Atmospheric Environment 51 (2012) 39–45

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Characteristics of water-soluble ions and carbon in fine and coarse particles collected near an open burning site

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ARTICLE INFO

Article history:
Received 23 August 2011
Received in revised form
4 January 2012
Accepted 23 January 2012

Keywords:
Biomass combustion
Particle size distribution
Agricultural waste
Smoke aerosol

ABSTRACT

This study investigates the chemical characteristics of particles that were collected from the open burning of wax apple agricultural waste, and evaluates the impact of such burning on regional air quality. The water-soluble ions, elemental carbon (EC), and organic carbon (OC) in fine ($D_p \leq 2.5$ μm) and coarse ($2.5 < D_p \leq 10$ μm) particles were collected using a micro-orifice uniform deposition impactor (MOUDI) and two Dichot samplers. The average $PM_{2.5}/PM_{10}$ ratio during open burning (0.90) was higher than those both before and after burning (0.57 and 0.55, respectively). The particle distributions before and during burning were bi-modal and uni-modal, respectively. During the open burning, the OC or K^+ content markedly increased; however, that of secondary aerosol (NH_4^+, NO_3^- and SO_4^{2-}) decreased. The Na^+/Cl^- molar ratios of fine particles before, after, and during the open burning 0.40, 0.18, and 0.24, respectively; however, the corresponding $(Na^+ + K^+)/Cl^-$ molar ratios were 0.74, 0.99, and 0.39, respectively. OC, K^+ and Cl^- were quite abundant in the open burning of agricultural waste (wax apple), and the OC/Na^+, K^+/Na^+, and Cl^-/Na^+ (mass) ratios in fine particles (318, 10.2, and 10.5, respectively) may be used as reference indexes associated with the open burning of wax apple waste.

1. Introduction

In Taiwan, and especially in Pingtung, the open burning of agricultural wastes (from the waste leafs, branches, and trunks of wax apple, rice, mango, and litchi trees) is a major source of air pollution. PM_{10}, $PM_{2.5}$, SO_x, NO_x, and NMHC represent 6.37%, 12.6%, 3.79%, 12.6%, and 5.95%, respectively, of all pollutant emissions in Pingtung city (Taiwan EPA, 2011; Kao et al., 2007; Lee et al., 2008). Fine particles – a major pollutant that is emitted in the burning of rice straw in the field – have harmful effects on human health (Pope et al., 2009) and the climate (Bond et al., 2004). When biomass is burned, elevated $PM_{2.5}$ and O_3 concentrations may cause significant air quality degradation in surrounding areas (Andreae et al., 1994; Liu et al., 1999; Chan et al., 2003; Lee et al., 2008; Oanh et al., 2011). The majority of the PM that is emitted in the field burning of rice straw is $PM_{2.5}$ with an emission factor (EF) of 5.1–0.7 g m^{-2} or 8.3–2.7 g kg^{-1} rice straw (Oanh et al., 2011). The most important components in $PM_{2.5}$ and PM_{10} are generally OC, water-soluble ions, and levoglucosan (Oanh et al., 2011). For example, smoke aerosols in Savanna contain large amounts of OC, EC, K^+, NH_4^+, and Cl^-, whereas the main contributors to atmospheric PM are BC, K, Zn, Cl, and Cu (Maenhaut et al., 1996; Andreae et al., 1998). However, the atmospheric PM composition is highly variable depending on location. The composition of particles formed by the burning of biomass in the Amazon basin is dominated by carbonaceous species associated with K, Cl, S, Ca, Mn, Zn, and ionic species (K^+, Cl^-, and SO_4^{2-}) (Artaxo et al., 1994; Yamasoe et al., 2000). In Europe, dominant ionic species in PM that is formed by the burning of agricultural waste are K^+, NO_3^-, and Cl^- (Ezcurra et al., 2001). Similarly, significant increases in K^+, Cl^-, OC, and fine particulate masses have been observed during biomass burning events in Gwangju, Korea (Ryu et al., 2004). Ryu et al. (2007) found mean OC/EC ratios of 4.9, 5.5, and 6.5 during normal (NM), haze (HZ) and biomass burning (BB) periods, respectively. In the BB period, concentrations of fine K^+, Cl^-, and NO_3^- were 326%, 100%, and 101%, higher than those in the NM period.

Less attention has been paid to atmospheric sampling close to open burning sites than to sampling during episodes of open burning in ambient air; moreover, few studies discussed the use of OC/Na^+, K^+/Na^+, and Cl^-/Na^+ ratios to characterize aerosols from the open burning of agricultural waste. Accordingly, this study investigates water-soluble ions (including five cations and three

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doi:10.1016/j.atmosenv.2012.01.053

anion species) and carbon in fine and coarse particles that are collected near a wax apple farm. The size distributions of particles, water-soluble ions and carbons in $PM_{2.5}$ and $PM_{2.5-10}$ were determined and compared.

2. Materials and methods

2.1. Collection of particles

Atmospheric particulate samples were collected at a wax apple farm in Pingtung City in southern Taiwan (X: 207383.17, Y: 2514565.27 (based on the Universal Transverse Mercator (UTM) system)). The area of the wax apple farm was 600 m^2 and the mass of the agricultural wax apple waste was 4.5 tons. The sampling time was divided into three periods – before open burning (background), during open burning, and after open burning (in March 2006). During the open burning period, the A, B, C, and D samples were taken from downwind locations at distances of 1, 3, 4, and 6 m, respectively, from the open burning site. A MOUDI (Model No.100; MSP Co., Minneapolis, MN) that was equipped with Teflon filters (Zefluor™, dia. = 37 mm, pore size = 1.0 μm, supported PTFE w/support pads) (Pall Co., Michigan, AA) was used to collect size-resolved aerosol samples. Silicon grease was applied to the surface of each filter installed in the MOUDI sampler, and the greased filter-strips were baked in a 60 °C oven for 90 min to stabilize the silicon grease before sampling to minimize particle bounce between the different stages of the MOUDI's during the sampling (Holsen et al., 1993). The relative humidity values were 61.88–84.55% (average = 74.55%) during the sampling period. These impactors effectively separated the particulate matter into ten size ranges (with a 50% efficiency) with equivalent cut-off diameters of 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, and 0.1–0.056 μm. The sampling flow rate for the MOUDI was 30 L min^{-1}. The MOUDI samples were collected at 1, 3, 4, and 6 m from the open burning site. Two Dichots (manual dichotomous samplers) that were equipped with Teflon and Quartz filters (diameters, 37 mm) were used to collect size-resolved aerosol samples. These samplers effectively separated particulate matter into two size ranges ($PM_{2.5}$ and $PM_{2.5-10}$). The Dichot sampling flow rates for $PM_{2.5}$ and $PM_{2.5-10}$ were 15.0 and 1.7 L per min, respectively. The filters were dried for 24 h in a desiccator at 25 °C and 40% relative humidity before and after each sampling. They were then weighed on an electronic balance (AND HM202) with a resolution of 10 μg. The suspended particulate substance concentration was determined by dividing the particle mass by the volume of the sampled air.

2.2. Water-soluble ion analysis and quality control

Before the property of the particle-bound water-soluble inorganic species ($Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-$, and SO_4^{2-}) had been determined quantitatively, collected particles from quarter sections of each quartz fiber filter (2500QAT-UP) were extracted using 10 mL of ultra-pure water (specific resistance 18.3 MΩcm). The water-soluble ions were extracted using an ultrasonic bath (UC-300) for 120 min. All extraction solutions were filtered through a cellulose acetate filter (ADVANTEC MFS, Inc., USA cat No., CO20A025A; pore size of 0.2 μm; diameter of 25 mm) and stored in plastic vials in a refrigerator at 4 °C until they were chemically analyzed. The inorganic species were analyzed by ion chromatography (IC) (DIONEX ICS-3000 with conductivity detection (DC detector/chromatography module, P/N 061767)). Cations were identified using a DIONEX IonPac® 4 × 50 mm CG12A guard column, a DIONEX IonPac® 4 × 250 mm CS12A analytical column, and a cation self-regenerating suppressor (CSRS® ULTRA II, 4 mm, AutoSuppression® Recycle Mode); the anions were identified using a DIONEX IonPac® 4 × 50 mm AG11 guard column, a DIONEX IonPac® 4 × 250 mm AS11 analytical column, and an anion self-regenerating suppressor (ASRS® ULTRA II, 4 mm, AutoSuppression® Recycle Mode). The eluents for the cation and anion analyses were 20 mM of methane sulfonic acid and 12 mM of NaOH, respectively. Analytical drift was monitored throughout the analytical procedures. Next, recovery efficiencies were determined using diluted samples that were spiked with known quantities of the ions of interest. Recovery efficiencies ranged from 93% to 107%. The method detection limit (MDL) was estimated by repeatedly analyzing a control solution of known quality. Replicate analysis of IC measurements was performed to calculate the MDL of each element using MDL =

$$2.681 \times S_{\text{pooled}}, \text{with}\, S_A^2/S_B^2 < 3.05.\; S_{\text{pooled}} = \left[\left(6S_A^2 + 6S_B^2\right)\Big/12\right]^{0.5},$$

where S_{pooled} denotes the pooled standard deviation; S_A represents the standard deviation of property of the prepared sample with a larger *F*-test value, and S_B is the standard deviation of the other sample. The detection limits in ng m^{-3} (estimated from MDL × volume of analyte solution (10 mL)/average sampling volume (2 m^3)) were Na^+, 70.0 ng m^{-3}; K^+, 120 ng m^{-3}; NH_4^+, 270 ng m^{-3}; Mg^{2+}, 130 ng m^{-3}; Ca^{2+}, 105 ng m^{-3}; Cl^-, 466 ng m^{-3}; NO_3^-, 286 ng m^{-3}; and, SO_4^{2-}, 616 ng m^{-3}. Both field and laboratory blank samples were prepared and analyzed for each sampling and analysis. All data were corrected with blanks.

2.3. Carbon content analysis and quality control

The carbon content of the aerosol samples was analyzed using an elemental analyzer. The sampling filters were quartz fiber filters (2500QAT-UP) that were supplied by the Pallflex Company (Putram, CT, U.S.A.). The quartz fiber filters were heated for 1.5 h at 900 °C before use, to reduce their carbon blank (Ohta and Okita, 1990). Thus, the background concentration in the quartz fiber filter and matrix, which could influence the analysis, was minimized. Analyses of carbon content of the filter samples were usually conducted within a week of sample collection. Until carbon analyses, the filter samples were stored in a freezer to prevent the loss of OC. One quarter of the quartz fiber filter was divided into two parts, which were weighed before the carbon analysis. All data were corrected with blanks.

3. Results

3.1. Concentration of particles formed in open burning

Table 1 presents the concentrations of particles in all samples before open burning (background), during open burning, and after open burning. The results indicate that the $PM_{2.5}$ concentrations at sampling sites A, B, C, and D during open burning were 8014, 6481, 4227, and 1303 μg m^{-3}, respectively; these values greatly exceeded the background value (47.5 μg m^{-3}) and the value after open burning (133 μg m^{-3}). The $PM_{2.5}$ concentrations at sampling sites A, B, C, and D during open burning were 169, 136, 89, and 27.4 times the background value, respectively, or on average, 105 times the background value. The $PM_{2.5}$ concentrations at sample sites A, B, C, and D during open burning were 60, 49, 32, and 9.8 times those after open burning, or 37.6 times higher on average. The average $PM_{2.5}/PM_{10}$ ratio during open burning (0.90) was higher than those before (0.57) and after burning (0.55), such that the fine particles increased as percentage of all particles in air, when wax apple tree branches were burned in an open space, although the