Atmospheric Environment 78 (2013) 93–104

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

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

Source indicators of biomass burning associated with inorganic salts and carboxylates in dry season ambient aerosol in Chiang Mai Basin, Thailand

Ying I. Tsai [a,b,*], Khajornsak Sopajaree [c], Auranee Chotruksa [b,c], Hsin-Ching Wu [b], Su-Ching Kuo [d]

[a] Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, 60, Sec. 1, Erren Rd., Rende Dist., Tainan 71710, Taiwan
[b] Department of Environmental Engineering and Science, Chia Nan University of Pharmacy and Science, 60, Sec. 1, Erren Rd., Rende Dist., Tainan 71710, Taiwan
[c] Department of Environmental Engineering, Chiang Mai University, Chiang Mai 50200, Thailand
[d] Department of Medicinal Chemistry, Chia Nan University of Pharmacy and Science, 60, Sec. 1, Erren Rd., Rende Dist., Tainan 71710, Taiwan

HIGHLIGHTS

- PM_{10} pollution in Chiang Mai, Thailand, during biomass burning.
- Two sites and two types of pollution (episodic and non-episodic) compared.
- Carboxylates show traffic, photochemical and biomass sources in PM_{10} episodes.
- Levoglucosan highs indicate biomass burning major cause of PM_{10} episodic pollution.
- Levo/Manno ratio shows hardwood burning, particularly, leads to PM_{10} episodes.

ARTICLE INFO

Article history:
Received 5 December 2011
Received in revised form
16 September 2012
Accepted 18 September 2012

Keywords:
Chiang Mai
Biomarkers
Carboxylates
Levoglucosan
Sugar alcohols
Soil biota

ABSTRACT

PM_{10} aerosol was collected between February and April 2010 at an urban site (CMU) and an industrial site (TOT) in Chiang Mai, Thailand, and characteristics and provenance of water-soluble inorganic species, carboxylates, anhydrosugars and sugar alcohols were investigated with particular reference to air quality, framed as episodic or non-episodic pollution. Sulfate, a product of secondary photochemical reactions, was the major inorganic salt in PM_{10}, comprising 25.9% and 22.3% of inorganic species at CMU and TOT, respectively. Acetate was the most abundant monocarboxylate, followed by formate. Oxalate was the dominant dicarboxylate. A high acetate/formate mass ratio indicated that primary traffic-related and biomass-burning emissions contributed to Chiang Mai aerosols during episodic and non-episodic pollution. During episodic pollution carboxylate peaks indicated sourcing from photochemical reactions and/or directly from traffic-related and biomass burning processes and concentrations of specific biomarkers of biomass burning including water-soluble potassium, glutarate, oxalate and levoglucosan dramatically increased. Levoglucosan, the dominant anhydrosugar, was highly associated with water-soluble potassium ($r = 0.75–0.79$) and accounted for 93.4% and 93.7% of anhydrosugars at CMU and TOT, respectively, during episodic pollution. Moreover, levoglucosan during episodic pollution was 14.2–21.8 times non-episodic lows, showing clearly that emissions from biomass burning are the major cause of PM_{10} episodic pollution in Chiang Mai. Additionally, the average levoglucosan/mannosan mass ratio during episodic pollution was 14.1–14.9, higher than the 5.73–7.69 during non-episodic pollution, indicating that there was more hardwood burning during episodic pollution. Higher concentrations of glycerol and erythritol during episodic pollution further indicate that biomass burning activities released soil biota from forest and farmland soils.

1. Introduction

Atmospheric particulate matter (PM) is a complicated mixture, mainly composed of inorganic substances and organic matter

* Corresponding author. Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, 60, Sec. 1, Erren Rd., Rende Dist., Tainan 71710, Taiwan. Tel.: +886 6 266 0208; fax: +886 6 266 0606.
E-mail address: mtsaiyi@mail.chna.edu.tw (Y.I. Tsai).

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http://dx.doi.org/10.1016/j.atmosenv.2012.09.040

resulting from the marine pathway, biomass burning, agriculture burning, automotive exhaust emissions and anthropogenic emissions (Khwaja, 1995; Chebbi and Carlier, 1996; Souza et al., 1999; Hsieh et al., 2008; Tsai et al., 2010). These emissions impact on regional air quality and visibility, ecosystems and human health, and climate change (Khwaja, 1995; Souza et al., 1999; Charlson et al., 2001; Tsai et al., 2007).

Low molecular weight carboxylic acids are ubiquitous and important components in aerosol particles (Chebbi and Carlier, 1996). The carboxylates in the particle phase in the atmosphere may result both from primary emissions (Kawamura and Kaplan, 1987) and from secondary photochemical reactions (Yao et al., 2004). The monocarboxylic acids formic and acetic acids constitute the most abundant carboxylic acids in the global troposphere (Khwaja, 1995; Souza et al., 1999). During daytime, vehicular emissions appear to be the primary source of acetic acid, whereas formic and pyruvic acids might be formed photochemically (Souza et al., 1999). Monocarboxylic acids present with a daytime maximum and a nighttime minimum (Khwaja, 1995; Chebbi and Carlier, 1996). The dicarboxylic acids (DCAs) are also important constituents of ambient particulate organic matter (Kawamura et al., 1996; Souza et al., 1999). Forest fires produce large amounts of DCAs (Pio et al., 2008; Kuo et al., 2011). Oxalic acid is the most abundant species, followed by succinic and/or malonic acid (Khwaja, 1995; Chebbi and Carlier, 1996; Hsieh et al., 2008, 2009; Tsai et al., 2008). Wang and Shooter (2004) suggested that emissions from coal and wood burning were the dominant source of maleic acid in an urban atmosphere while Tsai et al. (2010) reported wood burning as the dominant source of maleic acid in atmospheric aerosols.

During biomass burning, the biopolymer cellulose is combusted to yield a tarry material containing anhydrosugars (Santos et al., 2002). These combustion products, together with other thermal decomposition products from celluloses and hemicelluloses (e.g. levoglucosan, mannosan and galactosan), may be used as tracers of cellulose-containing biomass burning (Santos et al., 2002; Schmidl et al., 2008; Caseiro et al., 2009; Tsai et al., 2010). Levoglucosan (1,6-anhydro-β-D-glucopyranose), particularly, is recognized as a tracer of biomass burning in atmospheric aerosols. It is formed as a result of the thermal breakdown of cellulose, accompanied by generally less amounts of straight-chain, aliphatic and oxygenated compounds and terpenoids present in the biomass subjected to burning, and hence is specific to cellulose-containing biomass. Tsai et al. (2010) found that sugar alcohols could also be used as diagnostic markers of saccharide polyols for identifying the contribution of different types of biomass smoke. Furthermore, sugar alcohols such as arabitol and mannitol are structurally related to levoglucosan (Pio et al., 2008). Xylitol can also serve as a tracer for biomass burning (Tsai et al., 2010).

In Southeast Asia, biomass burning occurs in a vast region including India, Bangladesh, Myanmar, Thailand, Laos, Cambodia, Vietnam and southern China (Christopher and Kimberly, 1996; Streets et al., 2003; Srinivasan and Gadgil, 2002; Lee et al., 2011). This biomass burning produces the regional haze known as "Asian Brown Cloud" (Ramanathan and Crutzen, 2003) Chiang Mai, in northern Thailand, experiences severe biosmoke air pollution, primarily for a period of several weeks up to the beginning of April. Levels of $PM_{2.5}$ and PM_{10} in the Chiang Mai atmosphere are very high during the winter months, with daily $PM_{2.5}$ (24 h values) frequently exceeding 200–300 μg m^{-3}. There may be significant health implications associated with these high concentrations (Vinitketkumnuen et al., 2002), yet few formal studies have described atmospheric characteristics of particulate matter in Chiang Mai during the dry, biomass burning season (December to April). Chantara and Chunsuk (2008) noted the paucity of data related to water-soluble inorganic species in atmospheric particles and wet deposition and it can therefore be implied that a comparison of carboxylates, anhydrosugars and sugar alcohols in PM aerosol has not been reported in the literature. Chiang Mai sits in a basin and, with approximately 1 million inhabitants, is the largest city in northern Thailand. Farmers in the mountains surrounding the Chiang Mai Basin often still burn straw/leaves/agricultural waste or arbitrarily set fire to forests to facilitate manual harvesting. This biomass burning results in a great cloud of smoke spreading over the city and its surrounding area and causes serious air pollution. Furthermore, biomass burning in Southeast Asia affects air quality in other parts of the region as particulate matter is transported eastward by the prevailing westerly winds during the dry monsoon season in March and April every year. Lee et al. (2011), for example, reported impacts on air quality in East Asia, as detected at the Mt. Lulin Atmospheric Background Station in central Taiwan, West Pacific (LABS, 2862 m above sea level).

The main purpose of this study is to characterize the inorganic and organic components (carboxylates, anhydrosugars and sugar alcohols) of atmospheric aerosol during the dry, biomass burning season in Chiang Mai Basin, with a view to explaining the aerosol characteristics and identifying the profiles of biomass burning and anthropogenic pollution in Chiang Mai. Ultimately, this research can contribute to a better understanding of the sources of aerosol components detrimental to health.

2. Experimental

2.1. Sampling sites and sampling program

Aerosol samples were collected simultaneously at two sites on 47-mm Teflon filters (Zefluor, Pall) using Ecotech MicroVol 1100 Particulate Samplers with PM_{10} inlet and a constant volumetric flow rate of 3.0 L min^{-1}. One site, at latitude 18°47′54.90″ N and longitude 98°56′55.75″ E, was at Chiang Mai University (CMU). The sampling monitor was placed on a rooftop, set at a height of 12 m above ground. Located about 2 km west of Chiang Mai City, with medium traffic, and impacted by anthropogenic activities, the CMU site is characterized as urban. The other site, at latitude 18°41′ 40.04″ N and longitude 99°02′ 59.45″ E, was at TOT Public Company Limited (TOT). This site is located about 15 km southeast of Chiang Mai City, alongside a busy street and within the busy highway No. 11 and an industrial zone (including petrochemical, cement, ceramic and metal industrial parks), and is characterized as industrial. Locations of both sites are shown in Fig. 1. The prevailing winds in this region are from the NW and NNW with an approximately 25% occurrence of southeasterly winds and relatively low frequency of southwesterly and northeasterly winds. The prevailing winds cross mountains and forests located to the north and northwest of Chiang Mai before entering the city, while the southeasterly winds, with speeds between 2.1 and 3.6 m s^{-1}, have the potential to transport emissions from the industrial regions to the southeast of Chiang Mai into the city.

The sample collection period ran from 2 February to 2 April 2010, during which two PM_{10} aerosol samples were collected daily at both sites, one from 7 am to 7 pm (12 h: 'daytime') and one from 7 pm to 7 am (12 h: 'nighttime'). This period is hereafter referred to as the intensive observation period (IOP).

2.2. Sample handling

Before use, filters were stored at 23 ± 3 °C and 35 ± 5% RH for >24 h and then weighed at 50 ± 3% RH using a Mettler Toledo AT261 analytical balance with a sensitivity of ±10 μg and a Sartorius CP2P analytical balance with a sensitivity of ±1 μg, and this