Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2011, 23(8) 1334–1341
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Comprehensive characterization of ambient nanoparticles collected near an industrial science park: Particle size distributions and relationships with environmental factors

Yuhjeen Huang*, Lingyen Hsu, Yunghsun Chang

Department of Biomedical Engineering and Environmental Sciences, "National" Tsing Hua University, Hsinchu 30013, Taiwan.
E-mail: yjhuang@mx.nthu.edu.tw

Received 23 September 2010; revised 14 November 2010; accepted 19 January 2011

Abstract

We investigated the characteristics of ambient particles and their relationships with various environmental factors, including gaseous pollutants (CH_4, non-methane hydrocarbons (NMHC), total hydrocarbons (THC), NOx, CO, SO_2), meteorological parameters (humidity, temperature), and time (day/night, workday/weekend). We used an electrical low-pressure cascade impactor to measure the number and size distributions of ambient particles (0.007–10 μm) that were collected approximately 1 km northwest of Hsinchu Science Park in Taiwan between February and May 2007. The number concentrations of particles were enhanced through photochemical reactions during the day. In addition, high traffic flow during workdays increased the formation of particulates. Except for SO_2, all of the gaseous pollutants we studied (CH_4, NMHC, THC, NOx, CO) correlated positively with the total number concentrations of ambient particles during daytime, indicating that they might contribute to the particulate burden. The poorer relationship between the SO_2 level and the total number concentration of particles suggests that SO_2 might participate indirectly in the nucleation process during particle formation, The high enrichment factors for Zn, Pb, Cu, and Mn, which mostly comprised the ultrafine particles (diameter: < 0.1 μm) and fine particles (diameter: 0.1–1 μm), presumably arose from emissions from traffic and high technology factories. Heterogeneous reactions on solid particles might play a role in the removal of SOx and NOx from the atmosphere. Sulfides and nitrides can further react with these local pollutants, forming specific Cu-containing compounds: CuO (39%), $CuSO_4$ (34%), and $Cu(NO_3)_2$ (27%), within the ambient particles in this industrial area.

Key words: environmental factors; ambient particles; electrical low-pressure impactor (ELPI); XANES

DOI: 10.1016/S1001-0742(10)60558-X

Citation: Huang Y J, Hsu L Y, Chang Y S, 2011. Comprehensive characterization of ambient nanoparticles collected near an industrial science park: Particle size distributions and relationships with environmental factors. Journal of Environmental Sciences, 23(8): 1334–1341

Introduction

Air pollution is mostly generated from human activity and from natural sources (e.g., volcanic eruptions, biomass burning, dust storms). Gases and aerosols in the atmosphere can interact through homogeneous and heterogeneous processes to form ambient aerosols. The compositions and mixing states of these atmospheric aerosols fluctuate as a result of various physical or chemical processes. For example, nucleation, coagulation, and condensation processes, which lead to decreased number concentrations of aerosol particles, can also change their size distribution (Longley et al., 2005; Huggins et al., 2000). Different locations and emission sources can result in the feature different compositions of particles in their ambient atmospheres (Sun et al., 2010; Zhao et al., 2010). Thus, source apportionment is an important issue when determining the relative responsibility of anthropogenic contributions to the degradation of ambient air quality.

In northern Taiwan, the Hsinchu Science Park comprises over 450 high technology companies dealing with integrated circuits, computers and peripherals, telecommunications, optoelectronics, precision machinery, and biotechnology. Because residential areas surround this park, it would be beneficial to characterize the nanoparticles present in the area. Moreover, we wished to investigate the relationships between the particles and environmental factors, allowing us to explore the physicochemical processes affecting particle formation, identifying their original sources, and monitoring the subsequent evolution of ambient particles. Several previous studies have related particle number concentrations to traffic-related gaseous pollutants (CH_4, non-methane hydrocarbons (NMHC), total hydrocarbons (THC), NO, NOx, CO) and meteorological parameters (relative humidity (RH), temperature (TEMP)) (Longley et al., 2005; Morawska et al., 1998; Ketzel et al., 2003; Olofson et al., 2009; Favez et al., 2010;

* Corresponding author. E-mail: yjhuang@mx.nthu.edu.tw

Sanroma et al., 2010). Longley et al. (2005) indicated that it might be possible to reliably predict number concentrations of particulates on an hourly basis from knowledge of NO*x* and CO concentrations alone. Establishing such relationships would be useful when attempting to prove that these gaseous pollutants are potential co-pollutants with particulates within urban areas, sharing a common source (e.g., vehicle emissions). Moreover, enrichment factors (EFs) can be derived, based on the fact that metals originating from relatively well-defined sources (e.g., Al and Fe, which originate mainly from the Earth's crust) can be distinguished from those derived through other processes. Matter from the Earth's crust and salts from the soil or sea are significant contributors to aerosol compositions near the Earth's surface. Comparisons of aerosol compositions in relation to crustal compositions can allow the contribution of anthropogenic sources to be discriminated. Another powerful technique for exploring the characteristics of metallic species is X-ray absorption spectroscopy (XAS) (Manceau et al., 1992a, 1992b; Huggins et al., 1993, 2000; Huffman et al., 1994; Priggemeyer et al., 1995; Tohno et al., 1998; Qi et al., 2003), which provides information on the electronic structures of absorption atoms, reflecting their oxidation states and chemical speciation. For example, when Huggins et al. (2000) performed the speciation of elements in ash products from the combustion of coal (As, Cr), residual oil (Ni, Cr), and in airborne PM_{10}, they found that the chromium and arsenic atoms existed predominantly in the less-toxic oxidation states Cr(III) and As(V), respectively. Tohno et al. (1998) and Qi et al. (2003) used XAS to study the chemical states of S and Si in atmospheric aerosols and the local structures around Fe in atmospheric aerosols, respectively. Few of these XAS reports, however, provided further discussions of the mechanisms of formation of particulate anions associated with metals in practical ambient particulate matter (PM) samples.

Our main objective of this study was to observe the variations in the number concentrations and characteristics of series of particles, from the micro to the nano scale, in ambient air near the Hsinchu Science Park in Taiwan under various environmental factors, such as the time (day/night, workday/weekend), the levels of gaseous pollutants (CH_4, NMHC, THC, NO*x*, CO, SO_2), and meteorological parameters (RH, TEMP). We calculated EFs for key elements to explore their possible emission sources near the Industrial Science Park. We also used ion chromatography and the Cu K-edge X-ray absorption near-edge spectroscopy (XANES) to determine the soluble anions (NO_2^-, NO_3^-, SO_4^{2-}) and speciation of the Cu-containing compounds in this area.

1 Materials and methods

1.1 Sampling site

The city of Hsinchu, situated near the northwest coast of Taiwan, covers an area of approximately 100 km^2 and has a population of approximately 0.35 million. The Hsinchu Science Park, having an area of approximately 6.5 km^2, is located on the southern side of the city, lying between 2,739,000 and 2,743,000 m latitude and 247,000 and 252,000 m longitude; its height above sea level is approximately 50–120 m. Hsinchu Science Park is surrounded by urban areas (residential colonies, commercial complexes, university campuses).

In this study, the ambient particles were sampled approximately 1 km northwest of Hsinchu Science Park (24°47′32″N, 120°59′29″E). The sampling site of the Industrial Science Park is represented pictorially in Fig. 1. Sampling took place five days each month from February to May 2007 to avoid the influence of typhoons (July–September) or northeasterly monsoons (September–December). The samplings were also avoided on rainy day. The prevailing wind speed during the sampling period ranged from 14.3 to 15.9 m/sec; the wind direction was southwest (197 ± 70)°; the temperature varied in the range from 17.7 to 25.7°C; the relative humidity ranged from 73% to 81%.

1.2 Particle sampling

The number concentrations and size distributions of particles in 12 sets of aerodynamic diameters (ranging from 0.007 to 10.0 μm) were monitored directly using a Dekati Electrical Low Pressure Impactor (ELPI) equipped with an Al foil filter. The samples were then collected on Teflon filters by the ELPI, which grouped particles into three size ranges: ultrafine (diameter: < 0.1 μm; $PM_{0.1}$), fine (diameter: 0.1–1 μm; $PM_{0.1-1.0}$), and coarse (diameter: 1–10 μm; PM_{1-10}), for further chemical component analysis.

1.3 Gaseous pollutants and meteorological parameter measurement

Data for the gaseous pollutants (CH_4, NMHC, THC, NO*x*, CO, SO_2) and meteorological parameters (RH, TEMP) were obtained from environmental monitoring stations. The location is displayed in Fig. 1 at site c. NO*x* measurements were taken using an Ecotech 9841 chemiluminescent analyzer; CO was measured using a Horiba infrared absorption analyzer (Horiba Ltd., Japan). NMHC and THC measurements were taken using a Dani 462 flame ionization detector (DANI Instruments S.P.A., Italy). SO_2 was monitored using an Ecotech 9841 UV fluorescence analyzer. RH and TEMP data were recorded using a Metone 083C apparatus.

2 Analytical procedures

2.1 Water-soluble ions

To extract particles from filters, the samples were placed into high-purity 18.2-MΩ de-ionized (DI) water (4 mL) and then subjected to powerful ultrasonication until all of the particles had completely been removed from the filters. Ion chromatography (Dionex DX-1000) was used to analyze the soluble anions (NO_2^-, NO_3^-, SO_4^{2-}) from the samples; an anion exchange column (Dionex AS12) was used to measure the levels of these anions.

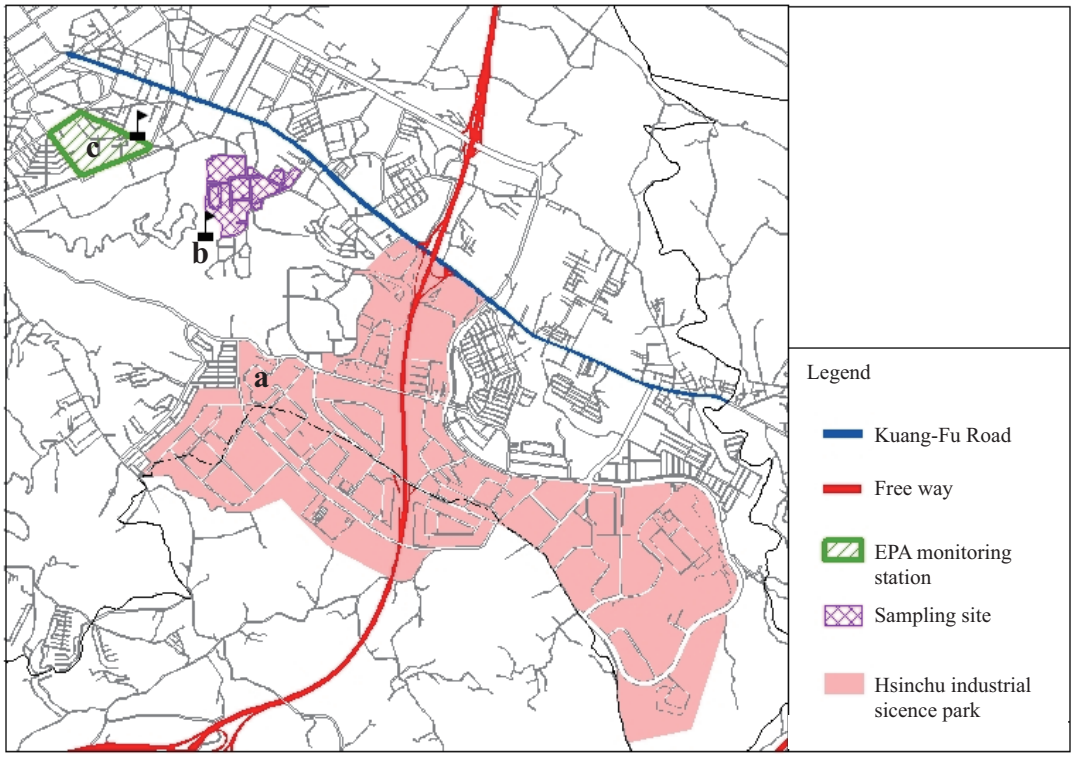

Fig. 1 Map displaying the Hsinchu Industrial Science Park (a), the sampling site used in this study (b), and the EPA monitoring station (c). Sampling period: February–May, 2007; temperature: 17.7–25.7°C; relative humidity: 73%–81%; wind velocity: 14.3–15.9 m/sec.

2.2 Heavy metals

A new wave Up-213 laser ablation (LA) instrument coupled with an Agilent 7500a inductively coupled plasma/mass spectrometer (ICP-MS) (USA) was used to analyze the trace elements in the particles. LA-ICP-MS offers direct multi-metal analysis of samples without the need for sample pretreatment. Nd:YAG lasers were employed for LA. The fundamental wavelength of the Nd:YAG lasers was 1064 nm; frequency multiplying was used to obtain wavelengths of 213, 266, 355, and 532 nm.

XANES spectra were recorded, using the Wiggler beamline of the Taiwan Synchrotron Radiation Research Center (SRRC), to explore the Cu species present in the particles. The electron storage ring was operated at energy of 1.5 GeV and a current of 120–200 mA. A Si (1 1 1) double-crystal monochromator was used to select the energy, with an energy resolution of 1.9×10^{-4} (eV/eV). The photon energy was calibrated using the characteristic pre-edge peaks in the absorption spectrum of Cu foil (8979 eV). The XAS data were analyzed using WinXAS 2.2 software. Principal component (factor) analysis was used in the data treatment to optimize the quantitative extraction of the relative concentration of Cu species (Ressler, 1997).

3 Results and discussion

Figure 2 presents the average values of the number and size distributions of the ambient particles, monitored downwind (southwest wind, 14.3–15.9 m/sec) of the Hsinchu Science Park during the daytime and nighttime on workdays and weekends. The total number concentrations of the particles were within the range from 1×10^4 to 6×10^4 particles/cm^3, close to the value reported by Shi et al. (2007) and Roth et al. (2008). Moreover, we found that the highest number concentrations occurred for the fine particles ($PM_{0.1-1.0}$), followed by the ultrafine particles ($PM_{0.1}$), which might be due to their higher coagulation rates, the lifetimes of ultrafine particles are very short (Bukowiecki et al., 2003). We also observed significant decreases in the number concentrations of ambient particles monitored on weekends, relative to those on weekdays. In Hsinchu Science Park, over 450 tenant companies employ more than 130,000 people, and automobiles or motorcycles are their main vehicles. Meantime, the rush-hour traffic flow (2280 passenger car units per hour) on the freeway exit near the Hsinchu Science Park on workdays is more than 1.5 times that found on weekends. These variations might correspond to the decreased levels of ambient particles on weekends.

Figure 3 displays correlation coefficients revealing the relationships between the total number concentrations and various environmental factors (TEMP, RH, CH_4, NMHC, THC, NOx, CO, SO_2). The total number concentrations and environmental factors are provided as hourly average values. Figure 2 shows that the ratio of the total number concentration at daytime to that at nighttime ranged between 3 and 6. The number concentrations of particles were higher during daytime hours, suggesting that nucleation and subsequent particle growth occurred more readily during the daytime via photochemical processes. This result is consistent with those reported by Kulmala et al. (2004), who monitored the formation and growth

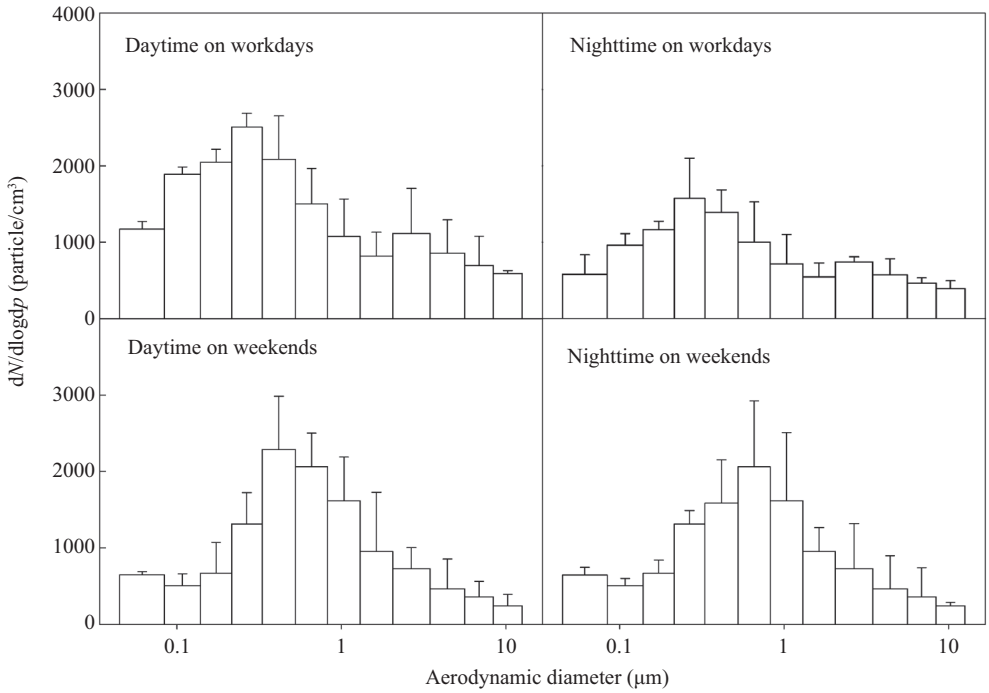

Fig. 2 Variations in mean number concentrations (N) and size (P) distributions of ambient particles collected downwind of the Industrial Science Park.

of particles over the last decade and found that almost all nucleation events occurred during the day. Boy and Kulmala (2001) concluded that solar UV radiation indirectly influenced the formation and growth of particles. Additionally, during the daytime, the total number concentrations of ambient particles were influenced significantly by the temperature and RH. In Fig. 2, however, we observe that only the number concentrations of the fine particles increased at night. The formation and growth of particles did not only depend on the temperature and humidity: other environmental factors were also important. In the absence of photochemical processes, gaseous environmental factors had poor relationships with the total particle number concentration, potentially limiting the formation and growth of particles at night. In contrast, all of the gaseous environmental factors that we studied (CH_4, NMHC, THC, NOx, CO) correlated positively with the particle number concentrations during the daytime, except for SO_2. Most photochemical process for organic aerosol formation involve the formation of semivolatile organic gases, originating from the gas phase reactions of parent hydrocarbons (CH_4, NMHC, THC) with OH radicals. Therefore, secondary organic aerosols might contribute significantly to the fine particulate burden. Acidic precursors (NOx) can enhance the amounts of organic materials that participate in the growth of nucleated particles (Kulmala et al., 2004). Therefore, in Hsinchu Science Park, high emissions of CO and NOx from mobile (e.g., vehicles) source (more than 1.5 times of traffic flow during workdays) tend to increase the formation of particulates.

Because the source and species of particles are various in different areas, it is essential to measure the constituents of ambient particles in Hsinchu Science Park. Figure 4 displays the variations in the concentrations of the anions NO_2^-, NO_3^-, and SO_4^{2-} in the particles from the Hsinchu Science Park. The concentration of nitrate ions was higher in the larger particles. During the particle growth process, nitrite ions in the particles were presumably oxidized to nitrate ions. Figure 4 also reveals that the total concentrations of NO_3^- in the fine and coarse particles at nighttime were higher than those during the daytime. Nitrate radicals are produced effectively at nighttime; they lead to the production of N_2O_5, which can react with water molecules on the surfaces of particles to form HNO_3 (Wark et al., 1998). Thus, more HNO_3 was adsorbed on the particles at nighttime.

We found that SO_2 had a poor correlation with the number concentration of accumulation-mode particles, indicating that SO_2 participates indirectly in the nucleation event. Generally, the oxidation of SO_2 in an unpolluted atmosphere is a slow process; therefore, other pollutant species must be involved in oxidation in an atmosphere polluted with SO_2. Heterogeneous reactions on solid particles should play a role in the removal of SO_2 from the atmosphere. The particle function as nucleation centers and act as catalysts that grow in size through the accumulation of reaction products. Meantime, the composition of the original particle may change. Heterogeneous reactions between SO_2 and the nanoparticles might dominate at Industrial Science Park, thereby oxidizing SO_2 into SO_4^{2-}. As a result, we found that most of SO_4^{2-} ions existed in the fine and coarse particles in the atmosphere at the Industrial Science Park. Because these S species were released by sea spray, from the soil, or from industrial sources (e.g., sulfuric fertilizer plants, power plant scrubbers, acid mine drainage), we sought to identify the possible sources of these pollutants and to realize their contributions to the total particle levels.

Element enrichment factors (EFs) were initially developed to determine the origins of elements in the

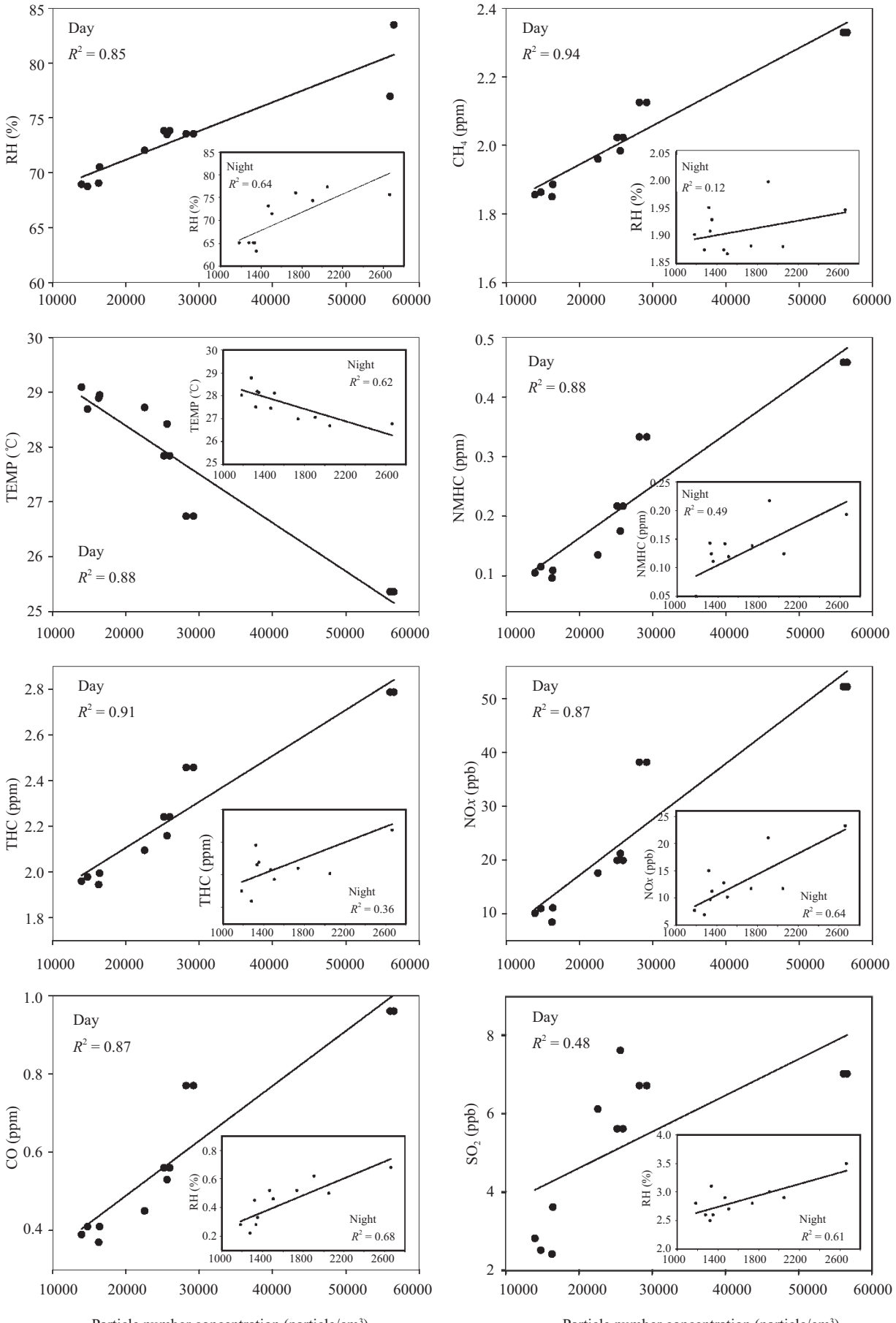

Fig. 3 Correlations between total number concentrations of ambient particles and environmental factors during the daytime and nighttime.

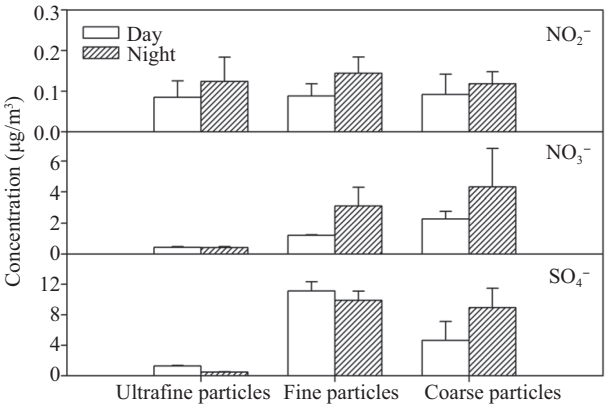

Fig. 4 Variations in concentrations of NO_2^-, NO_3^- and SO_4^{2-}anions in ambient ultrafine, fine, and coarse particles sampled near the Industrial Science Park during the daytime and nighttime.

atmosphere, with index elements from the Earth's crust (e.g., Si Al, Fe, Ti, Sc) selected for their stability and quantity. In this study, we used rustal EF to evaluate the relative strength between crustal (natural) and non-crustal (anthropogenic) sources in the Hsinchu Science Park. We chose Fe as the index element for the crust source. The abundances of the targeted crustal elements were obtained from the data provided by Taylor (1964). The EF for element X in the PM was calculated using Eq. (1):

$$\mathrm{EF} = \frac{(X/\mathrm{Fe})_{\mathrm{Atmosphere}}}{(X/\mathrm{Fe})_{\mathrm{Crust}}} \quad (1)$$

Figure 5 divides all of the elements into three broad categories based on their EFs: (1) low range (EF < 10; e.g., Ti, Cr, As, Se, Sr, Cd, Ba); (2) moderate range (10 < EF < 100; e.g., Mn, Cu, Pb); and (3) high range (EF > 100; e.g., K, Zn, Na). Most of the EFs of the crustal elements were less than 10. Hsinchu is located near the northwest coast of Taiwan. We suspect that natural pollutant sources, such as soil and marine salts, might be responsible for these results. The EFs calculated for the individual average concentrations of Zn, Mn, Cu, and Pb were all greater than 10, suggesting that these elements arose from anthropogenic sources. Accordingly, our results indicate that several sources, including vehicle-related emissions (Miguel et al., 1997; Wongphatarakul et al., 1998) and industrial activity, contributed to the levels of these metal elements in the study area. Some anthropogenic elements (e.g., Cu, Na) were present at higher concentrations on workdays than during the weekends. There are over 450 high technology companies in Hsinchu Science Park; for example, wafer manufacture, cleaning, or etching processes might release inorganic and volatile organic solvents or particles. We suspect that the exhaust of these anthropogenic elements might be deeply associated with factory operations. The EFs of metallic elements in the fine, ultrafine, and coarse particulates followed different distribution trends. Some of the EFs for metallic elements in the ultrafine and fine particulates were higher than those in the coarse particulates (e.g., Mn, Cu, Pb, Zn); others were higher in the coarse particles (e.g., Mg, Al, Ca, Na). Previous studies have considered the levels of Pb and Mn as a traffic pollutant index (Miguel et al., 1997; Wongphatarakul et al., 1998; Lu et al., 2003). Furthermore, there are over 391,600 mobile sources (including buses, trucks, passenger cars, pick-up trucks, specially constructed vehicles, and motorcycles) registered in Hsinchu City, with heavy traffic flows (averaging 2280 passenger car units per hour) on the freeway exit near the Hsinchu Science Park. The wearing of tires and brakes contributes to the Zn and Cu loads in street dust. In the semiconductor industry, large amounts of acidic or basic solvents and metal-containing materials (e.g., Cu, Pb) are used in production processes, thereby potentially changing the compositions of trace elements in the smaller particles. Because Cu-containing compounds are released from both high technology industries and vehicles, accumulating in the form of fine particles, we were interested in determining their compositions in the ambient particles. The component fits of the XANES

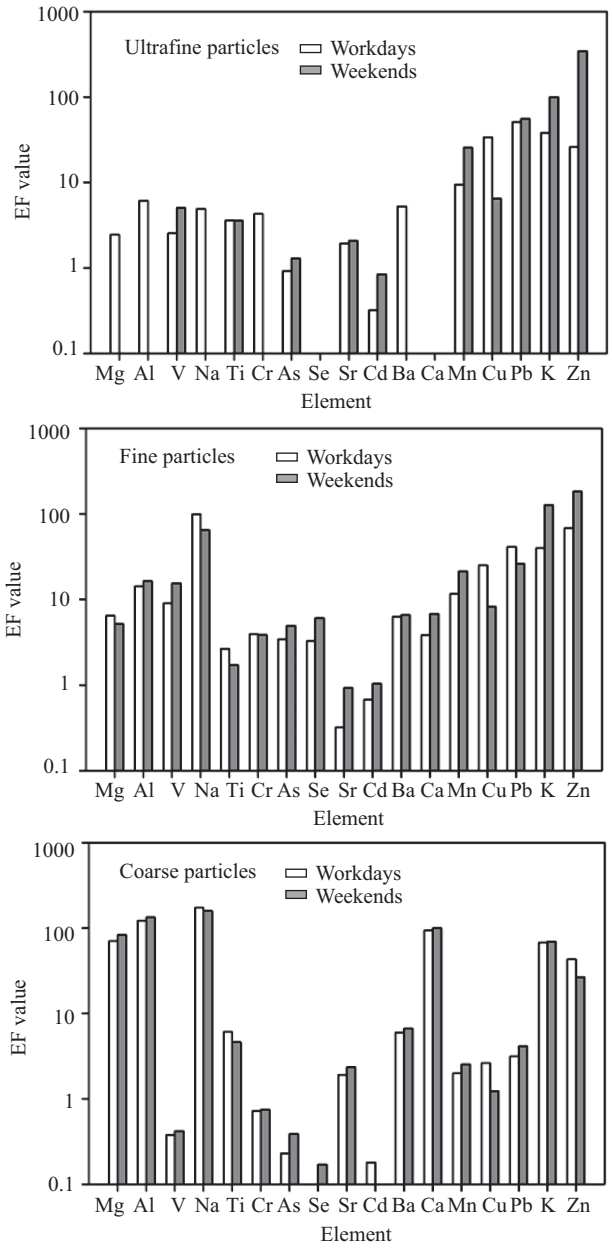

Fig. 5 Average enrichment factors (EFs) for various elements in ultrafine, fine, and coarse particles sampled during the daytime on workdays and weekends around the Industrial Science Park.

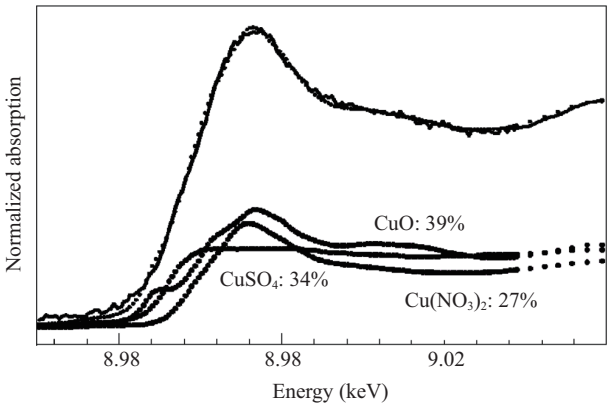

Fig. 6 XANES spectra of Cu species in the fine particles collected near the Industrial Science Park.

spectra (Fig. 6) revealed that CuO (39%), $CuSO_4$ (34%), and $Cu(NO_3)_2$ (27%) were present in the fine particles. Therefore, not all of the SO_4^{2-} or NO_3^- ions existed in the form of ammonium compounds. Once these acidic precursors, N or S species, absorbed onto the particles, they could recombine with the elements on the particles to form special compounds that are particularly characteristic of this area.

4 Conclusions

In the Hsinchu Science Park, we found that photochemical reactions indirectly influenced the formation and growth of particles, leading to higher total number concentrations of particles during the daytime. Human and factory activities both influenced the particle number concentrations, as evidenced by significant differences between workday and weekend levels. In addition, all of the gaseous pollutants that we studied (CH_4, NMHC, THC, NOx, CO) correlated positively with the particle number concentration, except for SO_2. Heterogeneous reactions of SO_2 and NOx with the nanoparticles might dominate in the Industrial Science Park, leading to SO_2 and NOx being oxidized to SO_4^{2-} and NO_3^-, respectively, thereby forming various unusual species (e.g., $CuSO_4$, $Cu(NO_3)_2$) during the particle growth process. Moreover, we found evidence suggesting that the hazardous heavy metals Zn, Pb, Cu, and Mn were exhausted from anthropogenic sources. The Cu-containing compounds CuO (39%), $CuSO_4$ (34%), and $Cu(NO_3)_2$ (27%) existed in the fine particles, presumably released from the high technology factories and/or vehicles, in the atmosphere at the Hsinchu Science Park; there should be concern regarding their potential hazards. The health of residents living near the Hsinchu Science Park might be threatened by the emission of these pollutants. Therefore, it will be necessary to monitor these pollutants over a long period.

Acknowledgment

We thank the "National" Science Council of Taiwan (NSC: 96-2113-M-007-029-MY) for financial support.

References

Boy M, Kulmala M, 2001. Nucleation events in the continental boundary layer: Influence of physical and meteorological parameters. *Atmospheric Chemistry and Physics Discussions,* 1(2): 239–276.

Bukowiecki N, Dommen J, Prévát A S H, Weingartner E, Baltensperger U, 2003. Fine and ultrafine particles in the Zürich (Switzerland) area measured with a mobile laboratory: An assessment of the seasonal and regional variation throughout a year. *Atmospheric Chemistry and Physics Discussions*, 3(3): 2739–2782.

Favez O, Haddad I E, Piot C, Boréave A, Abidi E, Marchand N et al., 2010. Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France). *Atmospheric Chemistry and Physics Discussions*, 10: 559–613.

Huffman G P, Huggins F E, Shah N, Zhao J, 1994. Speciation of arsenic and chromium in coal and combustion ash by XAFS spectroscopy. *Fuel Processing Technology*, 39(1-3): 47–62.

Huggins F E, Shah N, Zhao J, Lu F, Huffman G P, 1993. Nondestructive determination of trace element speciation in coal and coal ash by XAFS spectroscopy. *Energy Fuels*, 7(4): 482–489.

Huggins F E, Huffman G P, Robertson J D, 2000. Speciation of elements in NIST particulate matter SRM 1648 and 1650. *Journal of Hazardous Materials*, 74(1-2): 1–23.

Ketzel M, Wåhlin P, Kristensson A, Swietlicki E, Berkowicz R, Nielsen O J et al., 2003. Particle size distribution and particle mass measurements at urban, near-city and rural levels in the Copenhagen area and southern Sweden. *Atmospheric Chemistry and Physics Discussions*, 3(6): 5513–5546.

Kulmala M, Vehkamäki H, Petäjä T, Maso M D, Lauri A, Kerminen V M et al., 2004. Formation and growth rates of ultrafine atmospheric particles: A review of observations. *Journal of Aerosol Science*, 35(2): 143–176.

Longley I D, Inglis D W F, Gallagher M W, Williams P I, Allan J D, Coe H, 2005. Using NOx and CO monitoring data to indicate fine number concentrations and emission factors in three UK conurbations. *Atmospheric Environment*, 39(28): 5157–5169.

Lu H C, Tsai C J, Hung I F, 2003. Atmospheric lead concentration distribution in Northern Taiwan. *Chemosphere,* 52(6): 1079–1088.

Manceau A, Gorshkov A I, Drits V A, 1992a. Structural chemistry of Mn, Fe, Co, and Ni in manganese hydrous oxides. Part I: Information from XANES spectroscopy. *American Mineralogist*, 77: 1133–1143.

Manceau A, Gorshkov A I, Drits V A, 1992b. Structural chemistry of Mn, Fe, Co, and Ni in manganese hydrous oxides. Part II: Information from EXAFS spectroscopy and electron and X-ray diffraction. *American Mineralogist*, 77: 1144–1157.

Miguel E D, Llamas J F, Chacón E, Berg T, Larssen S, Royset O et al., 1997. Origin and patterns of trace elements in street dust: Unleaded petrol and urban lead. *Atmospheric Environment*, 31(17): 2733–2740.

Morawska L, Thomas S, Bofinger N, Wainwright D, Neale D, 1998. Comprehensive characterization of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants. *Atmospheric Environment*, 32(14-15): 2467–2478.

Olofson K F G, Andersson P U, Hallquist M, Ljungström E, Tang

L, Chen D et al., 2009. Urban aerosol evolution and particle formation during wintertime temperature inversions. *Atmospheric Environment*, 43(2): 340–346.

Priggemeyer S, Eggers-Borkenstein P, Ahlers F, Krebs B, Henkel G, Koerner M et al., 1995. XAS investigations on the iron-zinc center of purple acid phosphatase from red kidney beans. *Inorganic Chemistry*, 34(6): 1445–1454.

Qi J, Zhang M, Feng L, Li X, 2003. An EXAFS study on the local structure around iron in atmospheric aerosols collected in the Qingdao area. *Molecules*, 8(1): 31–39.

Ressler T, 1997. WinXAS: A new software package not only for the analysis of energy-dispersive XAS data. *Journal de Physique IV France*, 7(C2): 269–270.

Roth E, Kehrli D, Bonnot K, Trouvé G, 2008. Size distributions of fine and ultrafine particles in the city of Strasbourg: Correlation between number of particles and concentrations of NOx and SO_2 gases and some soluble ions concentration determination. *Journal of Environmental Management*, 86(1): 282–290.

Sanroma E, Palle E, Sanchez-Lorenzo A, 2010. Long-term changes in insolation and temperatures at different altitudes. *Environmental Research Letters*, 5(2): 024006.

Shi Z B, He K B, Yu X C, Yao Z L, Yang F M, Ma Y L et al., 2007. Diurnal variation of number concentration and size distribution of ultrafine particles in the urban atmosphere of Beijing in winter. *Journal of Environmental Sciences*, 19(8): 933–938.

Sun F F, Wen D Z, Kuang Y W, Li J, Li J L, Zuo W D, 2010. Concentrations of heavy metals and polycyclic aromatic hydrocarbons in needles of Masson pine (*Pinus massoniana* L.) growing nearby different industrial sources. *Journal of Environmental Sciences*, 22(7): 1006–1013.

Taylor S R, 1964. Abundance of chemical elements in the continental crust: A new table. *Geochimica et Cosmochimica Acta*, 28(8): 1273–1285.

Tohno S, Kawai J, Chatani S, Ohta M, Kitajima Y, Yamamoto K et al., 1998. Application of X-ray absorption fine structure (XAFS) spectrometry to identify the chemical states of atmospheric aerosols. *Journal of Aerosol Science*, 29(S1): S235–S236.

Wark K, Warner C F, Davis W T, 1998. Air pollution: Its Origin and Control. (3rd ed.). Addision Wesley.

Wongphatarakul V, Friedlander S K, Pinto J P, 1998. A comparative study of $PM_{2.5}$ ambient aerosol chemical databases. *Environmental Science and Technology*, 32(24): 3926–3934.

Zhao J P, Zhang F W, Chen J S, Xu Y, 2010. Characterization of polycyclic aromatic hydrocarbons and gas/particle partitioning in a coastal city, Xiamen, Southeast China. *Journal of Environmental Sciences*, 22(7): 1014–1022.