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Chemical Composition of the Size-resolved Particles in Buk-Ak Tunnel

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Abstract

The roadway tunnels in urban areas give rise to problems such as a localized air pollution. Here, we report the results of a case study of an urban roadway tunnel measurement. The size-resolved particle sampling was carried out with a two 2-stage filter pack samplers and an Andersen impactor sampler at the center of Buk-Ak tunnel in November 2001. Particle Induced X-ray Emission (PIXE) was applied to determine the elemental composition of size-resolved particles divided into soluble and insoluble fractions. The Thermal/Optical Reflectance (TOR®) method was also employed in analyzing of elemental carbon (EC) and organic carbon (OC). Mass concentrations of fine ($< 1.2\,\mu m$) and coarse ($> 1.2\,\mu m$) particles are 165 and 48 $\mu g\ m^{-3}$, respectively. Total elemental mass concentration (the sum of insoluble coarse, soluble coarse, insoluble fine, and soluble fine) is found to be 24 $\mu g\ m^{-3}$ and comprises only 11% of total particle mass concentration. The concentrations of EC, OC, and mass show the clear dependency on particle size with the maximum between 0.1 and 0.43 μm aerodynamic diameters. Total carbon (sum of EC and OC) accounts for approximately 70% of mass concentration.

Key words : Tunnel particles, PIXE, Elemental carbon, Organic carbon

1. INTRODUCTION

Air pollution is one of the widespread concerns in Seoul, with over 11 million individuals exposed to the air pollution. Among the pollutants in Seoul, particulate matter (PM) is represented by a broad class of physicochemically diverse substances. PM has so many sources such as motor vehicles, commercial ovens, boilers, materials-handling processes, agriculture, construction, mining, and so on. The effects of PM include the health problems like respiratory symptoms, aggravation of existing respiratory and cardiovascular disease as well as the environmental problems like visibility impairment and climate change. An increasing number of studies indicate that PM air pollution can have a severe effect on human health. Especially, the relationship between fine particles and health is a logical link because the efficiency of particle deposition in the respiratory tract is a function of particle size.

Emissions from engines powered by diesel and

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gasoline fuels are major sources of ambient particles. Because of technological improvement of engine, campaign of clean energy supply and rigorous emission regulation, emissions from motor vehicles have continuously changed over the last decade (Metz, 1993). Dust from paved roads, brake-lining dust, tire wear debris, and vegetative detritus from the dead leaves of urban plants can be also indirect materials of motor vehicle emissions (Rogge *et al.*, 1993). Diesel exhaust PM has been declared a probable human carcinogen by many agencies and organizations like the US Environmental Protection Agency (EPA) and the World Health Organization (WHO) (Pekkanen and Peters, 2002; Mauderly *et al.*, 1993). Recently, concerns about the health effects associated with motor vehicle exhausts have also been raised in Seoul, too.

Till now, few studies on PM have been carried out in the road tunnel in Seoul (Hwang, 1999). Thus there is very little data available on the production rate and airborne concentration in the urban roadway tunnel in Seoul. The primary goal of this study is to report the chemical composition of the size-resolved particles collected in a roadway tunnel located in a heavily industrialized metropolitan city.

2. MATERIALS AND METHODS

2.1 Tunnel description

Fig. 1 displays the entrance image of the Buk-Ak tunnel (looking East) and the scheme of the tunnel cross-section. Particle sampling was undertaken at the center of Bore 2 of Buk-Ak tunnel, which is one of the representative tunnels in Seoul and running between Chongro-Gu and Seongbuk-Gu on November 5, 2001. In order to avoid the influence of the turbulence by traffic density and wind speed on particle sampling, samplers were installed at 1.8 m above ground level in the Bore 2 (Fig. 1). Twelve automatic high volume blower fans with 40 HP was operating during sampling campaign. Average total

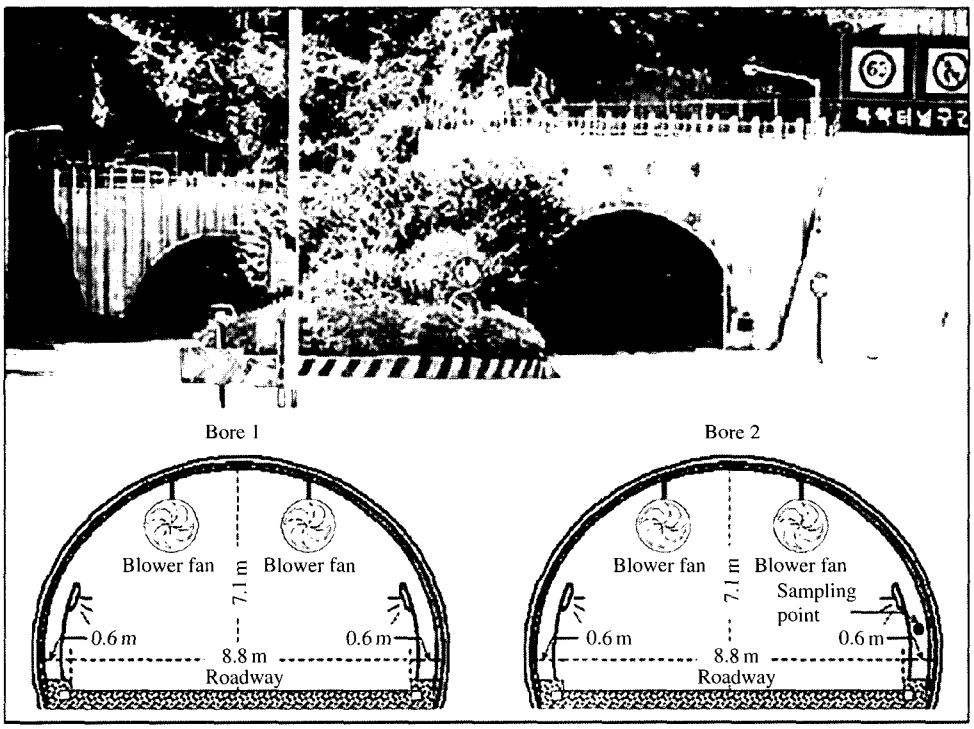

Fig. 1. Entrance image of the Buk-Ak tunnel (looking East) and the scheme of the tunnel cross-section.

Table 1. Characteristics of the Buk-Ak tunnel.

Item	Specification	Item	Specification
Run	East-West	Percent grade	1.5%
Lane	Four (bi-directional)	Number of blower fan	12 (40HP)[a]
Bore	Double	Type of ventilation	Transverse
Length	810 m	Traffic rate[b]	13750/day/bore
Width	10 m	Ratio of heavy duty[c]	39.5%
Height	7.1 m	Speed limit	60 km/hour

[a] All ventilation systems were operating during measurements
[b] A week day
[c] In the afternoon

traffic volume was 612 car/hour/Bore 2 with the speed of 60 km/hour. The ratio of heavy duty to total traffic volume is 32%. More details on tunnel characteristics are listed in Table 1.

2.2 Particle sampler and filter pretreatment

To collect the particles for elemental analysis, a 2-stage filter pack sampler was run for an hour. This sampler collected the coarse and fine fractions of the aerosols separately on a prefilter (a 47 mm diameter, 8 μm rated pore size polycarbonate filter (Nuclepore®) with 1×10^5 cm^{-2} pore density and 1 mg cm^{-2} nominal wt.) and a back-up filter (a 47 mm diameter, 0.4 μm rated pore size Nuclepore® filter with 1×10^8 cm^{-2} pore density and 1 mg cm^{-2} nominal wt.), respectively. The 50% cut-off diameter of the prefilter with 25 L min^{-1} flow rate was estimated to be 1.2 μm equivalent aerodynamic diameter (Ma *et al.*, 2001).

Additionally, for the size-resolved measurement of EC and OC, a 4-stage Andersen impactor sampler was also run. Aerosol particles were collected onto an 80 mm diameter quartz fiber filter (Whatman) at each stage. Sampling duration time was 6 hours and the airflow was maintained at approximately 23.8 L min^{-1}. The 50% cut-off sizes of each stage for the Andersen air sampler are 11 μm, 2.1 μm, 0.43 μm, 0.1 μm at stage-1, stage-2, stage-3, and back-up stage, respectively. To remove carbonaceous contaminants, by heating in an electric furnace at 700°C in air for 3 hours quartz fiber filters were pretreated.

Using our two different types of samplers, the size-classified particles were collected at once in a sampling campaign.

2.3 Analysis

PIXE with a proton beam of 6 mm diameter and 2.0 MeV energy from a Tandem Cockcroft accelerator was applied to the elemental analysis of soluble and insoluble fractions from bulk samples. Beam intensities from 10 to 60 nA were employed and the total dose were about 20 μC. X-ray with an energy of 14.8 keV emitted from the target was detected by a Si (Li) detector which had a resolution of 152 ev at 5.9 keV.

The aerosols deposited onto Nuclepore® filters were extracted ultrasonically with 10 mL of deionized water. And then the extracted water was filtrated through a 25 mm diameter Nuclepore® filter with 0.2 μm pore size to separate into the soluble and insoluble fractions. After filtration, the filtrate and residue were considered to be soluble and insoluble fractions, respectively. Blank filters were handled in the same manner as the samples. The more detailed analytical set-up and the procedures on sample pretreatment for PIXE analysis was given elsewhere (Ma *et al.*, 2003).

The TOR® method, which is a well-accepted technique for carbon analysis (Chow *et al.*, 1993), was employed in analyzing of EC and OC. Three 0.5 cm^2 punches were taken from the quartz filter set on each stage of the Andersen sampler and placed in the analyzer. After removing the oxygen in the oven atmosphere with helium, temperature is raised in several steps to 550℃ in a 100% helium atmosphere. The carbon evolved in each step is converted to methane, which is quantified by a flame ionization detector (FID). OC is defined as all carbon that evolves from the sample without added oxygen when heated up to 550°C. Two additional temperature steps of 700°C and 800°C are made. EC is defined as all carbon that evolves from the sample when heated up to 800°C in 2% oxygen in 98% helium atmosphere after the OC is removed. The optical absorption of the sample changes during the analysis, increasing during the steps without added oxygen and decreasing after oxygen is added. The optical absorption of the samples is monitored

throughout the analysis by the reflectance of a laser beam.

3. RESULTS AND DISCUSSION

Almost every vehicle on the road today exhausts particles less than 1 micron in diameter (PM_1) (Sucharov and Brebbia, 2001). For this reason, PM_{10} measurement is not a suitable for the impact of vehicle emissions as in a strongly traffic influenced environment. $PM_{2.5}$ measurements give more information about vehicle emissions but are still dominated by non-vehicle factors. Thus the particles fractionated into $d_p > 1.2\,\mu m$ and $d_p < 1.2\,\mu m$ by a two stage filter pack sampler employed in the present study is suitable instrument to estimate vehicle derived particles and non-vehicle derived particles, respectively.

3.1 Elemental composition

Fig. 2 shows the examples of PIXE spectra drawn by the soluble fractions of coarse and fine particles with the blank spectrum of a polycarbonate Nuclepore® film used as the substrate material. Relatively distinct peaks of Cl, Cr, and Mn were found at the blank spectrum of substrate material. However these background levels could be corrected by the ratio of integrated level of background counts to that of signal. The process assuring the measured values by PIXE was already described in elsewhere (Ma *et al.*, 2002) and was noted here briefly.

Generally, when the X-ray source is counted for a long time, the distribution of count rate can be fitted by the Poisson's distribution. In other words, the probability $P(N)$ which the number of X-ray proton (actual number = N_o) can be counted as $N(\geqq 0)$ is given as follow :

$$P(N) = (N_o^N/N!)\, e^{-No} \qquad (N_o > 0) \qquad (1)$$

Since the mean and dispersion are N in the Poisson's distribution, N_o can be written as

$$N-\sqrt{N} < N_0 < N+\sqrt{N} \qquad (68.3\%) \qquad (2)$$

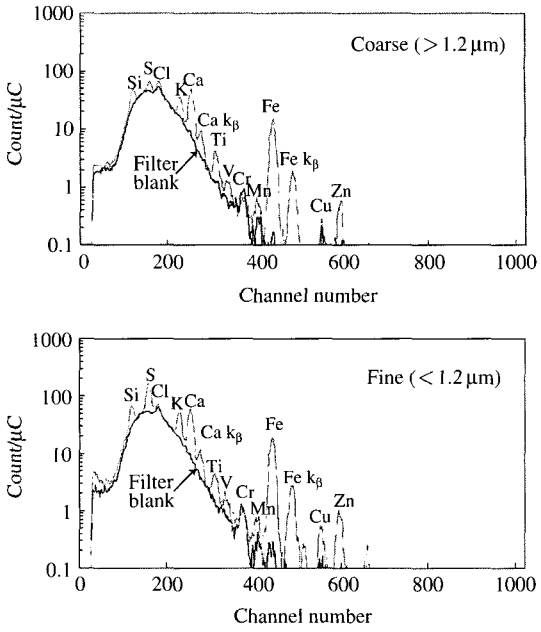

Fig. 2. Examples of PIXE spectra for the soluble fractions of coarse and fine particles collected in Buk-Ak tunnel.

$$N-2\sqrt{N} < N_0 < N+2\sqrt{N} \qquad (95.4\%) \qquad (3)$$

$$N-3\sqrt{N} < N_0 < N+3\sqrt{N} \qquad (99.9\%) \qquad (4)$$

In here, let's consider the case that the signal cannot be decided as peak or noise in one peak-width. If the integrated background count and integrated signal count are N_B and N_T, respectively, the integrated actual peak count can be written by $N_S = N_T - N_B$. In this study, if $N_S > 3\sqrt{N_B}$, the signal was considered as the actual peak.

The detection limits of each element calculated from the integrated background count of Nuclepore® filter, which was used as the backing material of particles, and elemental sensitivity was described in elsewhere (Ma *et al.*, 2002; Kasahara *et al.*, 1993).

Mass concentration (the sum of fine and coarse particles) in tunnel was 213 $\mu g\ m^{-3}$. This tunnel level of mass concentration is comparable to that of ambient level (57.1 $\mu g\ m^{-3}$) in Seoul (Ma *et al.*, 2001). The ratio of fine particles mass concentration to coarse particles mass concentration measured in

the present tunnel study (3.44) shows a quite different ratio from that of ambient measurements in the urban ambient air in Seoul (0.48) (Ma *et al.*, 2001). Since tunnel has a very distinct traffic variation depending on time series, we cannot fully discuss the particle mass concentration during a case of sampling campaign in this study. However, it is suggested that the high fine/coarse mass ratio within a tunnel was undoubtedly dominated by vehicular tailpipe, especially diesel trucks, emissions. Also since the inflow of outdoor air cannot be perfectly isolated from tunnel entrance, the effect of urban background air can be considered.

The determination of trace elements in tunnel particles with size-resolved characteristics and water solubility is helpful to understand their source profiles and to estimate their inflow from outside. Fig. 3 displays the elemental concentration of roadway tunnel particles divided into soluble and insoluble fractions as the functions of particle size. Total elemental mass concentration (the sum of insoluble coarse, soluble coarse, insoluble fine, and soluble fine) determined by PIXE is found to be 24 $\mu g\ m^{-3}$ and comprises only 11% of total aerosol mass concentration. The presence of soil origin components is strongly indicated by both coarse and fine fraction particles. As might be expected, the concentrations of Si, K, and Fe show enrichment in insoluble fraction. Fe probably occurs as a result of accumulation in street dust of small rust particles derived from automobiles and other iron objects. As stated by Rogge *et al.* (1993), mechanically generated soil dust particles are larger in size and, hence, deposit more easily by gravitational sedimentation or impaction. And those particles are expected to contribute to roadway tunnel dust accumulations. By the determination of elemental composition of vehicle and non-vehicle emissions, Hildemann *et al.* (1991) have reported that Al and Fe were also found in vehicle emission. In addition, several soil-derived elements were detected in fine aerosol emissions from highway vehicles (Nriagu and Davidson, 1986). Thus it is not unusual that soil origin components are enriched in tunnel dust.

In contrast to soil dust components, as the non-metallic elements, S and Cl show a major portion in soluble fraction and a minor portion in insoluble fraction, respectively. It seems reasonable to say that fine fraction S and Cl is formed by a gas-to-particle conversion in the tunnel atmosphere. On the one hand, their coarse fractions were formed by oxidization and absorption on coarse particle. Also it can be considered that the adsorption of their gas-phase onto the particles collected on prefilter during sampling.

Cr in insoluble fraction of fine particles was apparently detected and it might be derived from two sources, which are assigned as automobile exhaust and tire wear particles. Friedlander (1973) suggested that tire dust was also the major Zn source. Also Hopke *et al.* (1980) reported that the assignment of a component due to tire debris was based primarily on the presence of Zn, whose concentration was

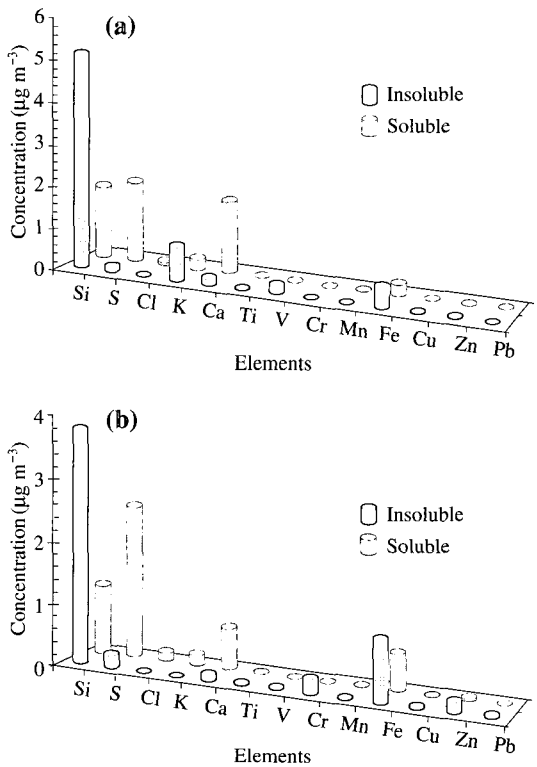

Fig. 3. Elemental concentration of coarse (a) and fine (b) particles divided into soluble and insoluble fractions.

ranged from 8 mg g^{-1} to 12 mg g^{-1} in the rubber. It could therefore be suggested that Zn determined as a level of 0.2 μg m^{-3} in insoluble fraction of fine mode particles was originated from tire wear particles.

Although it was banned to run leaded gasoline-powered vehicles in Korea, the burning of leaded gasoline for more than several tens of years has left a legacy of lead embedded in soils in urban areas, especially near and surface of roads with heavily congested automobile traffic. Thus lead in insoluble fine particles is probably derived from the past vehicle exhaust. Moreover, Rahn and Harrison (1974) have presented that the cement particles with enriched in lead were present in roadway dusts.

3.2 EC and OC

Size-resolved concentrations for EC, OC, and mass concentrations are given in Fig. 4. This figure clearly shows not only a strong size dependence of EC, OC, and mass concentrations, but also a high carbon fraction of particle mass. EC and OC concentrations have peaks at 0.1-0.43 μm particle aerodynamic diameter. The similar size distributions for mass, and carbonaceous compositions were reported in the former road and tunnel studies (Allen *et al.*, 2001; Rogge *et al.*, 1993). In the source profile study, Rogge *et al.* (1993) reported that the solvent-extractable organic compounds were found in fine particulate road dust. Also in the heavy traffic tunnel located in the San Francisco Bay area, the aerosol mass concentration mainly composed of EC and OC showed peak at 0.1-0.2 μm particle aerodynamic diameter (Allen *et al.*, 2001).

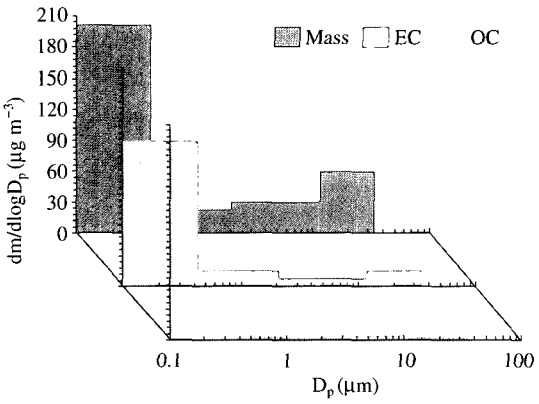

Fig. 4. Size distribution of EC, OC, and mass concentrations. D_p means aerodynamic particle diameter.

In fine fraction particles (<2.1 μm), the sum of EC and OC concentrations account for 80% of particle mass concentration. This mass concentration of carbonaceous components in tunnel can be compared with that of urban ambient particles (<2.1 μm) in Kyoto (52%) (Ma *et al.*, 2004).

Organic particulate carbon is both emitted in primary particulate form, and formed in the atmosphere through photochemical reactions. Low-volatility products from the gas-phase oxidation of reaction organic gases condense or absorb onto particle surfaces, or absorb into pre-existing particulate matter resulting in the addition of material to atmospheric particles. This is termed "secondary organic aerosol formation". This ratio between EC and OC is often used as a valuable tool for the identification of the secondary OC. However, it is difficult to accurately measure the particulate OC concentrations because particulate OC lost due to volatilization (i.e. negative artifacts) and adsorption of gas-phase organics onto the filter (i.e. positive artifact) during and/or after sampling.

4. CONCLUSIONS

A case study of tunnel particles, which was focused on the chemical composition of size-resolved particles, was performed in an urban roadway tunnel. Particle mass concentration in the tunnel atmosphere was compared to that of ambient air. The variation of traffic volume and vehicle type has a significant influence on the concentration of particles and the size distribution in tunnel. Thus detailed time-resolved measurement is strongly recommended to fully understand tunnel atmosphere. Also the studies on the gaseous pollutants emission and the calculation of various pollutants emission rate should be performed in a next step experiment. The trace elements in tunnel particles with size-resolved

characteristics and water solubility was successively determined by PIXE method. EC and OC concentrations are dominantly distributed in submicron particle fraction. In tunnel atmosphere, carbonaceous particles comprise majority of particle mass, while elemental components including heavy metals contribute slightly to the particle mass.

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