

## Aerosol Source Sampling in a Mid-Scale City, Gainesville, FL

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### Abstract

Five major sources for the ambient aerosol in Gainesville, FL were sampled by using a Micro-Orifice Uniform Deposit Impactor (MOUDI) and a University of Washington Mark III Cascade Impactor. The samples were analyzed for carbons and ions. Soil dust, unpaved road dust, cement dust particles and marine aerosols were mainly in the coarse mode, while particles from transportation showed a bi-modal or tri-modal distribution.

Carbon in soil dust was mainly organic, while carbon in unpaved road dust was mainly elemental. In transportation aerosols, carbons were mostly found in the ultra-fine range ( $< 0.18 \mu\text{m}$ ) and were likely from gasoline vehicles. For ionic species, soil dust was rich in  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ , and  $\text{Ca}^{2+}$ . In unpaved road dust,  $\text{Ca}^{2+}$  was the dominant species followed by  $\text{NO}_3^-$  and  $\text{K}^+$ . Marine aerosols were predominantly  $\text{Na}^+$  and  $\text{Cl}^-$ , and they were found primarily in the coarse mode. The major ionic species in the fine mode of the transportation aerosols were  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ , while  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$  were the key components in the coarse mode. In the cement dust,  $\text{Ca}^{2+}$  was the dominant species.

**Keywords:** MOUDI, Mass-Size Distribution, Source Distribution, Carbon Composition, Ion Composition.

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## **INTRODUCTION**

There have been numerous studies that reported the correlation between elevated levels of ambient particulate matter and various environmental and health effects. Examples include increased hospital admissions due to cardiopulmonary illness (Linn et al., 2000) and degradation in visibility (EPA, 1996), among others. Particle size and composition are the two major characteristics among various aerosol properties that determine the effects (Dodd et al., 1991). The deposition of aerosols in the respiratory system is controlled by various mechanisms such as impaction and diffusion, and the efficiency depends on particle size (Hinds, 1999). If the deposited particles are soluble, they are easily absorbed into the blood stream (Newhouse and Ruffin, 1978). Acidic aerosols can stimulate asthma (Ostro et al., 1991) while organic components can induce toxicity directly or via metabolism to genotoxic agents (Costa and Amdur, 1996). In terms of visibility reduction, submicrometer particles ( $0.1 \mu\text{m} < dp < 1 \mu\text{m}$ ) have the strongest scattering capabilities on the same mass basis and therefore are responsible for most visibility problems (Patterson and Wagman, 1977). To properly assess the environmental and health effects of aerosol, details of size-fractionated composition are of great importance. Many aerosol studies in terms of mass size distribution and composition focus on either large cities with high levels of pollution such as the Los Angeles Basin (Chow et al., 1996; Hering et al., 1997) or rural areas and desert (Dodd et al., 1991; Turpin et al., 1997) where no significant pollution sources exist. Investigations of mid-scale cities with limited pollution sources, however, are rather rare (Lijteroff et al., 1999).

Gainesville is a city located in Alachua county, north-central Florida, about 129 km southwest of Jacksonville, 193 km northwest of Orlando and approximately 225 km northeast of Tampa. With a household of 87,509, a population of 117,182 (as in 2003) and an area of 117.9 square km (The City of Gainesville, 2004), the city is considered as a mid-scale city surrounded by mainly agricultural and forest lands. The major anthropogenic stationary sources are power plants, a cement plant, sports equipment manufacturing, asphalt plants, medical waste incinerator and drilling equipment manufacturing, as given in a local emission inventory report (Alachua County Air Quality Commission, 1999). From the inventory, those stationary point sources produced about 170 tons of  $\text{PM}_{10}$  in 1997. Meanwhile, other area sources such as the road, both paved and unpaved, construction, managed burning and fires contributed 12,039 tons of  $\text{PM}_{10}$ , about 71 folds higher than the stationary point sources (Alachua County Air Quality Commission, 1999). However, these numbers were obtained solely by calculations following the inventory equations without verification by any source samplings. Furthermore, no studies have been conducted for this type of geographic location.

This study, therefore, aimed to establish the source profiles of five major sources in the area. Aerosols from the cement plant, transportation, soil, unpaved roads and the Atlantic Ocean were

sampled and analyzed for size distribution and size fractionated carbon and ion compositions. Such measurements are critical to the accurate assessment of the impact on local air quality, and the data are necessary for source apportionment modelling to determine the contribution of various stationary and area sources. Knowledge learned from this study provides a useful database that can be used to establish proper air quality policies for cities with a similar size and environment.

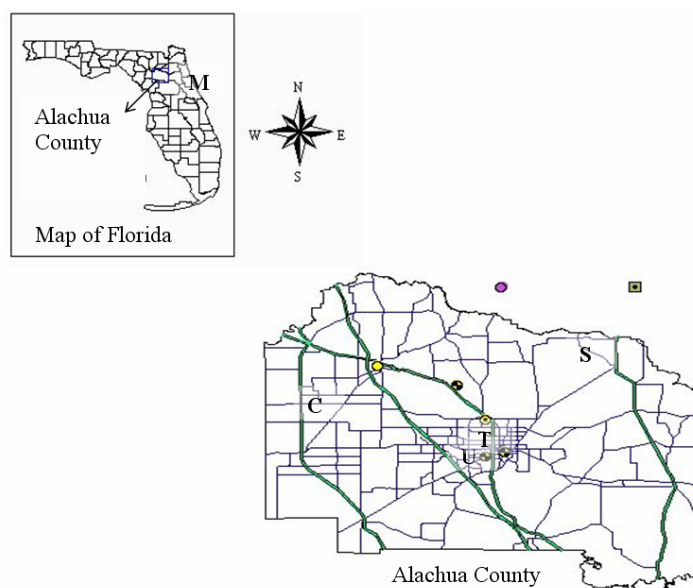
## **METHODS**

Aerosols from soil, unpaved road, transportation, and marine sources were obtained by using an 8-stage rotating Micro Orifice Uniform Deposit Impactor (MOUDI) (MSP Corporation, model 100) with the inlet located 0.5 meters above the ground level. The site locations were shown in Fig. 1. The sampling flow rate was 30 Lpm (liters per minute), and the corresponding cutsizes of the impactor stages were 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32 and 0.18  $\mu\text{m}$ . The soil dust sampling was conducted at an agriculture farm dominated by pine trees. The farm is on the border line of Alachua county and Bradford county, about 16.1 km from the Gainesville Regional Airport on state road number 225. A leaf-blower (Toro Air Blower, model 51591) was used to simulate natural wind. Since it was electrically powered, there was no contamination resulting from its emission. The sampling duration was 10 minutes and the wind was calm during that time.

The unpaved road dust sampling was performed at the corner of Center Drive and Mowry Road on the University of Florida (UF) campus for 10 minutes at calm wind condition, with the use of a blower as well. The transportation aerosol sampling was conducted for 4 hours on the footpath of 13<sup>th</sup> Street in front of College of Fine Arts, UF. The impactor was placed downwind, about 2 meters away from the street. The wind was from east-northeast and east with the average of 14.5 km per hour. There were no other major aerosol sources near the sampling site. The marine aerosols were sampled at Ormond Beach, Florida, for ion analysis. The wind was directly from the sea, which was east, east-southeast, and southeast with the average of 8.85 km per hour during 6 hours of sampling. Cement aerosols were isokinetically sampled from the stack of a local cement plant for 40 minutes by using a University of Washington Source Test Cascade Impactor (Mark III). The cutsize of each stage of the Mark III impactor was 13.6, 5.2, 2.6, 1.4, 0.8, and 0.4  $\mu\text{m}$ , respectively, at an operating flow rate of 27.3 Lpm and 97 °C.

Sampling for most sources was conducted for both carbon analysis and ion analysis. However, cement and marine sources were only sampled for ion analysis. For carbon analysis, 11- $\mu\text{m}$  thick aluminum foils (Fisher Scientific) were used as the collecting substrates. They were pre-baked at 450 °C for 24 hours to eliminate residual carbon since elemental carbon is oxidized above ~400 °C (Lavenchy et al., 1999). Quartz filter (SKC, Inc.) media used as the after-filter was pre-baked at 600 °C for 24 hours (Rogge et al., 1993). Regarding ion analysis, the 11- $\mu\text{m}$  thick aluminum

foil substrates were coated with 10% by wt Apiezon-L (Fisher Scientific) in toluene. The coated foils were then baked at 100 °C for 1 hour to remove any volatile compounds in the grease solution. A 5- $\mu\text{m}$  PVC filter (SKC, Inc.) was used as the after-filter. When the Mark III impactor was used for sampling cement aerosols, the collection plate inserts were fashioned from stainless steel because of the high in-stack temperatures at the sampling port (97 °C). The inserts were coated with a thin layer of Apiezon-H grease, 5% by mass, dissolved in toluene. All collection plate inserts and filters were placed in a furnace and baked at 200 °C for 1 hour. They were then dried in a desiccator for 24 hours before and after sampling. A CAHN microbalance (model 31), which had a sensitivity of 1  $\mu\text{g}$ , was used to measure their weights. The temperature in the weighing room was maintained in the range of 24-26 °C and the relative humidity was kept between 45-50%. Ion analysis was performed using capillary electrophoresis (Bio-Rad Laboratories, model BioFocus 2000). Carbon analysis was achieved by using an organic elemental analyzer (Carlo Erba, model NA1500). Blank and field blank filters and substrates, after preconditioning as stated above, were also analyzed for background content correction. Details of these analyses are presented elsewhere (Chuaybamroong, 2002).



**Fig. 1.** Sampling site locations: C = cement plant, M = marine, S = soil, T = transportation, U = unpaved road.

## RESULTS AND DISCUSSION

### *Mass-Size Distribution*

The particle size distributions by mass from these five major sources are shown in Fig. 2. Soil dust, unpaved road dust, cement dust and marine aerosols were mainly in the coarse mode.

Particles from transportation showed a bimodal or trimodal distribution. For plotting purpose, the lower limit of the after filter is set at 0.03  $\mu\text{m}$ , which is the typical value employed in similar studies (EPA 1999; Howell et al. 1998; Wagner and Leith 2001).

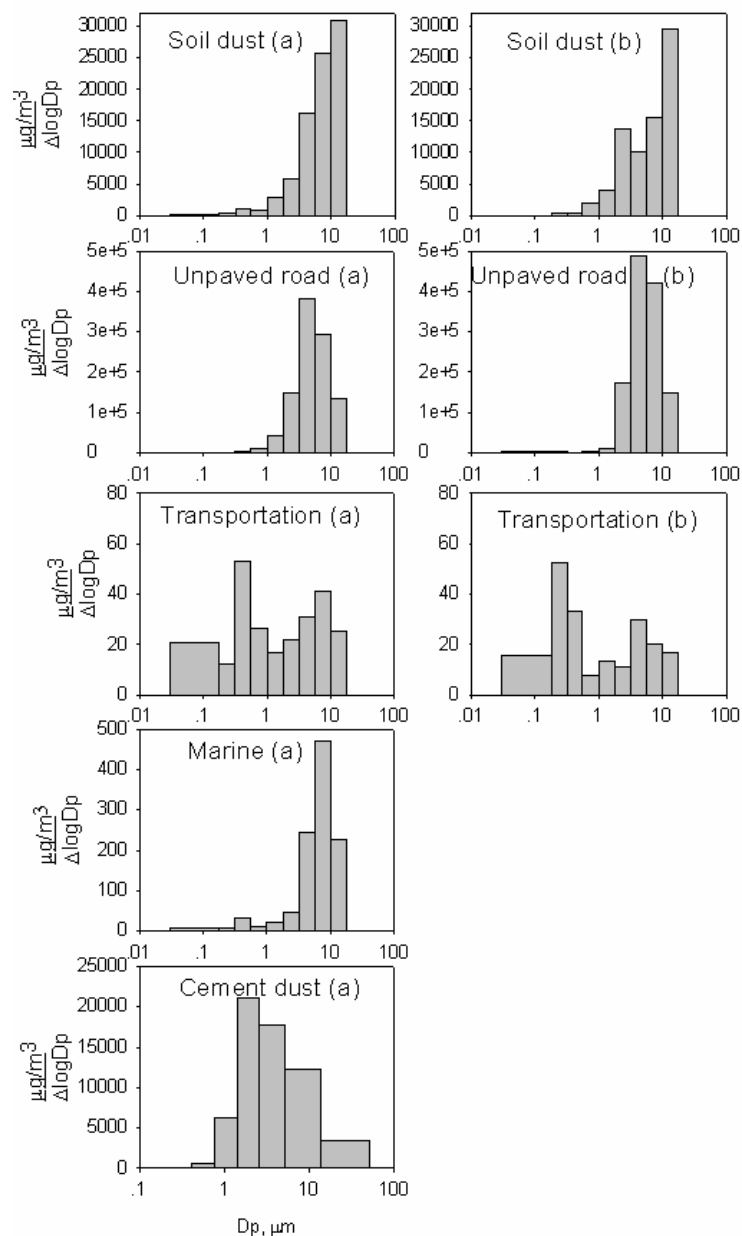
Most soil aerosol mass was found in the supermicron size range ( $> 1 \mu\text{m}$ ). Particle size distribution of soil is very broad, from  $<2 \mu\text{m}$  to 2 mm. Clay is classified as the one with the smallest particle size,  $<2 \mu\text{m}$ , while silt is in the range of 2 to 50  $\mu\text{m}$  (Taguas et al., 1999). The Florida top- and subsurface soils are reported to consist of fine sand (100 to 250  $\mu\text{m}$ ), while the subsoil is sandy clay loam with 3% silt and 25% clay (Brown, 2002).

A peak in the unpaved road dust size distribution was found at 3.2 to 5.6  $\mu\text{m}$ , which is smaller than the soil aerosol size distribution. The main material in the unpaved road is limestone, mixed with sand and soil. The frequent precipitation in Florida that washes out large particles on the road may be one reason that can explain the difference of the size distribution. In a study in Japan using a centrifugal particle size analyzer, it was reported that 70% of the particles on flooded unpaved road surface were  $< 3.9 \mu\text{m}$  (Kurashige and Fusejima, 1997). In contrast, unpaved road dust in a dry area has a larger particle size. By using a 5-stage Sierra-Anderson impactor, Sinha and Banerjee (1997) reported that 44% of unpaved haul road aerosols were  $>7 \mu\text{m}$  and about 28% were in the range between 3.3 and 7  $\mu\text{m}$ .

The transportation aerosols exhibited a tri-modal distribution with two peaks in the fine/ultrafine mode ( $< 0.18 \mu\text{m}$  and 0.32 to 0.56  $\mu\text{m}$ ), and the third peak in the coarse mode (5.6 to 10  $\mu\text{m}$ ). Many previous studies reported a bimodal distribution from transportation; for example, Bullin and Moe (1982) used a Lundgren impactor and found peaks at 0.4-1  $\mu\text{m}$  and 3-10  $\mu\text{m}$ . However, the ultra-fine ( $< 0.18 \mu\text{m}$ ) mode has been reported in studies using more advanced instrumentation. In Uji, Japan, the trimodal distribution was noticed by Hitzenberger and Tohno (2001) using a low-pressure Anderson impactor. They reported two submicron peaks at 0.15  $\mu\text{m}$  and 0.39  $\mu\text{m}$  and one peak in the coarse mode at 4.65  $\mu\text{m}$ . Ultra-fine aerosols are formed at high temperature in the vehicle engine and the exhaust pipe, with a peak  $< 0.1 \mu\text{m}$  (Kittelson, 1998). These ultrafine aerosols coagulate and/or grow by condensation to form larger particle sizes of 0.1 to 2  $\mu\text{m}$ , while the coarse particles are mechanically formed from the abrasion of road, tires, and brake linings (Wählin et al., 2001). Since a MOUDI could not classify the ultra-fine particles, all the ultra-fine particles present in the system were collected in the after-filter stage and, thus, the distribution could be considered a trimodal distribution with sizes of  $<0.18 \mu\text{m}$ , 0.18 to 1  $\mu\text{m}$ , and 1 to 18  $\mu\text{m}$ .

The distribution of marine aerosols showed a small peak in the submicron range and a huge peak at 5.6 to 10  $\mu\text{m}$  in the coarse mode. The supermicron particles, starting from the size of 1.8  $\mu\text{m}$  to 18  $\mu\text{m}$ , accounted for 70 to 92% of the total mass distribution. Similarly, McInnes et al. (1996) reported 61 to 86% of particles were in the size range of 1.0 to 10.0  $\mu\text{m}$ . The bursting of the air bubbles at the surface of the ocean can create salt particles as large as 20  $\mu\text{m}$  (Junge, 1963)

but they cannot travel over a distance much greater than 1 km (Ten Harkel, 1997). In contrast, the fine mode marine aerosol is produced from a different mechanism. Dimethyl sulfide gas in seawater can create very small particles of 0.01 to 0.045  $\mu\text{m}$  from photo-oxidation reaction (gas to particle conversion), although these particles tend to further undergo kinematic coagulation because of the wind. Their hygroscopic property also favors moisture pickup. A size of 0.3  $\mu\text{m}$  is likely to be the ultimate size generated at the sea surface interface at the RH of 60% (Piazzola and Despiau, 1997).



**Fig. 2.** Particle mass-size distribution from five sources: a) substrates were greased aluminum foil and PVC filter as an after-filter for ion analysis, b) substrates were ungreased aluminum foil and quartz filter as an after-filter for carbon analysis.

The fine distribution in marine aerosols agrees well with the study of Zhuang and Chan (1997) in Hong Kong although their coarse distribution was shifted to a smaller size. They found a bimodal distribution with the peaks at 0.3 to 0.6  $\mu\text{m}$  and 3 to 6  $\mu\text{m}$  by using a MOUDI located on the roof of a building that was 20 meters above the sea level. The study of Jennings et al. (1997) also showed a bimodal distribution at 0.4 to 0.5  $\mu\text{m}$  (23%) and 4 to 5  $\mu\text{m}$  (77%). A Berner low-pressure impactor located about 300 meters from the shore and 30 meters above the sea level was used in that study. These studies reported coarse particles in the smaller size range. The building height and meteorological condition might have depleted the large particles in their studies. In this study, the sampling location was much closer to the sea than those studies. It was placed on the seashore, about 6 meters downwind from seawater.

For the cement dust, it should be noted that the after-filter was not used in the stack sampling because it created an extremely high pressure drop during the sampling operation. The smallest particle size that could be collected in the last stage of the Mark III impactor was 0.4  $\mu\text{m}$ . The cement dust mass-size distribution had a peak at 1.4 to 13.6  $\mu\text{m}$ , indicating that on-site particle control devices were effective in removing larger particles that would be present in the cement production processes.

### **Carbon Analysis**

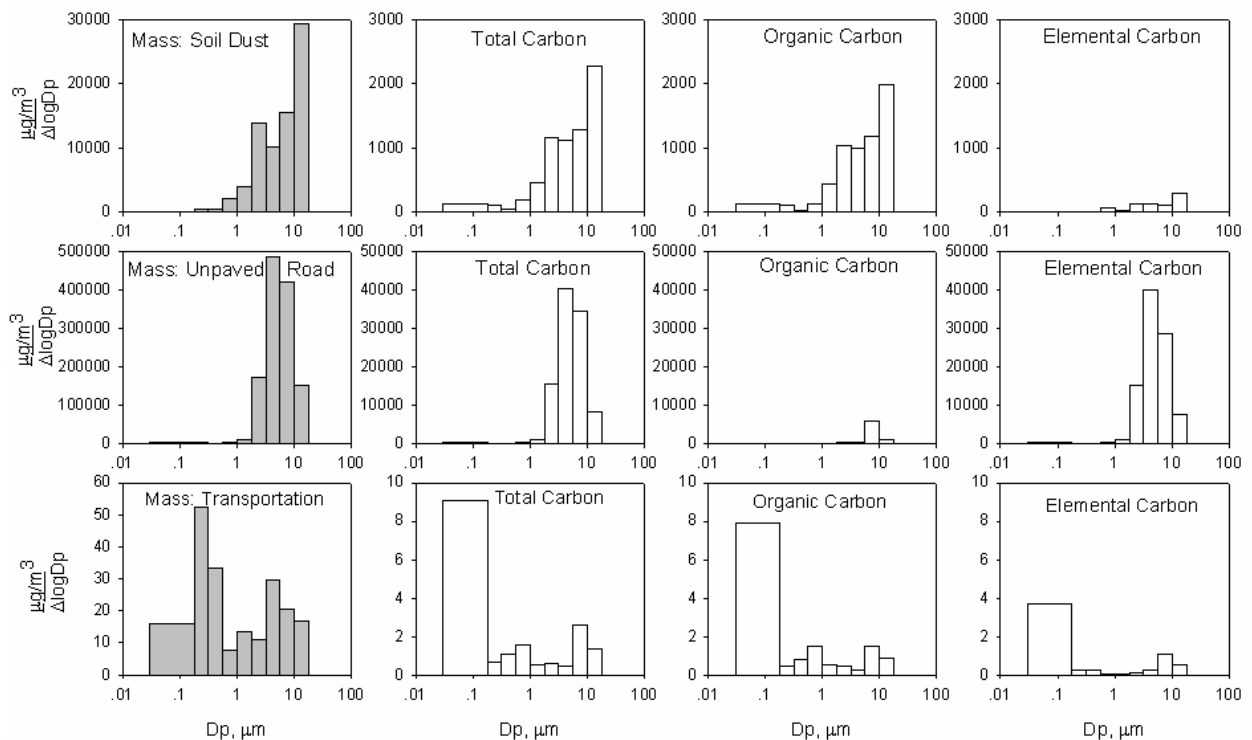
Fig. 3. shows the carbon distribution of particles from the various sources, and Table 1 lists the percentage of carbon content on each stage. Most of the carbon in the soil aerosols was organic carbon (OC), and it was mainly in the supermicron range. The OC content on each stage was from 6% to 96% of the mass, while the elemental carbon (EC) content was only around 1% to 3%, as shown in Table 1. Since the proportion of OC on each stage varied within a small range (6-12%) for aerosols larger than 0.32  $\mu\text{m}$ , the carbon size distribution also followed the same pattern of the dust mass distribution (i.e. increased as particle size increased, as in Fig.3). The OC content in soil can vary significantly from site to site, depending on various factors such as the annual precipitation, clay content, tree species, available water storage, evapotranspiration and temperature (Feng et al., 2002). The study of Cayet and Lichtfouse (2001) in France used sieves to classify soil particles by size. It reported that 87% of the OC in soil was in the size < 50  $\mu\text{m}$  and only 6% was in the size range of 50 to 200  $\mu\text{m}$ . In clay and silt, about 89% to 91% of the total OC was found with the particle size < 2 mm in soil samples in Brazil (Roscoe et al., 2001). Since FL subsoil is sandy clay loam (Brown, 2002), its OC is likely to come from the clay component.

Carbon in the unpaved road aerosols exhibited an opposite pattern to the carbon in the soil aerosols. It was mainly EC and the mass fractions were more consistent in every size range, mostly about 8% to 9%. One likely source for the EC could be the residues from vehicle combustion (Funasaka et al., 1998). The fractions of OC varied from 0.3%, in the size range of

3.2 to 5.6  $\mu\text{m}$ , to 3.5%, in the size range of 0.56 to 1  $\mu\text{m}$  as shown in Table 1. Due to the similar carbon fraction in every size range, the distribution shape of carbon is similar to that of the mass distribution as shown in Fig. 3. The mass ratio of carbon to dust between the fine mode, which was averaged from 1.8  $\mu\text{m}$  to the after-filter stage in Table 1, and the coarse mode, which was averaged from 3.2  $\mu\text{m}$  to >18  $\mu\text{m}$ , is about the same, 7.02% and 7.08% for EC, respectively, and 1.76% and 1.08% for OC, respectively. The similarity implies that the carbons were not freshly emitted; rather, they were aged ones (Turpin et al., 1997).

**Table 1.** Carbon composition of particles from different sources.

Particle size	Soil			Unpaved Road			Transportation		
	%TC	%EC	%OC	%TC	%EC	%OC	%TC	%EC	%OC
>18 $\mu\text{m}$	9.0	1.5	7.6	5.4	2.7	2.6	11.4	8.9	2.5
10-18 $\mu\text{m}$	10.2	1.3	8.9	8.2	7.1	1.1	7.9	3.1	4.8
5.6-10 $\mu\text{m}$	7.9	0.8	7.1	9.1	8.0	1.1	12.7	5.3	7.4
3.2-5.6 $\mu\text{m}$	11.1	1.2	9.8	9.1	8.8	0.3	1.5	0.9	0.5
1.8-3.2 $\mu\text{m}$	8.6	0.9	7.7	9.4	8.8	0.6	5.3	1.2	4.1
1.0-1.8 $\mu\text{m}$	13.0	0.8	12.2	9.6	8.9	0.7	0.2	0.2	0.01
0.56-1.0 $\mu\text{m}$	9.3	2.8	6.5	11.5	8.0	3.5	21.4	0.4	21.0
0.32-0.56 $\mu\text{m}$	7.5	1.3	6.2	6.5	5.0	1.4	3.3	0.8	2.5
0.18-0.32 $\mu\text{m}$	32.2	0.8	31.5	7.5	5.1	2.4	1.3	0.4	0.9
After filter	98.2	2.1	96.0	8.9	8.1	0.8	57.7	7.2	50.5



**Fig. 3.** Carbon distribution of particles from different sources.

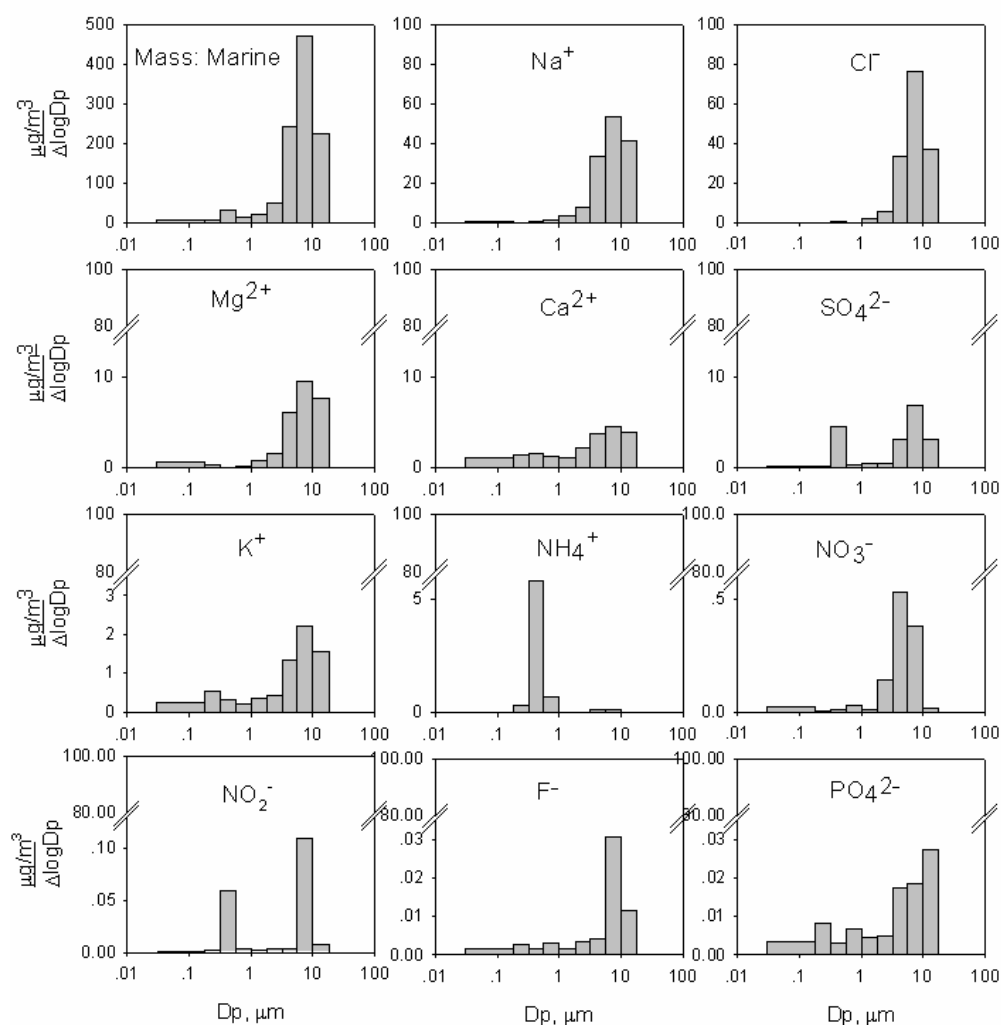
Table 1 revealed that carbon in the transportation aerosols was mainly found in the ultra-fine particles, 50.5% by mass for OC and 7.2% by mass for EC. In the sub-micron particles (0.18 to 1  $\mu\text{m}$ ), up to 21% by mass was OC and 0.4 to 0.8% by mass was EC. Only 0.01% to 7.4% by mass of OC was in the supermicron particles (1 to  $>18 \mu\text{m}$ ), and 0.2% to 8.9% by mass of EC was found in that mode. The fine OC from transportation particles, averaged from 1.8  $\mu\text{m}$  to the after-filter stage, was about four times higher than the coarse OC, averaged from 1.8  $\mu\text{m}$  up to  $>18 \mu\text{m}$ , 15% versus 3.9%, suggesting it was fresher emission than that found in the unpaved road carbon (Turpin et al., 1997). The fraction of fine OC from its mass in this study, 15%, is close to the fine OC fraction from vehicle exhaust in Los Angeles using a hi-vol dichotomous sampler which was reported to be 7.5% to 18.3% (Fraser et al., 1999). However, the fraction of EC from its mass is very different from other studies, which may be due to the amount of diesel engine vehicles. The EC fraction was 71% in the Osaka study (Funasaka et al., 1998), and 30% to 38% from the Caldecott tunnel in San Francisco (Hering et al., 1984), while in this study the average EC fraction of all size ranges was only 2.86%. It should be noted that the EC from gasoline light-duty vehicles was reported by Gillies and Gertler (2000) to be 6% to 7% by mass, which is much closer to this study. The comparison with these studies suggests the dominance of gasoline vehicles in the study area.

### ***Ionic Species Analysis***

Ionic species distributions for each source are shown in Figs. 4 to 8. In marine aerosols,  $\text{Na}^+$  and  $\text{Cl}^-$  were the prevailing ionic species, and they were mainly in the coarse mode, as displayed in Fig. 4. The  $\text{Cl}^-/\text{Na}^+$  ratio has been frequently used as an important indicator for assessing the aerosol production from a marine source. Junge (1963) reported the ratio to be 1.8 in seawater. However, chloride can be lost via reaction with gaseous  $\text{HNO}_3$  and/or  $\text{H}_2\text{SO}_4$  to form gaseous  $\text{HCl}$  ( $\text{NaCl} + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{HCl}$ ) as reported by Cheng et al. (2000). They found that the loss was 15% in summer and up to 20% in winter. With the loss, their  $\text{Cl}^-/\text{Na}^+$  ratio in seawater was 1.16 and that in aerosol was 0.88 in  $\text{PM}_{10}$ . In this study, the ratio was 0.99 for  $\text{PM}_{10}$  aerosol. Chloride depletion can occur in both the fine and the coarse modes, but it is more pronounced in fine particles due to the higher specific surface area, especially in a highly polluted location (Gustafsson and Franzén, 2000). In this study, the  $\text{Cl}^-/\text{Na}^+$  ratio varied from 0.55 in fine particles to 1.13 in coarse particles.

Regarding the other ionic species in marine aerosols, Fig. 3 showed that  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  were mainly in the coarse mode;  $\text{NH}_4^+$  had a distinctive peak in the submicron range, and  $\text{SO}_4^{2-}$  was bimodally distributed. The alkaline cations shared the same generation mechanism as  $\text{Na}^+$ , the bursting of air bubbles at the ocean surface, and therefore they have a similar distribution shape.  $\text{NH}_4^+$  is from gas-to-particle conversion of  $\text{NH}_3$  gas. Sulfate in the coarse mode is from the

bursting, whereas that in the fine mode is from the oxidation of dimethyl sulfide gas, as reported by EPA (1996).



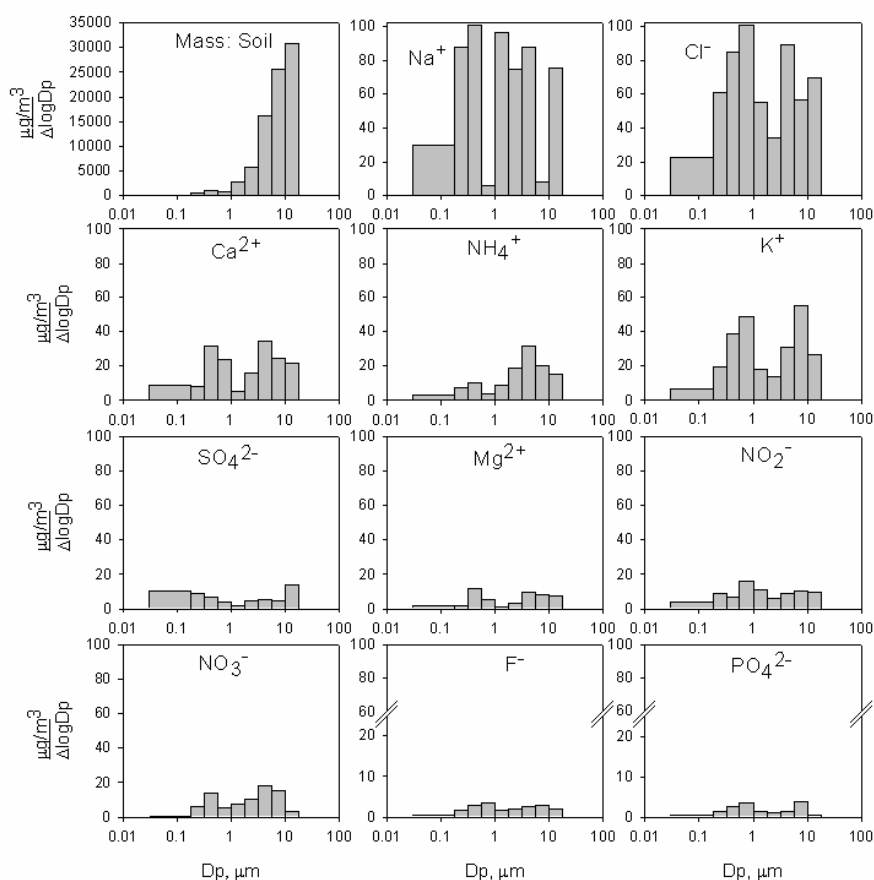
**Fig. 4.** Ionic species distribution in marine aerosols.

The composition of seawater was reported to be 30.7%  $\text{Na}^+$ , 55%  $\text{Cl}^-$ , 7.7%  $\text{SO}_4^{2-}$ , 3.6%  $\text{Mg}^{2+}$ , 1.2%  $\text{Ca}^{2+}$ , 1.1%  $\text{K}^+$  and 0.2%  $\text{Br}^-$  (EPA, 1996). In this study, the total ionic species from marine aerosols were 35% by mass. Its composition from that proportion was 37%  $\text{Na}^+$ , 41%  $\text{Cl}^-$ , 5%  $\text{SO}_4^{2-}$ , 7.2%  $\text{Mg}^{2+}$ , 5.9%  $\text{Ca}^{2+}$ , 2%  $\text{K}^+$  and 0.8%  $\text{NH}_4^+$ .

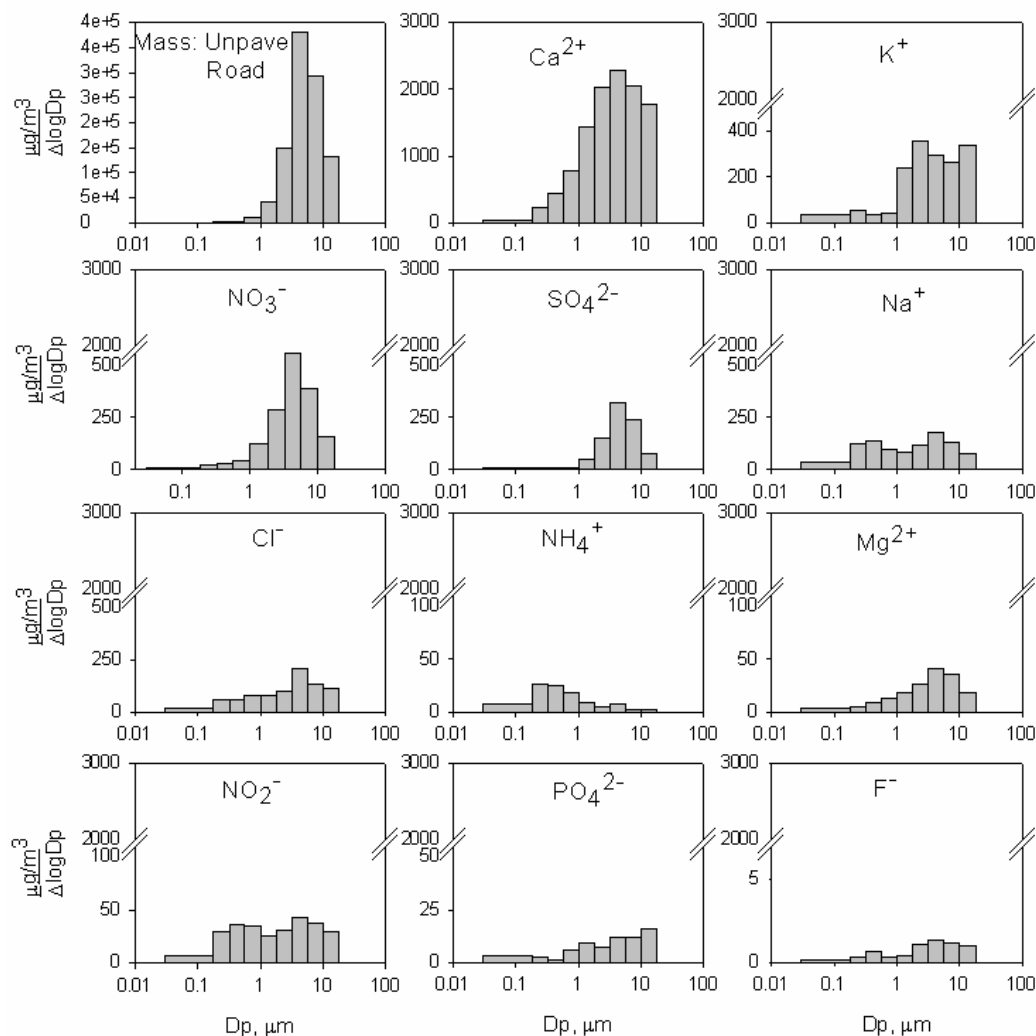
In soil dust particles, Fig. 5 revealed that every ion showed a bi-modal distribution. Topsoil composition is influenced by atmospheric inputs and further controlled by biogenic processes such as root uptake and biological immobilization. It is also affected by mineralization of organic matter and soil mineral weathering (Baumler and Zech, 1998). The high amount of  $\text{Na}^+$  and  $\text{Cl}^-$  suggests deposition of sea salt aerosols via precipitation (Carnol et al., 1997). The deposition could be as high as 100 kg  $\text{Cl}^-/\text{ha-yr}$  as in the southwestern coast of Norway, or as low as 1 to 2 kg  $\text{Cl}^-/\text{ha-yr}$  as in the Scandinavian mountain ridge (Johansson et al., 2001). Since Gainesville is only

less than 80 km away from the Atlantic Ocean from in the east and Gulf of Mexico in the west, it is not surprising to see high concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  as shown. Besides  $\text{Na}^+$  and  $\text{Cl}^-$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are related to each other via a nitrification and denitrification process by microorganisms (Baeumler and Zech, 1998). In this study, these two ionic species did exhibit similar size distributions.

Fig. 6. shows that  $\text{Ca}^{2+}$  was the dominant species in unpaved road aerosols since calcium containing compounds such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $(\text{CaSO}_4)_2 \cdot 2\text{H}_2\text{O}$ ) are the key components of the road materials in north central Florida. Calcium was present mainly in the coarse mode by mass. Potassium,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  were also important ionic species that showed their peaks in the coarse mode while  $\text{Na}^+$  was bimodally distributed. Sulfate being mainly present in the coarse mode indicates that it is likely due to the material of the road as discussed earlier or simply the reaction of lime rock ( $\text{CaCO}_3$ ) with  $\text{SO}_2$  (Ramadam et al., 2000). Querol et al. (1998) also reported that sulfate from suspended gypsum was mainly present in 1.2 to 5  $\mu\text{m}$ . Sodium and nitrite showed very similar size distribution profiles and were almost equal between the fine and coarse modes.  $\text{NH}_4^+$  was in the fine mode, perhaps from the deposition of the gas-to-particle conversion process in the atmosphere (Seinfeld and Pandis, 1998).



**Fig. 5.** Ionic species distribution in soil particles

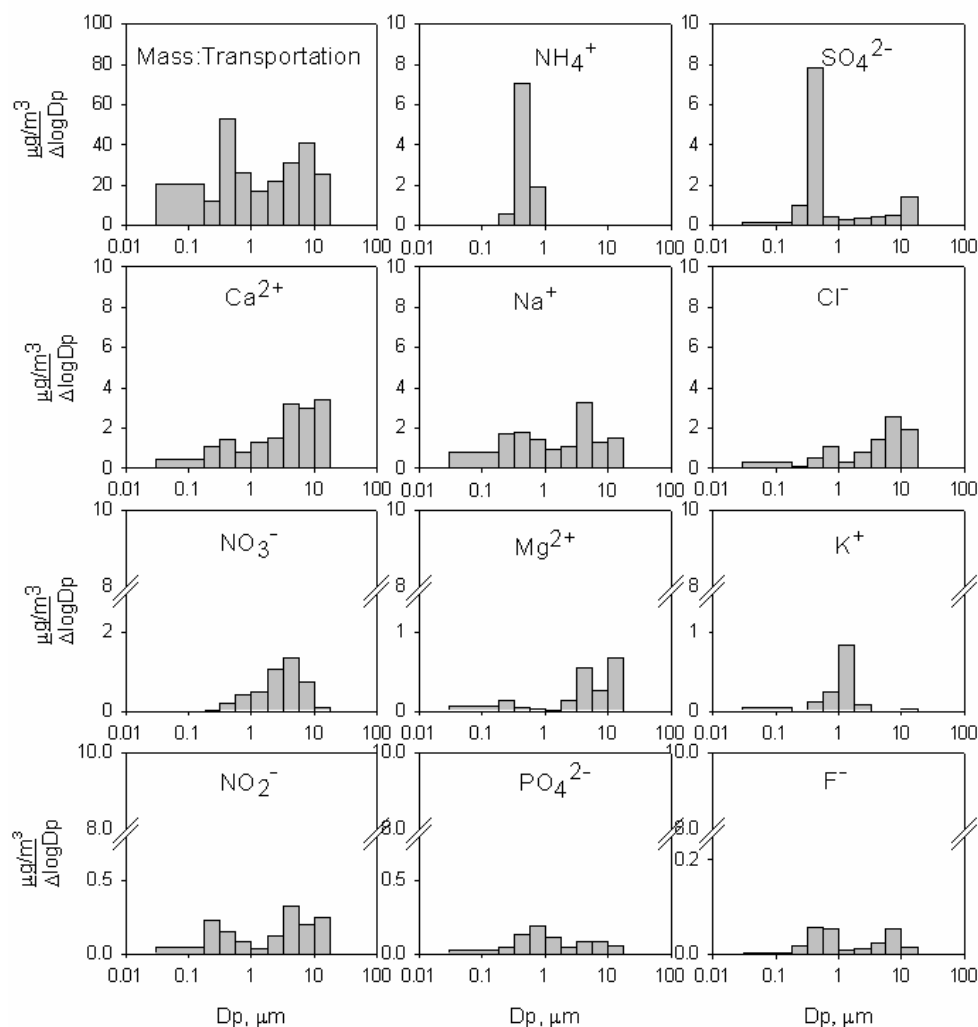


**Fig. 6.** Ionic species distribution in particles from unpaved road.

In contrast to the unpaved road,  $\text{SO}_4^{2-}$  in transportation aerosols was pronounced as fine particles, especially in the size range of 0.32 to 0.56  $\mu\text{m}$ , as shown in Fig. 7. It was reported that sulfate with diameter of  $<1 \mu\text{m}$  was produced by catalytic converters by oxidation of sulfur dioxide gas (Dzubay et al., 1979). Ammonium was only found in the fine mode. It is also possible that  $(\text{NH}_4)_2\text{SO}_4$ , a major component of ambient aerosol, might have come from the atmosphere. Calcium,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$  occurred mostly in the coarse mode, likely from the resuspended road dust. Nitrite and  $\text{Na}^+$  were about the same between the fine mode and the coarse mode.

Fig. 8. displays the ionic speciation from cement plant. As the major component of cement ( $\text{Si}_9\text{Al}_3\text{Ca}_{29.3}\text{S}_{0.8}\text{H}_3\text{Fe}_1\text{O}_{57}$ ),  $\text{Ca}^{2+}$  was the dominant ion in cement dust. The dominance of Ca in cement dust aerosol has also been reported by studies using Proton Induced X-Ray Emission (PIXE) spectroscopy for elemental analysis (Begum et al., 2004). The basic  $\text{Ca}^{2+}$  in cement dust

is a material that naturally scrubs out acidic gases. Hence, the size distributions of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  followed the similar size distribution profile of  $\text{Ca}^{2+}$ . The other important cations included  $\text{K}^+$  and  $\text{Na}^+$ , which are from the raw materials for cement production.

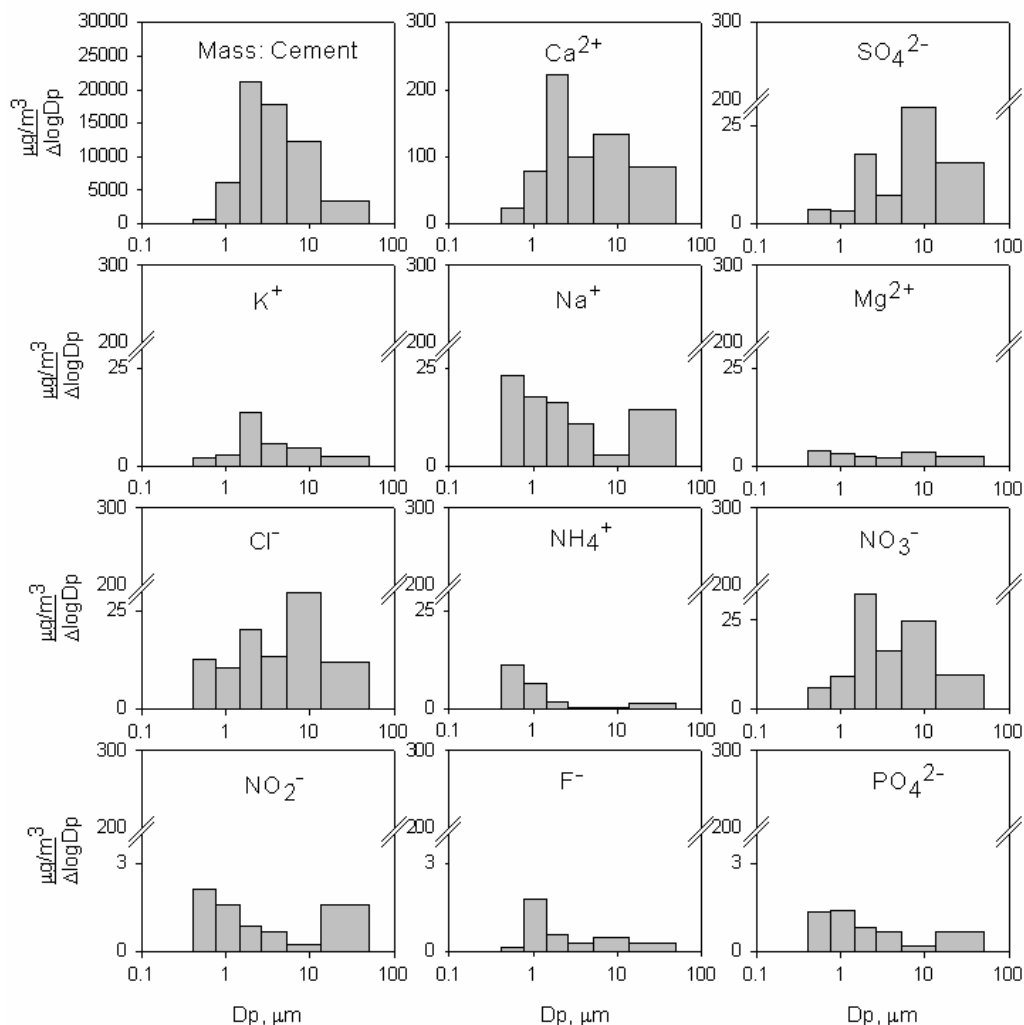


**Fig. 7.** Ionic species distribution in particles from transportation particles.

## CONCLUSIONS

In this study, five major sources for ambient aerosols in Gainesville were sampled and analyzed for their mass size distribution, carbons and soluble ionic species. Soil, unpaved road, cement and marine sources mainly contributed particles to the supermicron mode, while the transportation sources contributed particles to the ultrafine, submicron and supermicron modes.

The soil aerosols were rich in organic carbon in the supermicron particles, which likely came from the clay component. In contrast, the carbon in the unpaved road aerosols was mainly elemental carbon, which was likely aged residues from transportation. Carbon in the



**Fig. 8.** Ionic species distribution of particulate emission from cement plant.

transportation aerosols was mainly in the ultrafine range ( $< 0.18 \mu\text{m}$ ), and gasoline vehicles were the likely source that dominated the study area.

Regarding the ionic species, the marine aerosols were dominated by  $\text{Na}^+$  and  $\text{Cl}^-$ . The  $\text{Cl}^-/\text{Na}^+$  ratio was lower than that in sea water due to the loss of  $\text{Cl}^-$  via reaction to form gaseous  $\text{HCl}$ . In the soil aerosols,  $\text{Na}^+$  and  $\text{Cl}^-$  were also the dominating ionic species, indicating the importance of deposition of sea salt aerosols in the area. Calcium and  $\text{K}^+$  were also important ionic species in the soil which exhibited a bimodal distribution. In the unpaved road aerosols,  $\text{Ca}^{2+}$  was the dominant ionic species and was in the coarse mode. The other important ionic species ( $\text{K}^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) were also in the coarse mode. In transportation aerosols,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  were the key species and they were mainly in the fine mode. The other important ionic species in the

transportation aerosols were  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$ , which were likely from the resuspended road dust. In the cement dust,  $\text{Ca}^{2+}$  was the major ion.

The distributions of most major ionic species and carbons had a similar pattern to their mass distribution. The only exception of ionic species was the soil where the ionic species exhibited a bi-modal distribution while the mass size distribution increased as aerosol size increased. The only exception of carbons was the transportation aerosols where the mass exhibited a tri-modal distribution and the carbons were dominantly in the ultrafine mode. Ammonium was present in the fine mode in most sources. The only exception was the coarse  $\text{NH}_4^+$  in the soil particles due to different formation process (i.e. nitrification and denitrification by microorganisms instead of gas-to-particle conversion in the atmosphere). The presence of  $\text{SO}_4^{2-}$  in the fine mode or the coarse mode also depends on its formation mechanisms. If it was scrubbed by the basic material such as  $\text{Ca}^{2+}$ , as in the case of cement or unpaved road dust, it followed the size distribution of  $\text{Ca}^{2+}$ . If it was from gas-to-particle conversion in the atmosphere, as in the case of transportation and marine aerosols, it existed in the fine mode.

This study investigated various sources important to a mid-scale city in subtropical climate. Such a study provides valuable data of sources important to this type of city which are different and not available from the abundant literature focused on metropolitan areas. The size fractionated carbon and ionic speciation is useful in evaluating the impact on human health and visibility. As there is no data available for this size of city and type of geological location, such information is much needed for accurate assessment and for establishing strategies for better air quality in the area.

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## REFERENCES

Alachua County Air Quality Commission. (1999). *Alachua county air quality commission findings and recommendations*. November 8, 1999. Florida.

- Begum, B.A., Kim, E., Biswas, S.K. and Hopke, P.K. (2004). Investigation of sources of atmospheric aerosol at urban and semi-urban areas in Bangladesh. *Atmos. Environ.* 38:3025-3038.
- Baeumler, R., Zech, W. (1998). Soil solution chemistry and impact of forest thinning in mountain forests in the Bavarian Alps. *Forest Ecology and Management* 108:231-238.
- Brown, R.B. (2002), *Soil texture*, [http://edis.ifas.ufl.edu/BODY\\_SS169](http://edis.ifas.ufl.edu/BODY_SS169). Accessed 2/4/2002.
- Bullin, J.A., Moe, R.D. (1982). Evaluation of four types of samplers for aerosols along roadways. *J. Air Pollut. Contr. Assoc.* 32:733-737.
- Carnol, M., Ineson, P., Dickinson, A.L. (1997). Soil solution nitrogen and cations influenced by  $(\text{NH}_4)_2\text{SO}_4$  deposition in a coniferous forest. *Environ. Pollut.* 97:1-10.
- Cayet, C., Lichtfouse, E. (2001).  $\delta^{13}\text{C}$  of plant-derived *n*-alkanes in soil particle-size fractions. *Org. Geochem.* 32:253-258.
- Cheng, Z.L., Lam, K.S., Chan, L.Y., Wang, T., Cheng, K.K. (2000). Chemical characteristics of aerosols at coastal station in Hong Kong. I. Seasonal variation of major ions, halogens and mineral dusts between 1995 and 1996. *Atmos. Environ.* 34:2771-2783.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Countess, R.J. (1996). Sources and chemistry of  $\text{PM}_{10}$  aerosol in Santa Barbara County, CA. *Atmos. Environ.* 30:1489-1499.
- Chuaybamroong, P. (2002). Composition, Particle Size, and Source of Ambient Aerosol in Alachua County, Florida. *Ph.D. thesis*, University of Florida, Florida.
- Costa, D.L., Amdur, M.O., (1996). Air Pollution. In *Casarett & Doull's Toxicology, The Basic Science of Poison*, 5<sup>th</sup> edition, C.D.Klaassen (Ed.), McGraw-Hill, New York, pp.857-882.
- Dodd, J.A., Ondov, J.M., Tuncel, G., Dzubay, T.G., Stevens, R.K. (1991). Multimodal size spectra of submicrometer particles bearing various elements in rural air. *Environ. Sci. Technol.* 25:890-903.
- Dzubay, T.G., Stevens, R.K., Richards, L.W. (1979). Composition of aerosols over Los Angeles freeways. *Atmos. Environ.* 13:653-659.
- EPA-600/P-95/001aF. (1996). Air quality criteria for particulate matter, Vol I of III. Office of Research and Development, Washington, DC.
- EPA-625/R-96/010a. (1999). Sampling of ambient air for total suspended particulate matter (SPM) and  $\text{PM}_{10}$ , using high volume (HV) samplers, Washington, DC.
- Feng, Q., Endo, K.N., Guodong, C. (2002). Soil carbon in desertified land in relation to site characteristics. *Geoderma* 106:21-43.
- Fraser, M.P., Cass, G.R., Simoneit, B.R.T. (1999). Particulate organic compounds emitted from motor vehicle exhaust and in the urban atmosphere. *Atmos. Environ.* 33:2715-2724.
- Funasaka, K., Miyasaki, T., Kawaraya, T., Tsuruho, K., Mizuno, T. (1998). Characteristics of particulates and gaseous pollutants in a highway tunnel. *Environ. Pollut.* 102:171-176.

- Gillies, J.A., Gertler, A.W. (2000). Comparison and evaluation of chemically speciated mobile source PM<sub>2.5</sub> particulate matter profiles. *J. Air & Waste Manage. Assoc.* 50:1459-1480.
- Gustafsson, M.E.R., Franzén, L.G. (2000). Inland transport of marine aerosols in southern Sweden. *Atmos. Environ.* 34:313-325.
- Hering, S.V., Miguel, A.H., Dod, R.L. (1984). Tunnel measurements of the PAH, carbon thermogram and elemental source signature for vehicular exhaust. *Sci. Total Environ.* 36:39-45.
- Hering, S., Eldering, A., Seinfeld, J.H. (1997). Bimodal character of accumulation mode aerosol mass distributions in southern California. *Atmos. Environ.* 31:1-11.
- Hinds, W. C. (1999). *Aerosol technology: properties, behavior, and measurement of airborne particles*, John Wiley & Sons, Inc., New York.
- Hitzenberger, R., Tohno, S. (2001). Comparison of black carbon (BC) aerosols in two urban areas-concentrations and size distributions. *Atmos. Environ.* 35:2153-2167.
- Howell, S, Pszenny, A. A. P., Quinn, P., Huebert, B. (1998). A field intercomparison of three cascade impactors. *Aerosol Sci. Technol.* 29:475-492.
- Jennings, S.G., Geever, M., McGovern, F.M., Francis, J., Spain, T.G., Donaghy, T. (1997). Microphysical and physico-chemical characterization of atmospheric marine and continental aerosol at Mace Head. *Atmos. Environ.* 31:2795-2808.
- Johansson, E., Ebenå, G., Sandén, P., Svensson T., Öberg, G. (2001). Organic and inorganic chlorine in Swedish spruce forest soil: influence of nitrogen. *Geoderma* 101:1-13.
- Junge, C.E. (1963). *Air chemistry and radioactivity*, Academic Press, New York.
- Kittelson, D. B. (1998). Engines and nanoparticles: A review. *J. Aerosol Sci.* 29:575-588.
- Kurashige, Y., Fusejima, Y. (1997). Source identification of suspended sediment from grain-size distributions: 1. application of nonparametric statistical tests. *Catena* 31:39-52.
- Lavanchy, V.M.H., Gäggeler, H.W., Nyeki, S., Baltensperger, U. (1999). Elemental carbon (EC) and black carbon (BC) measurements with a thermal method and an aethalometer at the high-alpine research station Jungfraujoch. *Atmos. Environ.* 33:2759-2769.
- Linn, W., Szlachcic, Y., Gong, H. Jr., Kinney, P. and Berhane, K. T. (2000). Air Pollution and Daily Hospital Admissions in Metropolitan Los Angeles. *Environ. Health Perspect.* 108:427-434.
- Lijteroff, R., Cortinez, V. and Raba, J. (1999). Urban Development and Air Quality in San Luis City, Argentina, *Environ. Monit. Assess.* 57:169-182.
- McInnes, L.M., Quinn, P.K., Covert, D.S., Anderson, T.L. (1996). Gravimetric analysis, ionic composition, and associated water mass of the marine Aerosol. *Atmos. Environ.* 30:869-884.
- Newhouse, M.T. and Ruffin, R.E. (1978), Deposition and fate of aerosolized drugs. *Chest* 73:936-943.
- Ostro, B. D., Lipsett, M. J., Wiener, M. B., Selner, J. C. (1991). Asthmatic Responses to Airborne Acid Aerosols. *Am. J. Public Health* 81:694-702.

- Patterson, R.K. and Wagman, J. (1977). Mass and composition of an urban aerosol as a function of particle size for several visibility levels. *J. Aerosol Sci.* 8:269-279.
- Piazzola, J. and Despiiau, S. (1997). Contribution of marine aerosols in the particle size distributions observed in Mediterranean coastal zone. *Atmos. Environ.* 31:2991-3009.
- Querol, X., Alastuey, A., Puigercus, J.A., Mantilla, E., Miro, J.V., Lopez-Soler, A., Plana F., Artiñano B. (1998). Seasonal evolution of suspended particles around a large coal-fired power station. *Atmos. Environ.* 32:719-731.
- Ramadam, Z., Song, X-H, Hopke, P.K. (2000). Identification of sources of Phoenix aerosol by positive matrix factorization. *J. Air & Waste Manage. Assoc.* 50:1308-1320.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simoneit, B.R.T. (1993). Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. *Atmos. Environ.* 27A:1309-1330.
- Roscoe, R., Buurman, P., Velthorst, E.J., Vasconcellos, C.A. (2001). *Geoderma* 104:185-202.
- Seinfeld, J. H. and Pandis, S. N. (1998), *Atmospheric chemistry and physics: from air pollution to climate change*, Wiley, New York.
- Sinha, S. and Banerjee, S.P. (1997). Characterization of Haul Road Dust in an Indian opencast iron ore mine. *Atmos. Environ.* 31:2809-2814.
- Taguas, F.J., Martín, M.A., Perfect, E. (1999). Simulation and testing of self-similar structures for soil particle-size distributions using iterated function systems. *Geoderma* 8:191-203.
- Ten Harkel, M.J. (1997). The effects of particle-size distribution and chloride depletion of sea-salt aerosols on estimating atmospheric deposition at a coastal site. *Atmos. Environ.* 31:417-427.
- The City of Gainesville. (2004). *About Gainesville: General Facts*. [www.cityofgainesville.org](http://www.cityofgainesville.org)  
Accessed on April 13, 2004.
- Turpin, B.J., Saxena, P., Allen G., Koutrakis P., McMurry P., Hildemann L. (1997). Characterization of the southwest desert aerosol, Meadview, AZ. *J. Air & Waste Manage. Assoc.* 47:344-356.
- Wagner, J. and Leith, D. (2001). Passive aerosol sampler. Part II: Wind tunnel experiments. *Aerosol Sci. Technol.* 34:193-201.
- Wählin, P., Palmgren, F., Dingenen, R.V. (2001). Experimental studies of ultrafine particles in streets and the relationship to traffic. *Atmos. Environ.* 35:S63-S69.
- Zhuang, H., Chan, C.K. (1997). Size distribution of inorganic aerosols at a coastal site. *J. Aerosol Sci.* 28:S213-S214.

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