospheric conditions, Chem. Rev. 86 (1986) 69.

[72] M. Trainer, E.J. Williams, D.D. Parrish, M.P. Bhur, E.J. Allwine, H.H. Westberg, Models and observations of the impact of natural hydrocarbons on rural ozone, Nature 329 (1987) 705.

[73] D.J. Jacob, S.C. Wofsy, Photochemistry of biogenic emission over the Amazon forests, J. Geophys. Res. 90 (1985) 2380.

[74] W.L. Chameids, R.W. Lindsay, J. Richerdson, C.S. Kiang, The role of biogenic hydrocarbons in urban photochemical smog: Atlanta a case study, Science 241 (1988) 1473–1475.

[75] W.L. Chameids, R.J. Cicerone, Effects of nonmethane hydrocarbons in the atmosphere, J. Geophys. Res. 83 (1978) 947–952.

[76] J.A. Logan, M.J. Panther, S.C. Wofsy, M.B. McElory, Tropospheric chemistry: a global perspective, J. Geophys. Res. 86 (1981) 7210–7254.

[77] B. Rappengluck, P. Fabian, Nonmethane hydrocarbons (NMHC) in the Greater Munich Area/Germany, Atmos. Environ. 33 (1999) 3843–3857.

[78] F.W. Lurmann, A.C. Lloyd, B. Nitta, Modelling potential ozone impacts from natural hydrocarbons—II. Hypothetical biogenic HC emission scenario modeling, Atmos. Environ. 18 (1983) 1951–1963.

[79] J. Rudolph, A. Khedim, D. Wagenbach, The season variation of light nonmethane hydrocarbons in the Atlantic Troposphere, J. Geophys. Res. 44 (1989) 13,039–13,044.

[80] J. Rudolph, D.H. Ehhalt, A. Tonnissen, Vertical profile of ethane and propane in the stratosphere, J. Geophys. Res. 86 (1981) 7267–7272.

[81] D.D. Parrish, M. Trainer, E.J. Williams, D.W. Fahey, G. Hubler, S. Eubank, Measurement of NO_x-O_3 photostationary state at Niwot Ridge, Colorado, J. Geophys. Res. 91 (1986) 5361–5370.

[82] E.C. Apel, J.G. Calvert, F.C. Fehsnfeld, The nonmethane hydrocarbons intercomparison experiment (NMHICE): Task 1 & 2, J. Geophys. Res. 99 (D8) (1994) 16651–16664.

[83] E.M. Fujita, J.G. Watson, K.L. Mangliano, Receptor model and emission inventory source apportionment of nonmethane organic gases in California's San Jonquin Valley and San Francisco Bay area, Atmos. Environ. 29 (1995) 3019–3055.

[84] R.A. Harley, M.P. Hannigan, G.R. Cass, Respeciation of organic gas emissions and the detection of excess unburned gasoline in the atmosphere, Environ. Sci. Technol. 26 (1992), pp. 2395–1408.

[85] E.M. Fujita, L. Sheetz, G. Harshfield, T. Hayes, B. Zielinska, Hydrocarbon source apportionment in Western Washington, Prepared for State of Washington, Dept. of Ecology, Lacy, DA, Desert Research Institute, Reno, NV, 1997.

[86] E.M. Fujita, Z. Lu, Hydrocarbon receptor modelling for the 1996 Phoenix Ozone study, Prepared from ENSR corporation, Camarillo, CA, Desert Research Institute, Reno, NV, 1998.

[87] P.A. Scheff, R.A. Wadden, Receptor modelling of volatile organic compounds: emission inventory and validation, Environ. Sci. Technol. 27 (1993) 617–625.

[88] D.M. Kenski, R.A. Wadden, P.A. Scheff, W.A. Lenneman, Receptor modelling to VOC emission inventory validation, J. Environ. Eng. 121 (1995) 483–491.

[89] J.C. Chung, S.V. Hannan, N.K. Wilson, Development of ozone precursor relationships using VOC receptor modeling, Atmos. Environ. 30 (1996) 3167–3179.

[90] E.M. Fujita, Z. Lu, Analysis of data from 1995 NARSTO-Northeast study, vol. III, Chemical mass balance receptor modeling, Prepared for Coordination Research Council, Atlanta, GA, Desert Research Institute, Reno, NV, 1998.

[91] G. Fell, B. Jah, in: F. Guenter, J. Bward (Eds.), The Chemistry of Pollution, Wiley and Sons Ltd., 1987.

[92] K.R. Darnall, A.C. Llyod, A.M. Winer Jr., J.N. Pitts, Reactivity scale for atmospheric hydrocarbons based on reaction with hydroxyl radical, Environ. Sci. Technol. 10 (1976) 692–696.

[93] R. Atkinson, Gas-phase tropospheric chemistry of organic compounds, J. Phys. Chem. Ref. Data Monoger. 2 (1994) 1–216.

[94] R.L. Seila, W.A. Lonnema, S.A. Meeks, Project Summary: Determination of C2–C12 Ambient Air Hydrocarbons in 39 U.S. cities from 1984 through 1986, EPA. Rep., EPA/600/53-89/1058, Environ. Prot. Agency, Washington, DC, 1989.

[95] R. Fedele, I.E. Galbally, N. Porter, A. Weeks, Biogenic VOC emissions from fresh leaf mulch and wood chips of *Grevillea robusta* (Australian Silky Oak), Atmos. Environ. 41 (38) (2007) 8736–8746.

[96] D.D. Riemer, P.J. Milne, R.G. Zika, W.H. Pos, Photoproduction of nonmethane hydrocarbons (NMHCs) in sea water, Mar. Chem. 71 (3–4) (2000) 177–198.

[97] W.J. Broadgate, G. Malin, C. Kupper, A. Thompson, P.S. Liss, Isoprene and other nonmethane hydrocarbons from seaweeds: a source of reactive hydrocarbons to the atmosphere, Mar. Chem. 88 (1–2) (2004) 61–73.

[98] P. Crill, K. Backstrand, T.R. Christensen, M. Mastepanov, Growing season hydrocarbon flux dynamics at a subarctic mire, northern Sweden, Geophys. Res. Abstracts 9 (2007) 11450.

[99] B. Barletta, S. Meinardi, F.S. Rowland, Chuen-Yu Chan, X.g. Wang, S. Zou, Lo Yin Chan, D.R. Blake, Volatile organic compounds in 43 Chinese cities, Atmos. Environ. 39 (32) (2005) 5979–5990.

[100] S. Matthes, V. Grewe, R. Sausen, G.J. Roelofs, Global impact of road traffic emission on chemical composition and climate, Geophys. Res. Abstracts 6 (2004) 00335.

[101] J. Duan, J. Tan, L. Yang, S. Wu, J. Hao, Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing, Atmos. Res. Vol. 88 (1) (2008) 25–35.

[102] A. Guenther, C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, P. Zimmerman, A global model of nature volatile organic compound emissions, J. Geophys. Res. 100 (1995) 8873–8892.

[103] P.J. Crutzen, Overview of tropospheric chemistry: developments during the past quarter century and a look ahead, Faraday Discuss. 100 (1995) 1–21.

[104] F. Fehsenfeld, J. Calvert, R. Fall, P. Goldan, A. Guenther, C.N. Hewitt, B. Lamb, S. Liu, M. Trainer, H. Westberg, P. Zimmerman, Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, Global Biogeochem. Cycles 6 (1992) 389–430.

[105] S.A. Montzka, M. Trainer, P. Goldan, W.C. Kuster, F. Fehsenfeld, Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere, J. Geophys. Res. 98 (1993) 1101–1111.

[106] T. Kunhikrishnan, Mark G. Lawrence, Rolf von Kuhlmann, Mark O. Wenig, Willem A.H. Asman, Andreas Richter, John P. Burrows, Regional NO_x emission strength for the Indian subcontinent and the impact of emissions from India and neighboring countries on regional O_3 chemistry, J. Geophys. Res. 111 (2006) 15301, doi:10.1029/2005JD006036.

[107] S. Lal, L.K. Sahu, S. Venkataramani, Impact of transport from the surrounding continental regions on the distributions of ozone and related trace gases over the Bay of Bengal during February 2003, J. Geophys. Res. 112 (2007) D14302, doi:10.1029/2006JD008023.

[108] L. Sahu, S. Lal, Characterization of C_2–C_4 NMHCs distributions at a high altitude tropical site in India, J. Atmos. Chem. 54 (2) (2006) 161–175.

[109] Prabhat K. Gupta, Shvraj Sahai, Nahar Singh, C.K. Dixit, D.P. Singh, C. Sharma, M.K. Tiwari, Raj K. Gupta, S.C. Garg, Residue burning in rice–wheat cropping system: causes and implications, Curr. Sci. 87 (12) (2004) 1713–1717.

[110] J. Moriizumi, K. Nagamine, T. Lida, Y. Ikebe, Estimation of area flux of atmospheric methane in urban area of Nagoya, Japan, inferred from atmospheric radon-222 data, Atmos. Environ. 30 (10–11) (1996) 1543–1549.

[111] K. Sudo, M. Takahashi, Jun-ichi Kurokawa, H. Akimoto, CHASER: a global model of the troposphere, J. Geophys. Res. 107 (D17) (2002) 4339.

[112] D.E. Shallcross, P.S. Monks, New directions: a role for isoprene in biosphereclimate-chemistry feedbacks, Atmos. Environ. 34 (2000) 1659–1660.

[113] J.D. Fuentes, B.P. Hayden, M. Garstang, M. Lerdau, D. Fitzjarrald, D.D. Baldocchi, R. Monson, B. Lamb, C. Geron, New directions: VOCs and biosphere–atmosphere feedbacks, Atmos. Environ. 35 (2001) 189–191.

[114] M. Winer, J. Arey, R. Atkinson, S.M. Aschmann, W.D. Long, C.L. Morrison, D.M. Olszyk, Emission rates of organics from vegetation in California's Central Valley, Atmos. Environ. 26A (1992) 2647–2660.

[115] Michael G. Sanderson, Hadely Centre Technical Note on Emission of Isoprene, Monoterpenes, Ethene and Propene by Vegetation, 2002.

[116] Y. Rastigejev, M.P. Brenner, D.J. Jacob, Spatial reduction algorithm for atmospheric chemical transport models, Proc. Natl. Acad. Sci. (PANS) U.S.A. 104 (35) (2007) 13875–13880.

[117] K.C. Clemitshaw, A review of instrumentation and measurement techniques for ground based and airborne field studies of Gas phase tropospheric chemistry, Crit. Rev. Environ. Sci. Technol. 34 (1) (2004) 1–108.

[118] J.R. Hopkins, A.C. Lewis, K.A. Read, A two-column method for long term monitoring of non-methane hydrocarbons (NMHCs) and oxygenated volatile organic compounds (o-VOCs), J. Environ. Monit. 5 (2003) 8–13.

[119] B.C. Sive, Y. Zhou, D. Troop, Y. Wang, W.C. Little, O.W. Wingenter, R.S. Russo, R.K. Varner, R. Talbot, Development of a cryogen-free concentration system for measurements of volatile organic compounds, Anal. Chem. 77 (2005) 6989–6998.