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A Review on the Atmospheric Non Methane Hydrocarbons (NMHCs) Study in India

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Abstract

This study present extensive review on the atmospheric non methane hydrocarbons for the monitoring technology, source profile, and variability studies which have been done by various researchers at different research and development institutions all over the India. Most of the studies have reported that the concentration level in the urban environment is elevated at alarming level due to vehicular emission, refinery operation, secondary industrial process, LPG leakage and biomass burning. The elevated ambient concentration of NMHCs in an urban environment has a significant impact on climate change and human health. NMHCs levels are to be removed and limit the emission by using newer technology under specific industrial and practical conditions in the present time. This review aims at a summarizing discussion on the entire areas which come underneath the umbrella of NMHCs technologies and helpful to the future researchers and those findings will be helped to the formulate policies and implement for the enhancement of air quality in India.

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Introduction

In the present scenario urban air pollution becomes a prime concern across the world in both developed and developing countries. Urban sprawl, industrialization and extensive transportation in the urban areas have resulted the poor air quality that affects the both human health and the surrounding environment. Atmospheric nonmethane hydrocarbons (NMHCs) are major groups of air pollutants in the urban atmosphere[1]. NMHCs are a group of natural and anthropogenic aliphatic, aromatic and alkyl species usually having low molecular weight containing only hydrogen and carbon atoms ranging from C_2-C_{12} [2]. Methane is excluded from this group of chemicals due to its large emissions, low reactivity with OH radical as compared to NMHCs and its direct role in climate change[3]. The concentration of these compounds in the ambient atmosphere assumes special significance on account of the critical role they play in the atmospheric photochemistry and the adverse impacts they have on human health. They are highly reactive species because of their strong tendency to get oxidized by the OH radical and ozone present in the atmosphere [3].Thus NMHCs

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are acting as a key precursor of tropospheric O_3 formation through oxidation of OH radical and with nitrogen oxide (NOx)[4,5]. NMHCs sources and their environmental impacts and health effects has been describes in detail below.

Natural Source of NMHC

The biogenic sources of NMHCs are mainly emitted from vegetation[6] predominantly in the form isoprene, monoterpenes and sesquiterpenes[7]. Other sources of biogenic NMHCs include oceanic emissions[3] and those from microbial production[8]. According to Atkinson [9]biogenic volatile organic compounds (BVOCs) are almost ten times higher than the anthropogenic sources on the global scale. It is estimated that about 900-1115 TgC/yr of BVOC are emitted all over the world[8] shown in Table 1.

Anthropogenic Sources of NMHCs

In the current scenario, many scientists have been studies on the anthropogenic sources of NMHCs across the world and they have critically examined and which has been mentioned below. Kansal [11] has reviewd the motor vehicular exhausts, solvent evaporation, petro-chemical industries, Natural/LPG gas leakage are amongst the main sources of NMHCs. Wang *et al.,*[12] reported that motor vehicular exhausts and leakage of liquefied petroleum gas (LPG) are the primary sources of NMHCs in Taipei city in Taiwan. The types of emission mostly depend on the nature of the fuel and its combustion. Lewis *et al.,*[13] reported that incomplete combustion is usually the main cause of individual anthropogenic NMHCs emitted from petrol and diesel engines, stationary power generation plants, biomass burning and coal burning for cooking as well as heating. Pandit *et al.*[14] stated that the ambient air NMHCs concentration is mostly influenced by vehicle age/types, fuel used type, vehicle speed, and flow rate along with other environmental conditions. Apart from these, industrial processes are another major contributor of anthropogenic NMHCs emissions. On the global scale about 17-27 TgC/yr of NMHCs emission is released into the atmosphere due to industrial usage of solvents and household products such as paints,

Table 1: Quantitative estimation of global emissions of NMHCs[10,11]

Sources	Natural sources	Emission (tg-C/yr)
Oceanic production		
	1.Light hydrocarbons	5-10
	2. C_9-C_{28} higher hydrocarbons	1-26
Terrestrial emission		
	1.Microbial production	06
	2.Vegetation emission	1140
Total emissions		1183

Table 2: Quantitative estimation of global emissions of NMHCs [10,11]

Sources		Emission (tg-C/yr)
Anthropogenic sources		
	Vehicular exhausts	22
	Industrial processing, including natural gas production	17
	Organic solvents	15
	Biomass burning, forest fire	45
	Stationary sources	04
Total emissions		103

adhesives, coating and varnishes[10,11] shown in Table 2. NMHCs such as ethane, ethylene, acetylene, propane, propylene, n-butane, 1,3-butadiene, i-butane, cis-2-butene, trans-2-butene, pentane, i-pentane, cis-2-pentene, n-hexane, n-heptanes, benzene, toluene, m/p-xylene, o-xylene are major compounds in the atmosphere emitted from the mobile sources[10,11,15]. NMHCs emissions from landfilling are relatively low and in the environment their contributions have accounted less than 1 %. The quantitative estimation of global emissions of NMHCs from the various sources[10] and are reviewd by Kansal[11] shown in Table 2.

In the context of Asian cities, Streets *et al.,*[16] based on chemical reactivity and functional groups of NMHCs emissions, showed that alkanes accounted 27%, alkenes 22%, ethyne 5%, aromatics 17%, aldehydes and ketones 9%, halocarbons and other organic compounds 20% of total NMVOC emissions in all over Asia. The above disccusions have mentioned that NMHCs emissions have great impacts on the urban environment and percentage level of NMHCs in the urban ambient air. Thus the measurement, identification of their source profile and health risk exposure associated with NMHCs compounds should have well documented to undertake a proper planning, regulation and implementation of metropolis establishment by the government authorities.

Environmental Impact of NMHC

The impact of NMHCs on the environment may broadly be classified in terms of their role in atmospheric photochemistry and their adverse impacts on health of living organisms. The following sections specifically discuss their role in the photochemical ozone formation, occurrence of photochemical smog, including peroxy acyl nitrate (PAN) formation, and their impacts on vegetation and human health.

Role in Photochemical Ozone Formation

The basic process of atmospheric ozone formation involves the photolysis of NO_2 at wavelengths < 424 nm[17] and consists of the following reactions:

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

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

Where, M represents N_2 or O_2 or another third body which absorbs the excess energy to stabilize the ozone molecule. Liu *et al.,*[18] established the importance of NMHCs chemistry in ozone production in the rural atmospher. They presented a simplified scheme of reactions to illustrate the role of NMHCs in ozone formation in the following manner:

$$NMHC + OH + O_2 \rightarrow RO_2$$

$$RO_2 + NO + O_2 \rightarrow NO_2 + HO_2 + CARB$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$2(NO_2 + h\upsilon + O_2 \rightarrow NO + O_3)$$

$$\text{Net:} \quad NMHC + 4O_2 + h\upsilon \rightarrow 2O_3 + CARB$$

Where, R denotes the hydrocarbon radical and CARB stands for carbonyl compounds.

The above reaction scheme shows how two molecules are formed for every molecule of NMHC oxidized. Liu *et al.,*[18] further state that carbonyl compounds produced may result in producing still more ozone, through the production of hydrogen radicals. The tropospheric ozone formation starts with the oxidation of NMHCs by the hydroxyl radicals (OH) to result in the production of hydroperoxy radical (HO_2) and organo-peroxy (RO_2) radicals. The role of hydroxyl radical (OH) during ozone photochemistry in the troposphere is an important one which controls the oxidation of non-methane hydrocarbons, photochemical ozone production and secondary aerosol formation in the atmosphere[19]. The hydroperoxy radical (HO_2) and organo-peroxy (RO_2) radicals help to oxidise NO to NO_2 through various steps reaction to produce two molecules of NO_2 and finally which has been produced two molecules of ozone (O_3).

Role in the Formation of Peroxyacyl Nitrate

Peroxyacyl nitrates (PANs) are secondary photochemical atmospheric pollutants discovered in the 1950s as an important constituent of photochemical smog[17]. Their general chemical formula is given by: $RC(O)OONO_2$, where RC(O)OO stands for the peroxy acyl group. The first compound in this series is the peroxy acetyl nitrate i.e. $CH_3C(O)OONO_2$, also called PAN. Peroxyacetyl nitrate does not readily photodissociate in the troposphere and is relatively water insoluble[17]. For this reason, it behaves as a relatively stable species in the troposphere. PAN formation in the atmosphere takes place due to the oxidation of the carbonyl compounds such as the aldehydes by the hydroxyl radicals present in the atmosphere through the following sequence of reactions:

$$RCHO + OH \rightarrow RCO^{\cdot} + H_2O$$

$$RCO^{\cdot} + O_2 + M \rightarrow RC(O)OO^{\cdot} + M$$

The acyl peroxy radical formed above, then combines with NO2 to form PAN.

$$RC(O)OO + NO_2 + M \rightarrow RC(O)OONO_2 + M$$

NMHCs through their reactions described above which act as a source of carbonyl compounds such as aldehydes thus contributing to the formation of PAN. The primary loss of PAN in the atmosphere takes place through thermal dissociation, which is a high temperature dependent reaction:

$$RC(O)OONO_2 + M \rightarrow RC(O)OO^{\cdot} + NO_2 + M$$

At temperatures as low as in the upper troposphere, PAN lifetimes may be many months, making it a reservoir molecule of NO_2, thus helping in the long range transport of NO_2 [17]. PAN is a powerful oxidant and acts as phytotoxic in the presence of high concentration[20]. PAN is associated with the potential health risk to human beings. It is a strong eye irritant[21],[20] and also cited as a possible causative agent for the skin cancer [22].

NMHC Effects on Vegetation

As discussed above, NMHCs play a significant role in the formation of tropospheric ozone and PAN. But these compounds are known to cause adverse impacts on vegetation. Plant protection mechanisms in response to ozone exposure include reducing stomatal conductance or detoxification in sensitive tissues, but these mechanisms lead to a reduction in photosynthesis, increased senescence and damage to reproductive processes[17]. Studies have shown that elevated ozone levels can cause reduction in crop yield, tree growth (and thus its ability to sequester carbon), and may alter the species composition of a place[23]. In the Indian context, Sharma *et al.,*[24] reported reduction in the nutrient content of some vegetable crops. Further, negative association between stem growth and ozone exposure has been reported by Braun *et al.,*[25]. Van Dingenen *et al.,*[26] reported that the crop yields losses/decreases due to exposure of ozone.

NMHC Effects on Human Health

Exposure of NMHCs in human beings occurs through different pathways such as inhalation, ingestion and dermal, but inhalation and ingestion are the primary pathways through which human exposure occurs[27]. Inhalation being a major pathway of human exposure, a number of studies have reported adverse health impacts of hydrocarbons through inhalation. Glass *et al.,*[28] reported an excess risk of leukemia due to chronic exposure to relatively low levels of aromatic NMHCs like benzene. Kirkeleit *et al.,*[25] investigated health risk and suggested that benzene exposure could lead to increased risk of multiple myeloma among the workers in petroleum industry. White *et al.,*[29] showed an increased prevalence of asthma symptoms among school children who were living nearby petrochemical processing plant in Cape Town, South Africa. Several studies till date have reported death due to exposure to aliphatic hydrocarbons such as propane and butane[30]. NMHCs compounds such as benzene is known to cause several health impacts such as acute and chronic nonlymphocytic leukemia, chronic lymphocytic leukemia, anemia and other blood disorders as well as adverse impacts on the immune system[31,32] while exposure to xylene may lead to eye, nose and throat irritation, breathing problems and damage lung function as well as nervous system. Researchers also reported that benzene and 1,3-butadiene are considered to be highly toxic and carcinogenic to humans[31,33]. Nielsen *et al.,*[34] investigated the impacts of higher aliphatic hydrocarbons such as nonane exposure on rats and reported that nonane is causes damage of nervous system and with higher dosage even leading to death. Other NMHCs reported for adverse impact on human health are ethylene, propylene and hexane[35]. In addition to directly affecting the human health, NMHCs may indirectly influence human health through their derivatives and their role in ozone and PAN formation.

Indian Regulations Related To Hydrocarbons

India is considered as a developing country and they have huge pressure from both domestic and international forums to monitoring the emissions of NMHCs from various sources as we have mentioned in literature, which may help to formulate rules and regulation for controlling the level of NMHCs in the urban ambient air. Although we look into the global scenario, various researchers are going on NMHCs by researchers, organizations have discussed in the above, while no one have established the standard for NMHCs, even EPA is also not proposed any standard for ambient NMHCs. Despite the fact that World Health Organization and United State Occupational Safety and Health Administration (OSHA) have set up with a few guidelines for the NMHCs compounds but only suggestive. This is not essential for government to follow it [36].

In the Indian context monitoring and source profile identification of NMHCs and their control started late as compared to developed countries. These activities are mostly done in the academic sector as research and development programme. However, our review is to be reveals various research work published for an ambient air NMHCs.

We come across to past time of environmental regulation then we observed that India is the first country, they have a constitutional provision for the protection and enhancement of the environment. According to Article 48-A of the Indian constitution, state has directed to make intended for the protection and enhancement of the environment and for conservation the forest and wildlife of India. Another milestone prerequisite has inserted for the safeguard of the environment, as Artcles 51-A(g) of the Indian constitution and state every citizen of India has their Fundamental duty to protect and improve the natural environment, including rivers, lakes, forests and wildlife and to have compassion for living creature has given in CPCB Pollution Control Law series 2010[37]. Although environmental laws have been started in India since 1974, as a Water (Prevention and Control of Pollution) Act 1974, just after the Stockholm Conference on Human Environment in 1972. It's become a uniform law throughout the country for the broader environmental problems which has been threatening to the health and safety of our people and our flora and fauna as well. After the Water Act, the Air (Prevention and Control of Pollution) Act was enacted in the year of 1981 and mission of implementation of this legislation was again assigned to the same regulatory agencies made under the Water Act, 1974. Thus, Water (Prevention and Control of Pollution) Act, 1974 is known for the mother of all environmental laws in India.

General Regulations on Some of NMHC Compound

In view of the above discussion, the Central Pollution Control Board (CPCB) is a regulatory body of government of India which regulated on NMHC compounds such as benzene and other compound benzo (a)Pyrene which included in the National Ambient Air Quality Standard http://cpcb.nic.in/upload/Publications/Publication_514_air quality status 2009. pdf[38]. However, the standard value of benzene and benzo(a) Pyrene is to be 5 µg/m^3 and 1 µg/m^3 for Industrial residential, rural and ecologically sensitive area. Due to lack of epidemiological and toxicological evidence of NMHCs and VOCs compounds on the living beings except benzene and benzo (a) Pyrene not included under national standard. Some other decision has been imposed by the government of India for the reduction of air pollution, especially emitted from the vehicles and vehicular emission norm has been set up in 1991 as a Bharat Stage (BS) and the combine emission values of hydrocarbon and NOx was 0.35 and 0.18 g/km for the BS III and IV car passenger respectively, while the value 1.5 and 1.0 g/km for two and three wheelers. On the other hand 1.1, 1.6 and 0.96 g/km for BS II, III and IV respectively, to the diesel vehicles. Currently BS VI has been proposed for the entire country. The diesel engine generator sets are emitting more hydrocarbons and NOx and their impacts on urban air quality is more than that of rural air quality. Therefore, the emission limits of NMHC and NOx for the diesel engines greater than 800KW has been set up as 150 mg/N-m3; 1100 ppmv, 100 mg/N-m3; 970 ppmv and 100 mg/N-m3;710 ppmv in the year June 2003; July 2003 to June 2006 and July 2005, respectively.

Monitoring and Measurement of NMHC

Due to their very low concentrations in the atmosphere, NMHCs are considered as trace gas species and are generally measured in ppb, except in polluted atmosphere where their concentrations may even be detected in ppm[7]. Thus for the trapping of these compounds to the researchers' interest using highly sophisticated instruments, i.e., Gas chromatograph (GC) which is coupled with flame ionization detector (FID) and analysis protocol depending upon types of hydrocarbons have chosen by the researchers. In general various approaches are being followed for the sampling of NMHCs compounds. These approaches are may be active, passive and whole air sampling as per sampling devices accepted across the World.Generally, active sampling needs air flow control pumping sampler for the sampling period and in which air passes through the adsorbent for the adsorption tubes at the monitoring site. Passive sampling is done through the diffusion process of pollutant, the air is automatically adsorbed to the adsorbent tube. Although whole air sampling is done through both Tedlar bags and Summa Canister (Polished Stainless Steel canister) which is most commonly used by researchers all over the world. In general, research articles have cited that activated charcoal for the higher NMHCs and aromatic NMHCs while Tedlar bags and Summa Canister for the lower NMHCs, due to its volatility kept into their natural environment i.e., standard temperature pressure (STP). However, the selected aromatic NMHCs were analyzed by USEPA recommended method TO-14 or TO-17 and lower NMHCs there is no any specific recommended guideline by USEPA and their further analysis using GC-MS or GC-FID.

Study of NMHC Establish In India

In the Indian context, studies on monitoring, source identification of NMHCs are relatively few in number and it was started since mid 1990. In the Indian region very few studies have also been reported on the measurement of ozone and their precursors such as NMHCs. The prominent studies which have reported the presence of NMHCs in the ambient air in India.

For examples., Pandit and Rao[39] reported the C_2-C_5 hydrocarbons (HCs) were emitted from the petroleum driving auto-exhaust at the Deonar, Bombay. They also evaluated emission of C_2-C_5 HCs from the auto exhaust for contributing to the urban atmosphere in Bombay and found that 10 % of C_2-C_5 HCs was responsible for auto exhausts while only 1.2% responsible for isobutane.

Rao *et al.,*[39] measured NMHCs at industrial sites of Bombay, India, They reported the concentration of C_6-C_{10} NMHCs were higher that the C_2-C_5 at two industrial sites located in Thane areas of Bombay. Although, NMHCs C_2-C_5 were found higher in the refinery region near Mahul, Bombay.

The seasonal variations of ground level ozone and their precursor over the urban region of India has been studied by Lal *et al.,*[40]. Sahu and Lal[41] studied the distribution of C_2-C_5 NMHCs and other trace gases at a tropical urban site of Ahmedabad, India. They found the seasonal and diurnal variations in concentration levels of these NMHCs species have more winter season as compared to the summer months. It is due to changes in transportation pattern, boundary layer height and OH radical concentrations. The natural gas emission and liquid petroleum gas leakage were also be contributed to elevated levels of ethane and propane. They suggested that vehicular exhaust played a major role in the observed distribution of CO, ethane, propene and acetylene while contributions from biofuel and biomass burning were not found to be significant.

The characterization of nonmethane hydrocarbons C_2-C_4 has done by Sahu *et al.,*[41]at the high altitudinal site of India. They have estimated the annual mean mixing ratios of NMHCs species like ethane (1.22±0.58),ethene(0.34±0.24), propane(0. 46±0.20),propene(0.17±0.14), i-butane(0.21±0.18), acetylene(0.41±0.43) and n-(0.41±0.43) ppbv.

Pukarait *et al.,*[42] repeated the role of NMHCs for the formation of surface ozone at two sites in north east coast of India.They observed that the major sources of NMHCs compounds were industries, oil refineries, thermal power plant and heavy vehicular emissions.

Pandit *et al.,*[14] used principal component analysis (PCA) for source apportionment of atmospheric NMHCs in Mumbai, India. They identified 17 light NMHCs and their concentration was higher in the winter and low in the summer season. They identified five possible sources after factor analysis for NMHCs emissions viz. vehicular exhausts, refinery, petrochemical industries, paint solvent and polymer manufacturing industries contributing 33%, 21%, 15 %, 11% and 8% to the total variation respectively.

Sahu *et al.,*[43] studied seasonal variations in the latitudinal distributions of NMHCs over Bay of Bengal(BOB) and found the mixing ratios of major NMHCs significantly higher during the winter monsoon as compared to summer monsoon. In both season the distributions of NMHCs showed north-south decreasing gradients clearly over BOB. In summer season the latitudinal rising NMHCs mixing ratio were caused via the transport of pollutants from peninsular India to the BOB northern region while during the winter monsoon occurred owing to the dilution and photochemical loss.

Lal *et al.,*[43] measured light NMHCs (C_2-C_5) at two sites (Hissar and Kanpur) in the Indo-Gangetic Plain. They calculated propylene (propene) equivalents of NMHCs for their roles in ozone (O_3) photochemistry. On the basis of correlations among different species, they suggested that emissions of NMHCs were mainly from biomass, biofuel burning and fossil fuel combustion. They also compared with those results estimated over Ahmedabad, and found the total amount of these NMHCs was high in Ahmedabad and least at the Hissar while the total propylene-equivalent was the highest at Hissar and the lowest in Ahmedabad. Further, they reported that propene and ethene were the major component of NMHCs measured at Hissar & Kannur (72–77%) while the contributions of propene and ethene were only about 47% in case of Ahmedabad.

Nishanth *et al.,*[44] measured the TNMHCs and trace gages concentration in rural coastal sites Kannur,India. They estimated the maximum, minimum and mean concentrations of TNMHCs (25.45 ±6.56), (13.84 ±4.31) and (19.23 ±5.56)ppbv observational site.

Pandey *et al.,*[45] studied VOCs and NMHCs emissions from the biomass burning and their ozone forming potential (OFP) over India, using global biomass emission data base period from 1997 to 2009. They estimated annual emissions NMHCs (100-470 Gg yr^{-1}) and other OVOCs (46-211 Gg yr^{-1}). They found the agriculture residue burning was the major sources among the several biomass burning sources and isoprene is accounted 80% of total NMHCs.

Sarangi *et al.,*[46] had done observational of light nonmethane hydrocarbons (C_2-C_5) at high altitude site Nainital in the central Himalayas. They observed that the concentration of NMHCs was higher in winter and late autumn while lower during summer and monsoon. They also calculated the annual mixing ratios of ethane (1.8±1.0), ethene(0.7±0.9),propane (0.6±0.8),propene(0.6±0.7),i-butane (0.6±0.7),n-butane(0.5±0.6), acetylene(1.0±0.8), and i-pentane (0.5±0.6) ppbv at the Nainital, India.

Kumar *et al.,*[15] studied on the source profile of NMHCs using Principal Component Analysis (PCA) in the Metro city of Delhi. They found most of the NMHC in the urban environment of Delhi, was emitted from vehicular exhaust (23%), polymer manufacturing industries (19%), refinery operation/ gas station(14%), flare emissions(13%), natural gas emissions (10%), secondary industrial process, including paints, body soaps and metal fabricator and processing (8%) and remaining 13% from an unidentified source.

Conclusion and Upcoming Scope

This extensive review has focussed on the measurement, monitoring, source profile analysis of NMHCs and their role in tropospheric ozone formation. Their concentration level in the urban environment is elevated at alarming level due to anthropogenic sources, vehicular emission, refinery operation, LPG leakage and biomass burning. Although at the global level the natural sources of NMHCs are higher than that of anthropogenic sources. NMHCs are a key precursor of tropospheric ozone formation in the presence of high quantity of NO and OH radicals in the atmosphere. Thus the higher concentrations of NMHCs are also responsible for more production of tropospheric ozone. This situation was found an entire region of India. In this manner, the growth of nation in term of industrialization and urbanization can be achieved with proper preventative measure in emission from vehicles, types/age of vehicles and fuel used associated consequences. The government authorities have to be taken stringent steps and revise a existing policies time to time and implements in the public domain such as change the fuel used for petrol or diesel to CNG especially in the metro city, use four stroke engine will emit low pollution. They should also provide the better facility of public transport. Furthermore car pooling, use of metro train, especially metro city, proper training and awareness programs, proper monitoring all these activities will be change the level of NMHCs in the atmosphere.

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