

NH₄⁺, NO₃⁻, and SO₄²⁻ in roadside and rural size-resolved particles and transformation of NO₂/SO₂ to nanoparticle-bound NO₃⁻/SO₄²⁻

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ABSTRACT

This study investigates ammonium, nitrate, and sulfate (NH₄⁺, NO₃⁻, and SO₄²⁻) in size-resolved particles (particularly nano (PM_{0.01–0.056})/ultrafine (PM_{0.01–0.1})) and NO_x/SO₂ collected near a busy road and at a rural site. The average (mass) cumulative fraction of secondary inorganic aerosols (SO₄²⁻+NO₃⁻+NH₄⁺) in nano or ultrafine particles at the roadside was found to be three to four times that at the rural site. The above three secondary inorganic aerosol species were present in similar cumulative fractions in particles of size 1–18 μm at both sites; however, dissimilar fractions were observed for Cl⁻, Na⁺, and K⁺. The nitrogen ratios (NRs: NR = NO₃⁻-N/(NO₃⁻-N + NO₂-N)), sulfur ratios (SRs: SR = SO₄²⁻-S/(SO₄²⁻-S + SO₂-S)), dNR/D_p (derivative of NR with respect to D_p (particle diameter)), and dSR/D_p (derivative of SR with respect to D_p) at the roadside were higher than those at the rural site for nano/ultrafine particles. At both sites (particularly the roadside), the nanoparticles had significantly higher dNR/D_p and dSR/D_p values than differently sized particles, implying that NO₃⁻/SO₄²⁻ (from NO₂/SO₂ transformation or NO₃/SO₄²⁻ deposition) were present on these particles.

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1. Introduction

Primary aerosols may be directly emitted into the atmosphere from sources such as vehicles, factories, seas, and the earth's crust, while secondary inorganic aerosols that contain nitrogen or sulfur species (such as NH₄⁺, NO₃⁻, and SO₄²⁻) with diameters less OR than 2.5 μm are generated in the atmosphere in reactions with gaseous precursors. Raes et al. (2000) concluded that secondary particulate sulfates and nitrates were formed by the following two main pathways; (1) photochemical oxidation of SO₂ and NO_x precursors in the gas phase to highly soluble acids followed by uptake into pre-existing aerosols or cloud droplets and (2) oxidation in the aqueous phase, followed by evaporation of cloud droplets. In an urban atmosphere, the gas-phase pollutants (including hydrocarbons, CO, and NO_x) and ultrafine particles (D_p < 0.1 μm) emitted from traffic may cause serious air pollution (Dockery et al., 1993; Schwartz, 1991; Kittelson et al., 2004). The nano and ultrafine particles in an urban atmosphere come mainly from motor vehicle emissions (Palmgren et al., 2003).

Particles emitted from engines usually have sizes associated with nucleation (less than 30 nm) and ultrafine (30–100 nm) modes. These two modes commonly result from the coagulation of primary particles and the condensation of gaseous pollutants. The accumulation mode is chiefly composed of photochemical secondary inorganic aerosols (sulfates and nitrates) of larger sizes, in the range 0.1–2 μm (Palmgren et al., 2003). Ying and Kleeman (2006) found that, in the South Coast Air Basin (SoCAB), 83% of nitrates and 82% of ammonium ions in PM_{2.5} were formed from precursor gaseous species; furthermore, 67% of nitrates in PM_{2.5} came from mobile sources, including diesel engines (34.6%), non-gasoline engines unequipped with catalytic converters (4.7%), and gasoline engines equipped with catalytic converters (28.1%). Notably, the atmospheric conditions at a location also influence observations of secondary aerosol species.

Recent studies have demonstrated that secondary inorganic aerosols account for a significant portion of the concentration of PM_{2.5} in SoCAB (Christoforou et al., 2000; Schauer et al., 2002; Kim et al., 2000, 2002). This study determines whether (secondary) particulate NO₃⁻/SO₄²⁻ species transformed from gaseous NO₂/SO₂ are mainly present on smaller particles (particularly nano/ultrafine particles). Size-resolved nano, ultrafine, fine, and coarse particles were collected from the side of a heavily trafficked road and at

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a rural site using a micro-orifice uniform deposition impactor (MOUDI) and a Nano-MOUDI. Particle-bound water-soluble ion species (especially NH_4^+ , NO_3^- , and SO_4^{2-}) and atmospheric NO_x/SO_2 were analyzed by ion chromatography and using NO_x/SO_2 monitoring instruments, respectively. The nitrogen ratios (NRs), sulfur ratios (SRs), derivative of NR with respect to particle diameter (dNR/D_p), and derivative of SR with respect to particle diameter (dSR/D_p) were determined to evaluate the phase transformation of NO_2/SO_2 into particulate $\text{NO}_3^-/\text{SO}_4^{2-}$ on the size-resolved particles.

2. Experimental section

2.1. Collection of particulates

Atmospheric particulate samples were collected near a major road (20 m wide) in southern Pingtung city and at a rural site in southern Taiwan (Fig. 1). The traffic sampling site was about 8 m from the front of the main entrance of a college, and 10 m away from the centerline of the road, which has a speed limit of 50 km h^{-1} and had an average traffic loading of 72,000 vehicles per day during the sampling period from February to April 2004. In addition to the traffic, two major local sources of possible pollutant emission existed. One is the Pingtung Industrial Park (146 factories, mainly for manufacturing electronics, metals, and food and the other is a crematorium. These are approximately 2 km north and 1 km south, respectively, of the road sampling site. Some possible

pollutant sources at large distances from the study sites are located in Kaohsiung City and Kaohsiung County ($\sim 30 \text{ km}$ north of the sampling site), which have dense populations and four industrial parks that are associated with traffic and industrial pollutant emissions, respectively. The rural site is located on the roof of a three-storey building (9 m high) at the National Pingtung University of Science & Technology – roughly 15 km south of the urban site.

A MOUDI and a Nano-MOUDI (Model No.100 and 115, respectively; MSP Co., Minneapolis, MN), equipped with Teflon filters (with diameters of 37 and 47 mm, respectively), were used to collect size-resolved aerosol samples. These impactors effectively separated the particulate matter into 13 size ranges (at 50% efficiency) with the following equivalent cut-off diameters; 18–10, 10–5.6, 5.6–3.2, 3.2–1.8, 1.8–1.0, 1.0–0.56, 0.56–0.32, 0.32–0.18, 0.18–0.1, 0.1–0.056, 0.056–0.032, 0.032–0.018, and 0.018–0.010 μm . The particles were divided into four-size groups – coarse ($\text{PM}_{2.5-10}$), fine ($\text{PM}_{0.01-2.5}$), ultrafine ($\text{PM}_{0.01-0.1}$: $0.01 \mu\text{m} < \text{D}_p < 0.1 \mu\text{m}$), and nano ($\text{PM}_{0.01-0.056}$: $0.01 \mu\text{m} < \text{D}_p < 0.056 \mu\text{m}$). The sampling flow rates for the MOUDI and Nano-MOUDI were 30 L min^{-1} and 10 L min^{-1} , respectively. Sampling that covered four seasons (from August 2004 to May 2006) was performed seven times (for three days each time) at the traffic site and four times (six days each time) at the rural site, corresponding to 21 and 24 total sampling days, respectively, at the two sites. In each sampling period, the samplers were run for 15 (from 7:00 to 22:00) and 24 (from 7:00 to 7:00) hours daily at the roadside and rural sites, respectively. Silicon grease was applied to the surface of each filter that was installed in the MOUDI sampler and the Nano-MOUDI sampler. The greased filter-strips were baked in an oven at $60 \text{ }^\circ\text{C}$ for 90 min to stabilize the silicon grease before sampling, to minimize particle bounce between the MOUDI stages during sampling (Chang et al., 1999, 2001; Park et al., 2003), although the inevitable particle bounce may have caused sampling artifacts (even when Nano-MOUDI samplers were used (Park et al., 2003)). Before and after each sampling, the filters were dried for 24 h in a desiccator at $25 \text{ }^\circ\text{C}$ in 40% relative humidity. They were then weighed on an electronic balance (AND HM202) with a precision of $10 \mu\text{g}$. The concentration of suspended particulate matter was determined by dividing the mass by the volume of the sampled air. In this study, 143 samples (thirteen stages \times eleven runs) were obtained. The mean air temperature, relative humidity, and wind speed (in various directions, prevailing southwest ($\sim 40\%$)) were $22.0 \text{ }^\circ\text{C}$ ($15.2\text{--}29.1 \text{ }^\circ\text{C}$), 77.8% ($47.9\text{--}100\%$), and 2.0 m s^{-1} ($0.0\text{--}5.2 \text{ m s}^{-1}$), respectively, during the sampling period which was without rain.

2.2. Analysis of NO_x and SO_2 in an air quality-monitoring vehicle

An air quality-monitoring vehicle was adopted to determine the concentration of the atmospheric NO_x and SO_2 sampled close to the traffic. The NO_x and SO_2 monitoring instruments were HORIBA/APNA-360 and HORIBA/APSA-360, respectively. The monitors automatically recorded data every minute and calculated average values (in ppb) per hour with a detection limit of 0.5 ppb for both NO_x and SO_2 . Prior to sampling, the instruments were calibrated using multi-point calibration. Zero/span calibration and drift inspection were conducted before and after sampling.

2.3. Water-soluble ion analysis and quality control

Before the particle-bound water-soluble inorganic species (Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) were chemically analyzed, each Teflon filter with collected particles were quartered and then ultrasonically (UC-300) extracted in a 10 ml ultra-pure water bath (specific resistance $\geq 18.3 \text{ M}\Omega\text{cm}$) for 120 min. Although the greased surface of each filter somewhat reduced the contact

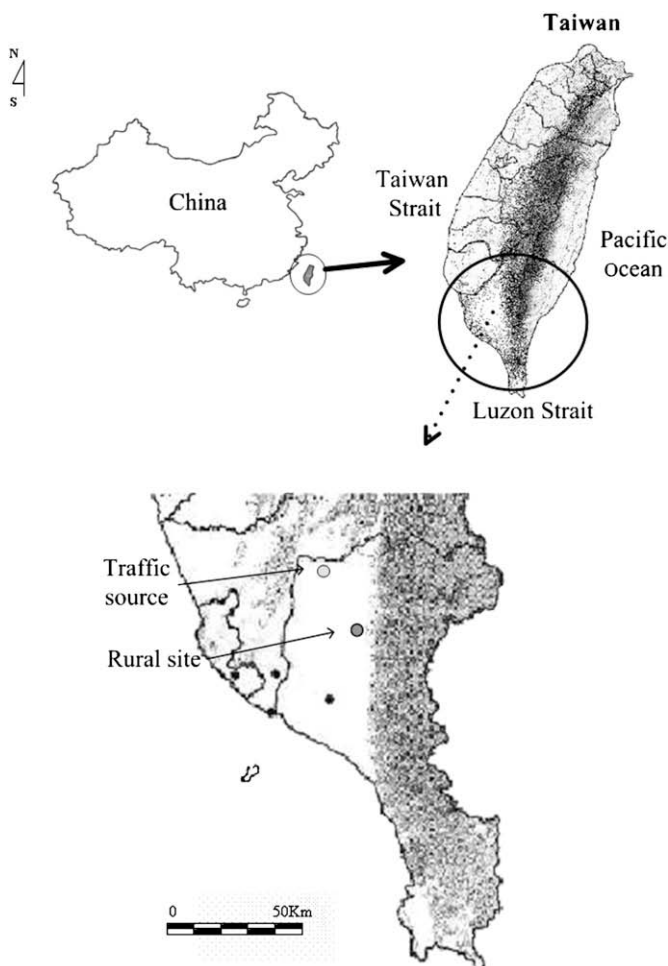


Fig. 1. Sampling sites.

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