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ScienceDirect
Environmental Research 103 (2007) 317–324
Environmental Research
www.elsevier.com/locate/envres

Contrasting reactive oxygen species and transition metal concentrations in combustion aerosols

S.W. See[a], Y.H. Wang[a], R. Balasubramanian[a,b,*]

[a]Department of Chemical and Biomolecular Engineering, National University of Singapore, Block E5, 4 Engineering Drive 4, 117576, Singapore
[b]Division of Environmental Science and Engineering, National University of Singapore, Block EA, 9 Engineering Drive 1, 117576, Singapore

Received 7 March 2006; received in revised form 2 August 2006; accepted 28 August 2006
Available online 2 October 2006

Abstract

The presence of reactive oxygen species (ROS) and 10 transition metals (Ag, Cd, Co, Cu, Fe, Mn, Ni, Ti, V and Zn) in both the acid-soluble and water-soluble fractions of fine particles of combustion origin were determined. ROS was analyzed using the dichlorofluorescin fluorescence technique. Particles emitted from on-road vehicles, gas cooking, incense burning, and cigarette smoke were characterized along with those in the background air of outdoor and indoor environments. In addition, this study evaluated the possible relationships between ROS and individual transition metals. It is found that cigarette smoke which had the highest concentration of metals also contained the highest concentration of ROS. Regression analysis performed showed that water-soluble metals including Cd, Co, Cu, Fe, Mn, and Ni showed better correlation with ROS concentration as compared to acid-soluble (total) metals. The findings demonstrated that water-soluble metals could be one of the species influencing ROS formation in ambient air.

Keywords: Air quality; Combustion particles; $PM_{2.5}$; Metals; Reactive oxygen species

1. Introduction

Research on airborne particulate matter (PM) has received increased concern in recent years after it was identified as a major component of the air pollution mix that is strongly associated with premature mortality and morbidity (Stieb et al., 2002; Hinwood et al., 2006). Particular attention has been paid to respirable particles with an aerodynamic diameter less than or equal to 2.5 μm ($PM_{2.5}$), which primarily originate from combustion sources (Afshari et al., 2005). These fine particles can penetrate deeply into the lungs and diffuse to other extrapulmonary target organs (Semmler et al., 2004). Anthropogenically derived combustion particles carry a multitude of harmful substances (Lima et al., 2005), and concentrations of these chemical components could be a better predictor of possible deleterious health effects than measurements of particulate mass (Burnett et al., 2000).

One group of particulate-bound chemical components of health concern is reactive oxygen species (ROS), which include molecules such as hydrogen peroxide (H_2O_2), ions such as hypochlorite ion (OCl^-), free radicals such as hydroxyl radical ($^{\bullet}OH$) and superoxide anion ($^{\bullet}O_2^-$), which is both an ion and a radical. Other than being produced endogenously within the body through normal metabolic processes (Nohl et al., 2003), ROS can also be formed exogenously without any biological activation from airborne inorganic or organic compounds through chemical reactions (Baeza-Squiban et al., 1999). One catalyst for ROS generation is transition metals (Prahalad et al., 2001; Hogervorst et al., 2006); others include polycyclic aromatic hydrocarbons (PAHs) (Lima et al., 2005) and carbonaceous soot (Jung et al., 2006). Collectively, their effects may be synergistic, additive, or even antagonistic. Transition metal particles are produced at high temperatures from combustion and high-temperature pyrolysis (Lighty et al., 2000; See and Balasubramanian, 2006), and generate $^{\bullet}OH$ via the Fenton reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-. \quad (1)$$

*Corresponding author. Department of Chemical and Biomolecular Engineering, National University of Singapore, Block E5, 4 Engineering Drive 4, 117576, Singapore. Fax: +65 6779 1936.
E-mail address: eserbala@nus.edu.sg (R. Balasubramanian).

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doi:10.1016/j.envres.2006.08.012

Thus, the abundance of transition metals from such sources can, in turn, increase ROS and cause harmful health effects.

ROS, with their strong oxidizing power, can react with and damage surrounding critical biological macromolecules within the body such as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) due to oxidative stress (Yu and Anderson, 1997; Martinet et al., 2004). Their participation as a fundamental component in tissue injury underlies their roles in a large number of diseases, including aging and carcinogenesis (Niwa et al., 1989; Vallyathan et al., 1998; Datta et al., 2000). At low concentrations, cells are normally able to defend themselves against ROS damage through the assistance of antioxidant enzymes such as superoxide dismutase (SOD) and catalase (Mates, 2000). However, when present at high levels, ROS cannot be removed adequately by intracellular defense mechanisms.

Therefore, it is essential to quantify ROS in PM for the benefit of health risk assessments and the protection of human health. Until recently, most of the investigations were focused on measuring ROS in the human body, usually by means of electron spin resonance (ESR) spectroscopy (Singh et al., 1995), or the rapid but highly sensitive chemiluminescence's assay using a non-fluorescent reagent dichlorofluorescein which becomes fluorescent when oxidized in the presence of ROS (Cathcart, 1983; Langlais et al., 1997). The latter method has been successfully used to measure ROS in airborne particles (Antonini et al., 1998; Hung and Wang, 2001; Kao and Wang, 2002; Huang et al., 2005; Venkatachari et al., 2005).

Kao and Wang (2002) and Venkatachari et al. (2005) demonstrated that the ozone (O_3) concentration in the ambient air is a major factor affecting the ROS concentration. However, no study has been conducted yet to look into the relationship between transition metals, one of the precursor pollutants, and ROS in particulates using the fluorescence assay. The primary objective of this work is to study the effect of transition metals on the production of ROS in $PM_{2.5}$ by determining the concentrations of ROS and metals. Both soluble and total metals were measured to evaluate their respective associations with ROS. $PM_{2.5}$ samples were collected from several outdoor and indoor combustion sources, including those emitted from on-road vehicles, food cooking, incense sticks, and cigarette smoke. $PM_{2.5}$ samples were also collected from the background air in both the ambient outdoor and indoor environments to assess the levels of particulate-bound transition metals and ROS with no combustion activities in the vicinity of sampling locations.

2. Materials and methods

2.1. Sampling site and measurements

Emissions of fine particles from four major combustion sources, namely, vehicular traffic, incense burning, cigarette smoke, and gas cooking were considered in this study. On-road vehicles were selected to be representative of outdoor combustion sources as they are a major contributor of fine particles and airborne metals at ground level in many urban regions (Mossetti et al., 2005; Zereini et al., 2005). In the case of indoor particulate air pollution, incense stick burning, which is a religious practice followed in Asia by Taoists, Buddhists, and Hindus during prayers, cigarette smoking, and gas cooking were picked as they are significant sources of airborne particles (Lofroth et al., 1991). In addition, air sampling was carried out in an outdoor as well as an indoor environment that is not strongly influenced by combustion-derived aerosol particles to represent the background concentration of particulate-bound transition metals and ROS. No background information was available for the cooking source as the food stall was closed during non-operating hours, but the outdoor background concentrations could be taken as representative of the indoor air quality in the kitchen since it is naturally ventilated. Two $PM_{2.5}$ samplers were used in parallel, which were placed 1.5 m apart and 1.5 m above the ground to simulate the breathing zone of humans. For all cases, measurements were made on clear days during the month of December 2005 for 3 h each from 10 a.m. to 1 p.m., except for cigarette smoking, in which case the air sampling lasted only for 15 min each, from 11 a.m. to 11:15 a.m. Efforts were made to carry out sampling within the same time frame as the levels of ROS are closely associated with the intensity of photochemical reactions involving light and O_3 which show a diurnal variation with a maximum between 12 noon and 1 p.m.

2.1.1. Urban aerosols

The site is located on the rooftop of one of the tallest buildings within the Kent Ridge campus of National University of Singapore (NUS) located 67 m above sea level at a latitude of 1°18′N and a longitude of 103°46′E. It is considered to be an urban background site, mainly affected by distant traffic and industrial emissions.

2.1.2. Traffic-influenced aerosols

A bus-stop in NUS, 2 m from the kerbside, was selected to collect traffic emissions as it is situated along a 4-lane, 2-way major road. The site is influenced by emissions from four internal and three public bus services, along with many other vehicles traveling along this steeply inclined stretch of road. The average traffic flow during the sampling days was counted to be 198 vehicles per hour, with 52% of them being diesel vehicles, which include buses, vans and trucks. The remaining 48% were gasoline-powered vehicles, which include passenger cars and motorcycles. The tall buildings located in front of and behind the bus-stop increase the roughness of the terrain and cause a reduction in wind speed, leading to poor dilution and dispersion of air pollutants in this region. A combination of all these factors could cause a build-up of airborne particles in this area.

2.1.3. Gas cooking emissions

A Chinese food stall in one of the canteens in NUS serving noodles was chosen as the sampling site. This site was chosen because the only cooking method employed in the commercial kitchen is boiling; different cooking methods give rise to different particulate pollutant levels indoors (See et al., 2006). The 24 m^3 stall is naturally ventilated through the back door and front counter at ~1.7 ACH. There are two boilers over two liquefied petroleum gas (LPG) stoves on one side of the kitchen and the samplers were placed about 0.4 m away on the opposite side of the gas stoves. No exhaust fume extractor or other mechanical dilution devices were present in the kitchen.

2.1.4. Indoor aerosols

The indoor background site is situated one storey below the outdoor background site. The 8 m^3 room is mechanically ventilated at ~0.5 air change per hour (ACH) by drawing ambient air through a network of air handling units, implying that the indoor air quality is affected by the migration of outdoor pollutants indoors as well as a build up of particles from old wall paint, tiled floorings, furniture, and other structures in the room (Kemp et al., 1998). ACH was estimated by injecting a known amount of SF_6 into the kitchen and calculated using the following equation by measuring its decay in concentration over time:

$$C_t = C_0 e^{-(ACH)t}, \quad (2)$$