Environmental Pollution 239 (2018) 499–511

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Toxicity and mutagenicity of exhaust from compressed natural gas: Could this be a clean solution for megacities with mixed-traffic conditions?☆

Avinash K. Agarwal [a,*], Bushra Ateeq [b], Tarun Gupta [c], Akhilendra P. Singh [a], Swaroop K. Pandey [b], Nikhil Sharma [a], Rashmi A. Agarwal [d], Neeraj K. Gupta [a], Hemant Sharma [a], Ayush Jain [a], Pravesh C. Shukla [c]

[a] Engine Research Laboratory, Department of Mechanical Engineering, Indian Institute of Technology Kanpur, Kanpur, 208016, India
[b] Department of Biological Sciences and Bioengineering, Indian Institute of Technology Kanpur, Kanpur, 208016, India
[c] Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur, 208016, India
[d] Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, 208016, India

ARTICLE INFO

Article history:
Received 17 October 2017
Received in revised form
4 April 2018
Accepted 5 April 2018

Keywords:
Toxicity
Mutagenicity
Particulates
Polycyclic aromatic hydrocarbons
Unregulated emissions

ABSTRACT

Despite intensive research carried out on particulates, correlation between engine-out particulate emissions and adverse health effects is not well understood yet. Particulate emissions hold enormous significance for mega-cities like Delhi that have immense traffic diversity. Entire public transportation system involving taxis, three-wheelers, and buses has been switched from conventional liquid fuels to compressed natural gas (CNG) in the Mega-city of Delhi. In this study, the particulate characterization was carried out on variety of engines including three diesel engines complying with Euro-II, Euro-III and Euro-IV emission norms, one Euro-II gasoline engine and one Euro-IV CNG engine. Physical, chemical and biological characterizations of particulates were performed to assess the particulate toxicity. The mutagenic potential of particulate samples was investigated at different concentrations using two different *Salmonella* strains, TA98 and TA100 in presence and absence of liver S9 metabolic enzyme fraction. Particulates emitted from diesel and gasoline engines showed higher mutagenicity, while those from CNG engine showed negligible mutagenicity compared to other test fuels and engine configurations. Polycyclic aromatic hydrocarbons (PAHs) adsorbed onto CNG engine particulates were also relatively fewer compared to those from equivalent diesel and gasoline engines. Taken together, our findings indicate that CNG is comparatively safer fuel compared to diesel and gasoline and can offer a cleaner transport energy solution for mega-cities with mixed-traffic conditions, especially in developing countries.

1. Introduction

Vehicular pollution is considered to be a major source of air pollution in mega-cities like Delhi. Exhaust from vehicles is a complex mixture of gases and particulates. The adverse morbidity and mortality effects of these chemical species emitted by engines/vehicles significantly influence the health of residents of mega-cities like Delhi and neighboring satellite towns (Sindhwani and Goyal, 2014). A continuous increase in the population of Delhi from ~13 to ~17 million during the first decade of 21st century has led to explosion in the vehicular density in the city, which increased from ~3.6 million to ~7 million (Hosamane and Desai, 2013). This increased the average ambient $PM_{2.5}$ concentration more than three folds from ~75 $\mu g/m^3$ in 2001 to ~250 $\mu g/m^3$ in 2010 (Air Quality Monitoring; Organization, 2013). Particulate emissions from various combustion sources have caused global concerns due to their adverse health effects, including cancer, asthma, and predisposition to various genetic diseases (Organization, 2011). Respiratory infections caused by particulates pose another set of challenges, which may potentially lead to death of children under 5 years of age (Organization, 2013; Organization, 2011). The World

☆ This paper has been recommended for acceptance by Dr. Hageman Kimberly Jill.

* Corresponding author.
E-mail address: akag@iitk.ac.in (A.K. Agarwal).

https://doi.org/10.1016/j.envpol.2018.04.028

Bank estimated that in 1995, one person died in every 70 min because of air pollution in Delhi, which reduced to ~60 min in late 1990's (Sindhwani and Goyal, 2014; Organization, 2013; Organization, 2011; Greenstone et al., 2015). This forced researchers to look for sources of pollution and it emerged from numerous studies that vehicular exhaust emissions were one of the main culprits. Relatively lower fuel injection pressure (FIP) in the engines powering diesel engines leads to higher particulate emissions in conventional direct injection compression ignition engines (Sharma and Agarwal, 2017; Agarwal et al., 2013a).

Particulates originating from engine exhaust consist of solid and liquid organic compounds, carbonaceous matter, vaporized/ pyrolysed fuel and lubricating oil, trace metals and sulfates (Sharma et al., 2005). Particulates have different sizes, morphology, and composition, having a wide range of inorganic and organic species, including polycyclic aromatic hydrocarbons (PAHs) adsorbed onto the carbonaceous core. Most particulates emitted by internal combustion (IC) engines are nano-particles ($D_p < 10$ nm) hence they can be easily inhaled and hence they penetrate deep into the inner structures of the lungs (Baldauf et al., 2016). Singh et al. (2016) carried out a comparative analysis of particulates emitted from diesel, gasoline and CNG fueled engines and reported that diesel engines (without any diesel particulate filter) emit relatively bigger particulates compared to gasoline engines. However, particulate mass (per unit mass of fuel consumed) emitted from diesel engines were an order of magnitude higher compared to the gasoline engines (McClellan, 1987; Maricq et al., 1999a, 1999b; Ban-Weiss et al., 2008). Experimental studies have demonstrated that smaller particulates induce stronger biological effects than larger ones of similar composition due to their larger surface area-to-volume/ mass ratio (Kunzi et al., 2015). However, a correlation for variations in surface area cannot account for variations in the biological reactivity among particulates of different chemical compositions (Osornio-Vargas et al., 2003; Schwarze et al., 2007). The capacity of particulates to induce mutagenic responses is largely related to their number density, concentration and cumulative effect of chemical components, especially PAHs adsorbed onto their surface (Niu et al., 2017; You et al., 1994). Formation of PAHs and their associated toxicity largely depends on the engine type, fuel properties, engine operating conditions and effectiveness of exhaust gas after-treatment devices. PAHs are of particular concern due to their mutagenic and carcinogenic potential and associated health effects. PAHs are formed due to incomplete combustion of hydrocarbons (Finlayson-Pitts and Pitts, 1986). Their mutagenic effects are further compounded by the fact that they may readily undergo reactions with oxygen, ozone and nitrogen oxides in the atmosphere and produce secondary aerosols that may be even more mutagenic than the parent PAHs (Agarwal et al., 2013b). These chemical structures generally exist in the gas phase above 150 °C and condense over the emitted fine particulates in relatively lower temperature environment (Lioy and Greenberg, 1990). Once inhaled and deposited in the human respiratory system, these PAHs may transform into a variety of metabolites via reactive epoxide intermediates. Further activation into a diol epoxide, which is considered a precursor to the product, can interact with the nucleic acid bases present in the DNA (Gupta et al., 1982). This reaction takes place primarily with the exocyclic 2-amino group of guanine, and this bulky PAH substituent on the DNA base interferes with replication merely because of its size (Phillips, 1983).

With time, emission legislations have become stringent in order to improve urban air quality, especially in mega-cities like Delhi, Tokyo, Beijing and New York (Mage et al., 1996; Sakai et al., 2002; Voorhees et al., 2000; Kathuria, 2002, 2004). Significant evidence corroborates the adverse health impacts of particulates originating from internal combustion (IC) engines used in vehicles and stationary auxilliary power sources, comprising of fine and ultra-fine particles (50 nm < D_p < 1000 nm), which have been linked to the production of oxidative stress in the cells through the formation of reactive oxygen species (ROS) (Li et al., 2003; Nel, 2005). In mega-cities, gasoline engines are preferred over diesel engines in the vehicles due to the fact that gasoline engines emit lesser particulate mass. However, gasoline engine particulates can cause DNA damage and can create DNA adducts, which enhances micronucleus formation and promotes chromosome aberration that has been thought to be associated with carcinogenesis (Tsai et al., 2000; Hoek et al., 2002; Pope et al., 2002). Condensates from gasoline exhaust were found to be mutagenic in one of the study (Ye et al., 2000). Moreover, different particulate characteristics appear to be involved in various biological effects *in-vitro*. Betha et al. (2012) investigated the effects of particulates generated from a stationary engine fueled with mineral diesel and biodiesel. They suggested that particulate formation is a complex phenomenon, in which fuel properties affect the particulate structure and its toxicity. They reported that biodiesel fueled engines showed significantly higher toxicity and ROS compared to mineral diesel fuelled engines. Adverse effects of particulates on human health are potentially associated with their size-surface area distributions and chemical constituents such as trace metals and PAHs (Crebelli et al., 1991). Allergic responses tend to be associated more with the organic fraction of particulates, whereas inflammatory reactions seem to be associated more with trace metals from particulates and endotoxins. Literature also confirms that many trace metals such as cadmium (Cd) elicit toxicity via free radical-induced damage, but these trace metals do not generate free radicals directly (Yang et al., 2008). Nitric oxide (NO), a fundamental molecule that interplays with ROS, may be associated with trace metal induced cytotoxicity (Nazarewicz et al., 2007).

In view of the above, many countries are adopting various control measures to combat the twin issues of energy security and emission control. Use of gaseous fuels such as compressed natural gas (CNG) and liquefied petroleum gas (LPG) has become popular worldwide with a view to improve urban air quality. Nylund and Lawson (2000) reported that the level of greenhouse gases (GHGs) emitted from CNG fueled vehicles was 12% lower than mineral diesel fueled vehicles when the entire life-cycle of the test fuels were considered. Based on similar results reported in the literature, Supreme Court of India ruled in 2000 that all public transport vehicles in Delhi should switch over to cleaner fuels such as CNG by 31st March 2001. All buses of Delhi Transport Corporation and other Private bus owners, autos and taxis were therefore converted to CNG in a short span of time. Due to an introduction of CNG vehicles in Delhi and with the implementation of several other emission control measures, a significant reduction in PM_{10} levels in the ambient air of Delhi was witnessed in the following years (Kathuria, 2004). Mega-city of Delhi consumed 800,000 MT liquid transportation fuels (gasoline and diesel) and 500,000 MT CNG in 2009-10 and which increased to 831,000 MT liquid transportation fuels and 717,000 MT CNG in 2014-15 (Book, 2011; All India Study, 2013). This shows that currently, a very large fraction of private transport vehicles and entire public transport system has switched over from conventional liquid fuels to CNG. However, particulates emitted by vehicles (PM_1) on Delhi roads have not been significantly affected due to increase in number of vehicles and increased fuel consumption. This has triggered another debate amongst researchers about the comparative severity of health effects from particulates emitted by diesel, gasoline and CNG engines.

Many researchers have speculated that while CNG looks cleaner, it would cause far more severe health effects because of large number of finer nano-particles it emits. Globally, a number of studies have been carried out to correlate particulates emitted by