行政院國家科學委員會補助專題研究計畫成果報告

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※　　　都會區大氣中超細粒徑微粒之特性探討(II)　　　※
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行政院國家科學委員會專題研究計劃成果報告

都會區大氣中超細粒徑微粒之特性探討(II)

Characterization of Ultrafine Particles in Urban Atmosphere (II)

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中文摘要

本研究主要目的在於測量都會區周界大氣中超細粒徑（在本研究中定義為 $d_p < 0.18$ μm）微粒之質量濃度與不同粒徑之微粒其反應性含氧物種(Reactive Oxygen Species, ROS)的濃度，同時探討可能影響ROS濃度之因素。

人行道與柴油引擎排氣採樣結果均顯示在相同的微粒質量下較小的微粒中ROS含量較高。而大氣中微粒相ROS濃度與光化學反應強度呈現良好之正相關性。此種現象顯示光化學反應是影響大氣中較小微粒之ROS含量的主要因素，尤其是對超細粒徑微粒而言。此外，微粒上所量測到的ROS濃度會隨著微粒樣本暴露在空氣中的時間增加而衰減。推測空氣中含有之還原性化學物質可能是造成ROS濃度衰減之主要因素。

關鍵詞：都會氣膠，新鮮氣膠，老化氣膠，反應性含氧物種

Abstract

The objective of this study was to measure the mass concentration of ambient ultrafine particles (defined in this study as the particles with aerodynamic diameter < 0.18 μm) and the concentration of reactive oxygen species (ROS) in various size fractions for the Taipei aerosols and diesel exhaust particles. The factors affecting the concentration of ROS in particles were also investigated.

For the same mass concentration of particles, the ROS content was found to be higher in smaller particles, except for ultrafine particles. This pattern was observed both in the particles sampled at the sidewalk and from diesel exhausts. The concentration of ROS in ambient particles had good correlations with the intensity of photochemical reactions. The correlation coefficient between the ROS concentration and the O_3 concentration was higher for smaller particles. This indicates that the intensity of photochemical reactions is an important major factor affecting ROS concentration in smaller particles, especially in ultrafine particles. Moreover, Measurements of ROS concentrations in particle samples aged for different periods of time showed that the ROS concentration was higher for the 'fresh' particles analyzed 1 h after sampling as compared to the particles 'aged' for a longer period of time.

Keywords: urban aerosol, fresh aerosol, aged aerosol, ROS

Introduction

Highly reactive oxygen-containing species and their derivatives, collectively described as reactive oxygen species (ROS), originate from various sources and have different lifetimes in the atmosphere. ROS

appear in both gas phase and particulate phase. Several studies on ROS in the gas phase and in rain and cloud droplets have been reported (Sakugawa and Kaplan, 1990), but concentration data on ROS in the particulate phase are limited.

Particles in diesel emissions and those generated by photochemical reactions generally contain high concentrations of ROS. These particles are mostly in the submicrometer range and therefore have a relatively high rate, about 20~30 %, of lung deposition. As a result, toxicants in these particles can be efficiently transferred to the lungs (Friedlander and Yeh, 1998). ROS are also produced naturally in biological systems to defend against foreign organisms and other environmental challenges. High ROS concentrations can induce cell injury that may trigger a cascade of free radical reactions promoting the disease process. Consequently, a central role has been implicated for ROS in the pathogenesis of many pulmonary diseases.

Exposure to reducing compounds in air is an important factor that affects the concentration of ROS in particles. It has been well documented that freshly fractured silica dust has a higher concentration of free radicals, which decays with time by first-order kinetics and exhibits a half life of ~30 h when the dust was exposed to air after grinding (Shi et al., 1988). Compared to aged silica dust, freshly ground silica dust shows a greater biological effect on respiratory systems (Vallyathan et al., 1995).

Rapid quantitation of ROS can be made with a fluorogenic probe. Dichlorofluorescin ($DCFH_2$) is a non-fluorescent reagent that becomes fluorescent dichlorofluorescein (DCF) when oxidized in the presence of ROS. This fluorometric method has been widely applied in measurements of oxidative activity in biological systems. Its application in the quantitation of ROS in aerosol particles has been made recently (Antonini et al., 1998).

The objective of this study was to use the fluorogenic probe to determine the concentrations of reactive oxygen species in various size fractions of Taipei aerosol and diesel exhaust particles. The factors affecting the concentration of ROS in particles were also investigated. These factors include the intensity of photochemical reactions and the aging of particles.

Results and Discussion

The results for aerosols sampled at a Taipei sidewalk show that the mass concentrations of very fine (2.9~36.7 $\mu g/m^3$) and ultrafine (3.4~22.1 $\mu g/m^3$) particles were higher than fine (1.8~11.2 $\mu g/m^3$) and coarse (3.4~13.9 $\mu g/m^3$) particles. Table 1 shows the average ROS concentrations expressed in terms of H_2O_2 concentrations (nanomoles of H_2O_2 per cubic meter of air sampled, $nmol/m^3$) were 0.064, 0.058, 0.322, and 0.163 $nmol/m^3$, respectively, for the coarse, fine, very fine, and ultrafine particles. Since very fine particles (0.18~1 μm) had higher mass concentrations and ROS concentrations per unit mass of particles than those of other size fractions, it is not surprising that the ROS concentrations per unit volume of air were higher in ambient particles of this size range.

The concentrations of ROS in particles (nanomoles of H_2O_2 per unit mass of particles, nmol/mg) of different size intervals of particles sampled at a sidewalk and from diesel emissions were compared using the fluorescence measurements for liquid suspensions of sampled particles having identical mass concentration of 10 $\mu g/ml$. For the purpose of comparison, ROS concentrations in particles collected at the sidewalk were categorized into two subgroups, one with corresponding average O_3 concentrations below 20 ppb (representing weak photochemical reactions) and one with corresponding average O_3 concentrations above 20 ppb (representing intense photochemical reactions). Figure 1 shows the concentrations of ROS in particles sampled at a sidewalk and from diesel

emissions. During periods of intense photochemical reactions, the ROS concentrations in very fine particles were higher than those in fine and coarse particles at the sidewalk. Such a relationship between the ROS concentration and the particle size was seen in particles larger than 0.18 μm, but not in ultrafine particles that have larger surface areas per unit mass than very fine particles. Nevertheless, for the same particle mass concentration, the ROS concentration in smaller particles was still higher than those in larger particles.

The pattern that smaller particles contain higher levels of ROS per unit mass of particles was also observed on the particles sampled from diesel emissions. The particles collected at the sidewalk during periods of weak photochemical reactions showed a slightly higher level of ROS per mass of particles in smaller particles. On the other hand, the ROS concentration in smaller particles sampled at the sidewalk during periods of intense photochemical reactions was significantly higher than those sampled from the diesel exhaust and at the sidewalk during periods of weak photochemical reactions.

Figure 2 shows the decay of ROS with time in particles of different size intervals sampled at the sidewalk. The ROS concentration was higher for the 'fresh' particles analyzed 1 h after sampling as compared to the particles 'aged' for 115 h. For particles of different size intervals, the ratio of ROS concentration in 'aged' particles to that in 'fresh' particles was 0.27~0.38. Limited by the number of available samplers, only two different "ages" of particles collected at the sidewalk were analyzed. Figure 3 shows the decay of ROS with time in very fine and ultrafine particles sampled from diesel emissions. The result also indicates that the ROS concentration was higher for the 'fresh' particles analyzed 0.5 h after sampling as compared to the particles 'aged' for 4, 20, and 168 h. For very fine and ultrafine particles, the decay of ROS was fast in the first 4 hours.

Self-evaluation of Results

The goals of this study, which included measuring the mass concentration, and the concentration of reactive oxygen species in atmospheric ultrafine particles in an urban environment, were completed. In addition, the concentration of ROS was also determined for diesel exhaust particles of different size fractions. A paper based on the results of this study has been accepted by Journal of Aerosol Science for publication.

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Table 1 Equivalent hydrogen peroxide concentrations of ROS in aerosol particles collected at a sidewalk. (n: sample size)

Size interval (μm)	n	Equivalent H_2O_2 concentration, nmol/m^3		
		Range	Mean	SD
3.2~10 (coarse)	32	0.006~0.138	0.064	0.033
1~3.2 (fine)	31	0.016~0.146	0.058	0.040
0.18~1 (very fine)	32	0.043~0.991	0.322	0.249
< 0.18 (ultrafine)	32	0.026~0.592	0.163	0.155

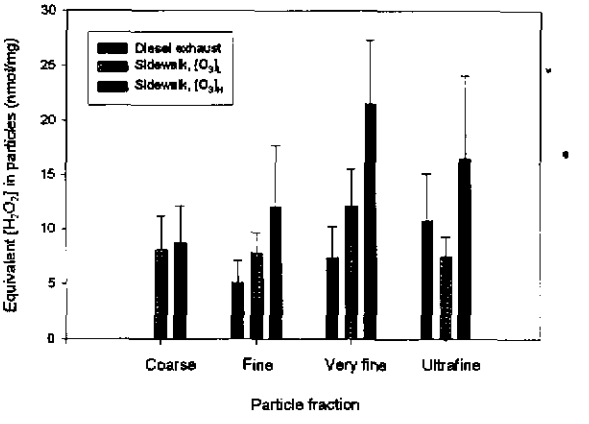

Fig. 1 ROS concentrations in 10 μg/ml liquid suspensions of particles obtained from diesel, and sidewalk samples expressed in terms of equivalent hydrogen peroxide concentrations. Values were mean ± SD. $[O_3]_L$ and $[O_3]_H$ represented periods of weak and intense photochemical reactions, respectively.

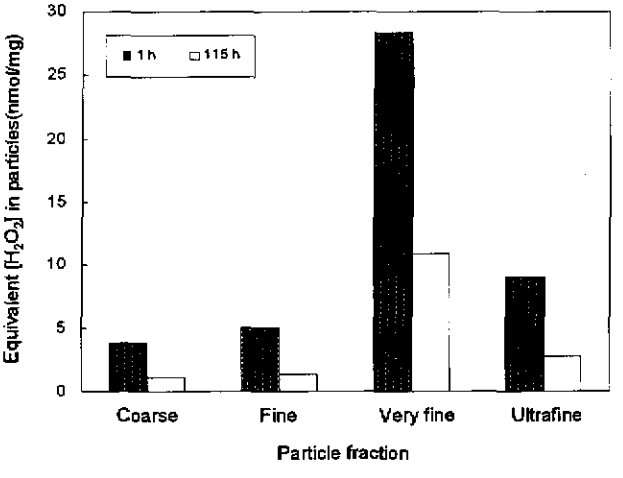

Fig. 2 Equivalent hydrogen peroxide concentrations in aerosol particles (nmol/mg) collected at an sidewalk. The concentration of ROS was determined 1 h and 115 h after particle collection.

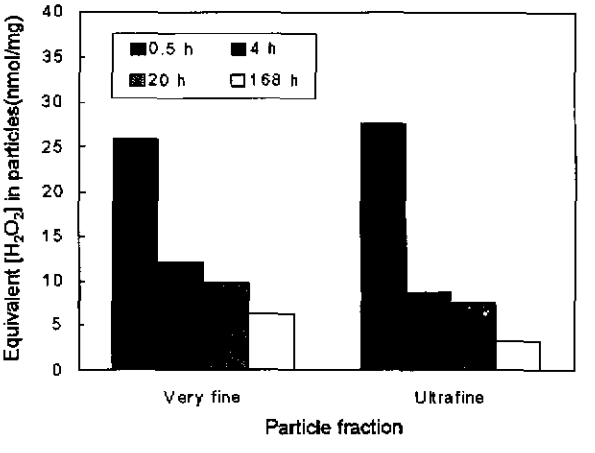

Fig. 3 Equivalent hydrogen peroxide concentrations in aerosol particles (nmol/mg) collected from diesel emissions. The concentration of ROS was determined 1 h, 4h, 20 h, and 168 h after particle collection.