Indoor Air Quality of Public Places in Mumbai, India in Terms of Volatile Organic Compounds

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Received: 30 May 2006 /Accepted: 30 October 2006 / Published online: 8 February 2007 \circledcirc Springer Science + Business Media B.V. 2007

Abstract Indoor air quality at nine locations viz. food courts, restaurant, bar, conference room, office and theater, which can be classified as public places have been monitored for Volatile Organic Compounds (VOCs) content. Forty VOCs have been identified and one fourth of these are classified as Hazardous Air Pollutants. Levels of most VOCs are observed to be below the guideline values for public places and offices, as adopted by Hong Kong. Consumer goods are found to be predominant source of chlorinated VOCs in indoor air. Levels of benzene and carbon tetrachlorides were observed to be above the guideline values at all the locations. Effect of ozonisation on Total VOC concentrations have also been studied.

Keywords Indoor air pollution . VOC . Benzene . Ozonisation . Naphthalene . Mumbai

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1 Introduction

Indoor Air Quality (IAQ) in urban areas of India is fast deteriorating. As more than 80% of our time is spent indoors, IAQ is a major cause of concern in the modern concretized world. A rapid change in the urban lifestyle has given rise to a new genre of indoor air pollutants. Majority of these pollutants is linked to organic chemical contaminants termed as Volatile Organic Compounds (VOCs). VOCs are a wide range of hydrocarbons possessing a characteristic ability to vaporize at low temperatures also room temperature. In Indoor environment, these originate from various sources including paints, adhesives, solvents, pressed wood, combustion of cooking fuel, household pesticides, deodorizers and also tobacco smoking. Certain VOCs, e.g. benzene, toluene, ethylbenzene, have been classified in the USEPA Air Toxics Programme, due to their toxic effects on humans and environment. Toxicity in humans, range from acute symptoms to chronic conditions, affects all vital systems of human body (Atkinson [2000](#page-10-0); Kuran and Sojak [1996](#page-10-0)). Some VOCs are also known to have carcinogenic and teratogenic effects (HSDB [1993](#page-11-0); USEPA [1994](#page-11-0)). Thus, it is critical to manage the concentrations of VOCs in indoor air. Ozonisation units are often used to reduce VOCs in indoor and improve the air quality. Some scientific evidence show that, at concentrations that do not exceed public health standards, ozone has little or no effect on the removal of indoor air contaminants (Boeniger [1995](#page-10-0); Esswein and Boeniger [1994](#page-10-0); Shaughnessy et al. [1994](#page-11-0)) While there are few scientific studies, which support the claim that ozone effectively removes odors, Ozone was found to react readily with certain chemicals, including some chemicals that contribute to the smell of new carpet (Weschler et al. [1992a](#page-11-0); Zhang and Lioy [1994](#page-11-0)). Ozone is also believed to react with acrolein, one of the many odorous and irritating chemicals, found in secondhand tobacco smoke (USEPA [1995](#page-11-0)). For many chemicals, with which ozone does readily react, the reaction can form a variety of by products (Weschler et al. [1992b](#page-11-0); Weschler and Shields [1996](#page-11-0); Zhang and Lioy [1994](#page-11-0)).

The present study attempts to identify VOC levels at indoor locations of the public places when ozonisation units were in use and not in use. Levels of ozone were also monitored.

2 Study Area

Mumbai is located on the west coast of India on latitude 18.9°N and longitude 72.8°E. Mumbai is one of the largest metropolises of the world with a population of more than 12 million and which is expected to reach 14.4 million by 2011. Mumbai is the commercial capital of India housing many national and multinational companies. Over the last few years, Mumbai has seen an increase in the development of commercial estates in the form of Corporate Parks, Entertainment Malls etc. with highend public service utilities, which include among others central air conditioning, water coolers and food courts. Keeping this trend in mind, nine air-conditioned locations were selected, which basically fall into public place category, including offices, theatre hall, restaurant, bar rooms, food courts and conference rooms. Most of these were located in commercial zones, across various parts of the city. All these locations were using engineered ozonisation system during this study.

Mumbai has a tropical savanna climate with relative humidity ranging between 57 and 87% and annual average temperature of 25.3°C, with a maximum of 34.5°C in June and minimum of 14.3°C in January. Average annual precipitation is 2,078 mm, with 34% of total rainfall occurring in July. Prevailing wind directions are from west and northwest with west and southwest shifts during monsoon. Some easterly component is observed during winter.

3 Ozonisation Unit

Multi plate duct mounted ozone generators are used at these locations. The ozone generation is modulated using TVOC sensors/controller which ensures generation just adequate to oxidize the VOCs generated inside the space. The ozonisation unit uses automatic controllers to regulate ozone generation. It uses residual ozone monitor and has a 'High Ozone Cut-Out' device to deactivate ozone generator in the event of high ozone levels. Method of ozone production is by the principle of corona discharge, with multiple number of double-sided corona plates. Production density of ozone per unit surface area of corona surface is very low. Ozone is produced from supply air of the AHU/ fan. Air pressure over the corona surface does not exceed air pressure in the duct. The ozonization units, at all locations, were in the duct of air-conditioning system and thus the supply of air to it was a mixture of re-circulated indoor air and dilution air taken from outside to maintain carbon dioxide levels as per the guidelines of American Society of Heating Refrigeration and Air- conditioning Engineers (ASHRAE).

4 Method of Estimation

At all of the above mentioned locations air was sampled for a period of 4 h into cartridges containing absorbing media – Chromosorb[®] 106, using a low volume sampler. VOCs were estimated using USEPA TO-17 method (USEPA [1999](#page-11-0)).

Battery operated personal air sampler (model Staplex PST 3000 A) was used to sample air at the rate of 20 ml/min through an adsorption cartridge containing Chromosorb® 106. Uniform flow rate was maintained using a rotameter. The monitoring was carried out during peak occupancy hours. The cartridges were fabricated from stainless steel pipe (SS-316) having a length of 15 cm with an internal diameter of 4 mm and external diameter of 6 mm and with caps on both sides. Approximately 800 mg of preheated cooled Chromosorb® 106 was filled in the cartridge with glass wool plugs on either side of the sorption cartridge. Desorption from sorbent cartridge was carried out by heating at 200°C for 20 min. Two tubes were connected in series. When the concentration in the second tube was more than 5% of total concentration, that is sum of measured concentrations in both tubes, it was assumed that breakthrough had occurred. At none of the locations breakthrough was observed. As soon as the pump was turned off, the cartridges were removed, capped tightly and sealed in plastic bags. The tubes and blank cartridges were stored in refrigeration. Concentrations

 $({\cal J} = \text{VOC Identified};$ # = VOC Quantified; * = VOC Listed in USEPA Hazardous Air Pollutants List)

of VOCs in blank tubes were observed to be lower than $0.02 \mu g/m^3$.

Analysis was carried out on Varian make GC-MS subsequent to thermal desorption at 180°C. The column used was DB-624. The carrier gas used was Helium, with a flow rate of 1 l/min and a split ratio of 1:25. The GC oven temperature was programmed for 35°C and held for 2 min. The ion trap temperature was maintained at 125°C. The peaks obtained were identified using the NIST Database Library. First three abundances were matched to identify the peaks. Quantification was done by calibration with liquid

standards of VOC MIX-15 of Dr. Ehrenstorfer from Perkin Elmer.

Ozone was estimated using alkaline potassium iodide method recommended by American Public Health Association (APHA) Intersociety Committee (Methods of Air Sampling and Analysis – 2nd edition edited by Morris Katz [1989](#page-10-0)). Air was absorbed in 10% sodium hydroxide with a flow rate of 1 l/min, adjusted with the help of the rotameter for a period of 8 h. Yellow colour of iodine is developed on the addition of phosphoric–sulphamic acid, which was measured at 352 nm.

Fig. 1 Concentrations of VOCs at monitored indoor locations (concentration in μ g/m³)

5 Results and Discussions

As many as 40 VOCs were detected. One fourth of the total VOCs identified are classified as Hazardous Air Pollutants in USEPA Air toxic programme (Table [1](#page-2-0)). It is observed that carbon tetrachloride, methylene chloride, chloroform, trichloroethylene, benzene, toluene, ethyl benzene, xylenes and 1,3,5 trimethyl benzene have been identified in all the samples at all the locations. Concentrations of these VOCs are given in Fig. [1](#page-3-0). Table 2 gives the concentrations of the VOCs quantified using Ehrenstorfer standard VOC Mix 15. Time Weighted Average (TWA) Threshold Limit Values of (TLVs) these ubiquitous VOCs along with risk levels as given by World Health Organization (WHO) are given in Table [3](#page-5-0). Table [4](#page-5-0) presents indoor outdoor ratio (I/O) of these VOCs. Average concentrations of the VOCs in outdoor air are taken from Srivastava et al. [\(2004](#page-11-0)) and Srivastava [\(2004](#page-11-0)). It is observed that I/O for

chlorinated VOCs are greater than one while those for benzene, toluene, ethyl benzene, xylene and 135 trimethyl benzene are less than one. Presence of chlorinated VOCs in the indoor environment can be attributed mainly to the use of consumer products like paints, varnishes, aerosols, insecticides floor polishes etc. Some contribution may as well be from outdoor air with oceanic emissions and fuel burning emissions. However, high I/O ratio indicates predominant indoor sources of these VOCs. Trichloroethylene is used in paints, spot removers, carpet cleaning fluids, metal cleaners and varnishes [\(dhfs](#page-10-0) [Chemical Fact Sheet](#page-10-0)). Methylene chloride is also a constituent of paints and varnish thinners, cleaning solutions, degreasers, aerosols, pesticides fumigants, insecticides, refrigeration and air conditioning equipments [\(AFSCME Health and Safety Fact Sheet](#page-10-0)). Some consumer products like lacquers solvents, floor polishers, resins, gums, metal degreasers, dry cleaning fluid etc. contain carbon tetrachloride and chloroform

Table 2 Concentrations of VOCs at different indoor locations $(\mu g/m^3)$

VOCs	Office room	Food court A	Food court B	Food court C	Theater $\mathbf{1}$	Theater $\overline{2}$	Restaurant	Conference room	Bar floor
Benzene	44.92	7.44	5.43	1.65	27.44	30.95	2.58	113.89	27.18
Carbon tetrachloride	57.50	215.00	237.50	51.67	223.33	124.17	304.44	288.33	176.67
Chloroform	24.17	94.03	135.28	8.86	115.92	178.64	118.25	148.33	91.77
Methylene chloride	1,251.67	4,219.17	4,498.33	884.17	4,341.67	3,530.00	2,941.11	5,406.67	1,895.98
Benzene, (1-methylethyl)					0.01	0.01			0.01
Benzene, (1-methylpropyl)	0.01				0.01	0.01		0.02	
Benzene, 1,2,4-trimethyl	0.01	0.24	0.02		0.04	0.06			0.01
Benzene, 1,2-dichloro		0.24	0.13		0.24	0.10			0.06
Benzene, 1,3,5-trimethyl	0.10	0.06	0.16	0.08	0.30	0.30	0.04	0.06	0.09
Benzene, 1,3-dichloro					0.01	0.01			
Benzene, 1,3-dimethyl	0.04	0.06	0.08	0.03	0.17	0.29	0.03	0.14	0.16
Benzene, butyl		0.01		0.01	0.01	0.17			
Benzene, tert-butyl						0.02	0.00	0.00	
Ethane, 1,1,2-trichloro					0.05			0.03	
Ethane, 1,2-dibromo				0.02	0.02				0.01
Ethyl benzene	0.06	0.12	0.16	0.13	0.45	0.67	0.04	0.57	0.34
Naphthalene	0.02	0.01	0.07		0.05	0.04	0.07		0.02
p-Xylene	0.03	0.05	0.07	0.01	0.13	0.23	0.01	0.06	0.16
Toluene	0.82	0.88	0.37	0.42	0.76	3.35	0.22	3.61	2.60
Trichloroethylene	0.08	1.28	1.05	0.15	0.64	1.52	0.82	0.17	0.51
1-Propene, 3-chloro				0.02					
Benzene, (1,2-dimethoxyet)					0.25				
Benzene, 1,2,3-trichloro						0.02			
Benzene, 1-chloro-4-methy									0.02
Methane, bromodichloro			0.03						

VOCs	AICGH TWA $(\mu g/m^3)$	OSHA TWA $(\mu g/m^3)$	RFC	RFD
Trichloroethylene	0.269	0.054	Not established	Not established
Carbon tetrachloride	0.031	0.315	Group B2 carcinogen RFC not established	RFD Group B2 carcinogen 0.0007 mg/kg/day based on tetrious in rats
Chloroform	0.049	0.244	Group B2 carcinogen $REL - 35 \mu g/m^3$	Group B2 carcinogen 0.01 mg/kg/day
Benzene	0.002	0.003	No safe level Group A carcinogenic	No safe level Confirmed carcinogen effect on humans
Ethyl benzene	0.434	0.434	Group D carcinogen 1 mg/m ³	Group D carcinogen 1 E-1 $mg/kg/day$
p-Xylene	0.434	0.434	Group D carcinogen 0.1 mg/m ³	Group D carcinogen 0.2 mg/kg/day
Toluene	0.188	0.754	Group D carcinogen 0.4 mg/m^3	0.2 mg/kg/day
Benzene, 1,3,5-trimethyl	0.123	0.123		

Table 3 Threshold limit values and risk levels of some VOCs

RFC Provisional Reference concentration that is likely to be without appreciable risk of deleterious non cancer effects during a life time RFD Provisional Reference close

Group A Confirmed carcinogenic effect on humans by all routes of exposure

Group B2 Probable human carcinogenic

Group D Not classified as to human carcinogenicity

Source :

• USEPA 1994 Integrated Risk Information System (IRIS) online Office of Health and Environment Assessment, USEPA, Cincinnati, OH

• American Conference of Governmental Industrial Hygienists – www.acgih.org

• Occupational Safety and Health Administration – www.osha.gov

as solvents. [\(National Safety Counci](#page-10-0)l, Online Library, and Chronic Toxicity Summary, Batch 2A, December 2000).

I/O ratio for benzene, toluene, ethyl benzene, xylene and 1,3,5 trimethyl benzene are observed to be less than one, at most locations, except conference rooms and bar floor. Benzene, toluene, ethyl benzene, xylene and 1,3,5 trimethyl benzene are constituents of vehicular exhaust. The source of these pollutants is thus mainly outdoor air and to a some extent indoor tobacco smoking. (conference room and bar floor)

Comparison of observed indoor levels of VOCs, identified at all the locations, with the Indoor Air Quality guidelines objectives for office and public

Table 4 Indoor outdoor ratio of some VOCs

VOCs	Office	Food	Food	Food	Theater	Theater	Restaurant	Conference	Bar
	room	court A	court B	court C		2		room	floor
Trichloroethylene	3.8	63.8	52.5	7.5	32.0	75.8	41.1	8.6	25.5
Carbon tetrachloride	21.7	81.1	89.6	19.5	413.6	229.9	114.9	108.8	66.7
Chloroform	8.9	34.4	49.6	3.2	60.4	93.0	43.3	54.3	33.6
Methylene Chloride	248.8	838.8	894.3	175.8	727.2	591.3	584.7	1074.9	376.9
Benzene	0.9	0.2	0.1	0.0	0.2	0.2	0.1	2.5	2.8
Ethyl benzene	0.3	0.6	0.8	0.7	1.6	2.3	0.2	2.8	1.7
p-Xylene	0.0	0.1	0.1	0.0	0.8	1.4	0.0	0.1	0.2
Toluene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
Benzene, 1,3,5-trimethyl	0.1	0.1	0.2	0.1	0.5	0.5	0.1	0.1	0.1

Fig. 2 Comparison of concentrations of some VOCs with IAQ guidelines of Hong Kong, 2003

Fig. 3 Percentage reduction of TVOC concentration on ozonisation at monitored indoor locations

Bar floor		Concentration $(\mu g/m^3)$		Percent $(\%)$ reduction
Sr. No	Compound name	Without ozonization	With ozonization	
1	Chloroform	91.772	62.756	32
2	Benzene	27.180	13.950	49
3	Trichloroethylene	0.510	0.180	65
4	Toluene	2.600	0.728	72
5	Ethane, 1,2-dibromo-	0.008	0.007	13
6	Ethylbenzene	0.341	0.223	35
7	Benzene, 1,3-dimethyl-	0.156	0.089	43
8	p-Xylene	0.163	0.039	76
9	Benzene, (1-methylethyl)-	0.005	0.003	34
9	Benzene, 1,2,4-trimethyl-	0.012	0.011	8
10	Benzene, 1-chloro-4-methyl	0.016	0.012	22
11	Benzene, 1,3,5-trimethyl-	0.089	0.026	70
12	Benzene, 1,2-dichloro-	0.060	0.039	35
13	Naphthalene	0.020	0.074	-270
14	Carbon tetrachloride	176.667	138.333	22
15	Methylene chloride	2,162.778	1,895.980	14

Table 5 Concentrations of VOCs and their percentage reduction at bar

places as adopted by Hong Kong Government, shows (Fig. [2](#page-6-0)) that levels of most VOC are well within the limits. However, concentrations of chloroform were found to exceed at Theater 1 and benzene levels exceeded, at almost all locations. Carbon tetrachloride levels were also found to exceed at almost all the locations monitored.

Figure [3](#page-6-0) shows percentage reduction in the Total VOC concentration on ozonisation at different locations. Overall reduction in TVOC is achieved up to 89%, with a maximum reduction observed at Food Court 'B' & restaurant. Negative percentage reduction is observed at Bar indicating thereby the rate of destruction of pollutants (VOCs) is lower as compared

Fig. 4 Concentration of naphthalene at monitored indoor location with percentage increase on ozonisation

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	Methylene chloride		Benzene		14 1,3,5-Trimethyl benzene
າ	3 Methyl Pentane	8	Trichloroethylene		15 t-Butylbenzene
3	Chloroform	9	Toluene	16	Undecane
Δ	n-Pentane	10	Ethylbenzene		Naphtalene
5	Cyclohexane		m-Xylene		15 t-Butvibenzene
6	Carbon tetrachloride	12	p-Xvelene	16	Undecane
		13	Pentadecane		Naphtalene

Fig. 5 a Typical chromatograph of indoor air sampled at restaurant – without ozonisation. b Typical chromatograph of indoor air sampled at restaurant – with ozonisation

to the rate at which VOCs were added to the indoor air of the Bar room. Percentage reduction of individual VOCs observed in Bar shows that all the VOCs, excepting Naphthalene get reduced on ozoni-sation (Table [5](#page-7-0)). Figure [4](#page-7-0) shows that concentrations of naphthalene increase on ozonisation. At office, Bar and Food Court, concentrations of naphthalene increase more than one hundred per cent. Maximum increase is observed at Bar, which makes the percentage reduction of TVOC negative. This may be due to the degradation of higher VOCs.

Kajornsak et al. [\(2004](#page-10-0)) and Jintawat et al. [\(2005](#page-10-0)) have reported removal of formaldehyde and acetaldehyde from contaminated air stream using corona discharge. Uncertainty prevails regarding the mechanism of degradation of aromatic hydrocarbons in upper atmosphere. (Andino et al. [1996](#page-10-0); Bartolotti and Edney [1995](#page-10-0); Koltz et al. [1997](#page-10-0)). Photo catalytic conversion of toluene, n-butane, 1, 3 dichloroethene, n-hexane, methyl-ethyl-ketone, n-decane, propanal, 1 butanol, trichloroethylene, ethylene, ammonia have been studied individually (Hall et al. [1998](#page-10-0)). However, very little work has been published on simultaneous conversion of contaminants in mixture. In a mixture of VOCs, differences in the binding ability of the compounds will affect the reaction rates. In the tropospheric degradation of VOCs, ring opened compounds have been reported (Atkinson [1994](#page-10-0); Becker et al. [1992](#page-10-0); Beirbach et al. [1994a](#page-10-0), [b](#page-10-0); Yu and Jeffries [1997](#page-11-0); Yu et al. [1997](#page-11-0)). Representative reconstructed ion chromatogram of VOCs identified at Restaurant with and without ozonization unit, is shown in Fig. [5](#page-8-0). The figure shows a reduction in peak heights. This clearly demonstrates the degradation of VOCs represented by these peaks. However, the available literature does not provide any detail insight into the reaction mechanism of the observed reduction of VOC levels. It may be postulated that ozone decomposes partly into OH radicals as follows :

 O_3 + hv \rightarrow O_2 + O(CD) (λ = 335 nm) $O(^1D) + M \rightarrow O(^3P)$ (M = N₂, O₂), O(¹D) – extracted oxygen $O(^3P) + O_2 + M \rightarrow O_3 + M (M = air)$ $O(^1P) + H_2O \rightarrow 2OH$

 $O(^3P)$ is formed by deactivation of $O(^1D)$ atom to ground state oxygen. These OH radicals form hydroxyl adducts for further reactions (Atkinson [2000](#page-10-0)). Further investigation to understand the reaction mechanism is required.

The levels of ozone monitored at different locations are given in Table 6. It is observed that, at all locations at all times, the levels of ozone were within the prescribed limits of OSHA (0.1 ppm). Low levels of ozone encountered on ozonization may be due to the location of the ozonization unit. The ozonization units, at all locations, were in the duct of air-conditioning system and not directly in indoors.

Table 6 also shows that the carbon dioxide levels reduce on ozonization. This may be due to interaction of carbon dioxide with OH radicals formed due to decomposition of ozone. Vesela and Wilhelm [\(2002](#page-11-0)) have reported that in aqueous media $CO₂$ interacts with reactive nitrogen species and reactive oxygen species. In the presence of super oxide, NO reacts with oxygen to form peroxynitrite, that reacts with $CO₂$ to give nitrosoperoxy carbonate. This compound rearranges into nitro carbonate which is prone to further reactions. When nitrogen reacts with oxygen in absence of a super oxide a nitrating species N_2O_3 is formed. CO_2 reacts with N_2O_3 to produce nitrosyl compounds. It is thought that similar reactions may be occurring in air environment also. The present observations are not based on controlled chamber study but on real indoor environment. The urban indoor environment monitored is too complex to visualize all reactions that may be taking place. The exact process of $CO₂$ removal is not clearly understood and warrants further chamber studies.

Table 6 Concentrations of ozone and carbon dioxide in indoors with and without ozonisation unit

Location	Concentrations $(\mu g/m^3)$								
	With ozonization		Without ozonization						
	Ozone	CO ₂	Ozone	CO ₂					
Office room	1.20E-05	1.10E-05	3.14E-06	2.88E-06					
Food court A	3.93E-07	3.60E-07	1.96E-07	1.80E-07					
Food court B	1.35E-05	1.24E-05	1.30E-05	1.19E-05					
Food court C	1.37E-05	1.26E-05	3.93E-07	3.60E-07					
Theater 1	1.96E-07	1.80E-07	1.96E-07	1.80E-07					
Theater 2	3.93E-07	3.60E-07	1.96E-07	1.80E-07					
Restaurant	9.23E-06	8.46E-06	2.16E-06	1.98E-06					
Conference room	7.85E-07	7.20E-07	1.96E-07	1.80E-07					
Bar floor	9.03E-06	8.28E-06	1.57E-06	144E-06					

(Ozone TLV−TWA/8 h=0.000196319)

6 Conclusion

Out of 40 VOCs were identified, more than one fourth, is classified in the USEPA Air Toxic Programme as Hazardous Air Pollutants (HAPs). Some compounds, including HAPs, like benzene, toluene, ethyl benzene, chloroform and carbon tetrachloride have been observed, in appreciably high concentrations, even in the absence of a predominant source. When compared with standard limiting values, as stated in the Hong Kong Indoor Air Quality Guidelines (Hong Kong Government 2003), concentrations of most VOCs were found to be within limits. Concentration of benzene in outdoor air was observed to be high, much above the guideline value of 5 μ g/m³ defined for outdoor ambient air. Also, excessive use of consumer products leads to higher indoor concentrations of chlorinated VOCs, namely, viz chloroform and carbon tetrachloride.

Concentrations of TVOC decrease on ozonization. Reduction of individual VOC, levels defined in the IAQ objective, contribute to a reduction of TVOC concentrations. This indicates that ozone reacts with these compounds to reduce their concentration. The mechanism of reactions needs to be studied in detail.

In order to achieve healthy indoor environment, it is thus necessary not only to have clean outdoor air but also restrict the use of consumer products containing VOCs in Indoor. In the long run, it is advisable to look for alternative safe solvents in consumer products.

Acknowledgement Special thanks are due to Dr. G. H. Pandya and Mr. S. Kashyap for their assistance in analysis of samples on GC-MS. Deep gratitude is expressed to Director, NEERI for encouraging this work.

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