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Polar and non-polar organic aerosols from large-scale agricultural-waste burning emissions in Northern India: Implications to organic mass-to-organic carbon ratio

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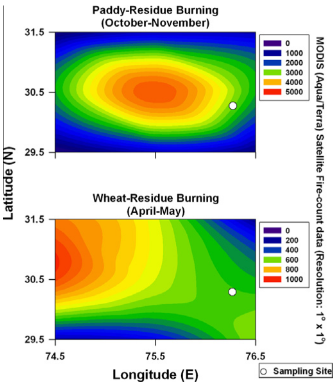
HIGHLIGHTS

- Chemical characteristics of organic aerosol from paddy- and wheat-residue burning.
- Mass contribution of polar organic aerosols is dominant (~85%).
- OM/OC ratio is close to 1.9 for agricultural-waste burning emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

This study focuses on characteristics of organic aerosols (polar and non-polar) and total organic mass-to-organic carbon ratio (OM/OC) from post-harvest agricultural-waste (paddy- and wheat-residue) burning emissions in Northern India. Aerosol samples from an upwind location (Patiala: 30.2°N, 76.3°E) in the Indo-Gangetic Plain were analyzed for non-polar and polar fractions of organic carbon (OC1 and OC2) and their respective mass (OM1 and OM2). On average, polar organic aerosols (OM2) contribute nearly 85% of the total organic mass (OM) from the paddy- and wheat-residue burning emissions. The water-soluble-OC (WSOC) to OC2 ratio, within the analytical uncertainty, is close to 1 from both paddy- and wheat-residue burning emissions. However, temporal variability and relatively low WSOC/OC2 ratio (Av: 0.67 ± 0.06) is attributed to high moisture content and poor combustion efficiency during paddy-residue burning, indicating significant contribution (~30%) of aromatic carbon to OC2. The OM/OC ratio for non-polar (OM1/OC1 ~ 1.2) and polar organic aerosols (OM2/OC2 ~ 2.2), hitherto unknown for open agricultural-waste burning emissions, is documented in this study. The total OM/OC ratio is nearly identical, 1.9 ± 0.2 and 1.8 ± 0.2, from paddy- and wheat-residue burning emissions.

1. Introduction

Organic aerosols (OA) contribute significantly (~20–90%) to the total fine particulate matter ($PM_{2.5}$: particle with aerodynamic diameter $\leqslant 2.5$ μm) in the troposphere (Andreae and Crutzen, 1997; Duce et al., 1983; Kanakidou et al., 2005). Based on their chemical characteristics, OA can be broadly subdivided into polar

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and non-polar compounds. The polar nature of OA has relevance to their enhanced activity as cloud condensation nuclei (CCN) (Jimenez et al., 2009; Saxena and Hildemann, 1996; Sullivan et al., 2004). A recent study addresses the issue related to polar nature of OA and its CCN efficiency; an increase in the degree of polar character enhances their nucleating property (Lathem et al., 2012). The impact of OA, with varying contribution of polar and non-polar fractions, on the direct and indirect radiative forcing has been suggested due to water uptake capacity of organic particles (Jacobson et al., 2000). In this context, the anthropogenic aerosols from different emission sources can have different fractions of polar and non-polar OA (Russell, 2003).

The available information on mass fractions of polar (hydrophilic) and non-polar (hydrophobic) OA has been utilized for assessing their direct radiative forcing impact (Ming et al., 2005). One of the major outcomes of their study suggests that if all of the OA are non-polar (hydrophobic), leading to a complete deprivation of water uptake, then radiative forcing at top-of-the atmosphere (TOA) would reduce by $\sim$20%. Based on theoretical estimates reported in literature (Turpin and Lim, 2001), their study utilizes organic aerosol mass-to-organic carbon (OM/OC) ratio of 1.7 for polar and 1.3 for the non-polar organic aerosols. The OM/OC ratio is of immense significance in assessing the global distribution of OA. This in turn has impact on the estimation of atmospheric radiative forcing and deposition of nutrients associated with OA (N and P) to the open ocean (Kanakidou et al., 2012). In general, the chemical transport models for representing the global distribution of atmospheric OA and their impact on the radiative forcing use a theoretical estimate of OM/OC ratio of 1.6 ± 0.2 over urban and 2.1 ± 0.2 over non-urban regions (Kanakidou et al., 2005; Turpin and Lim, 2001). However, recent studies characterizing the ambient organic aerosols from Atlanta (El-Zanan et al., 2009), in northeastern Asia and in the Caribbean (Russell, 2003), suggest that the OM/OC ratio over urban and non-urban regions can be significantly different than that estimated theoretically (Turpin and Lim, 2001). A large spatial variability in OM/OC ratio reported in the literature, varying from 1.2 to 2.3 (El-Zanan et al., 2009; Japar et al., 1984; Kiss et al., 2002; Russell, 2003; Turpin and Lim, 2001) demands a better assessment of this parameter in ambient aerosols from different sources. With this rationale, we report here on the characterization of polar and non-polar OA and OM/OC ratio in ambient aerosols ($PM_{2.5}$) from open biomass burning emissions in the Northern India. The open biomass (post-harvest agricultural-waste) burning of paddy- and wheat-residue are dominant sources of particulate matter over Northern India during October–November and April–May, respectively (Rajput et al., 2011).

2. Methodology: Solvent extraction approach

2.1. Solvent extraction of organic aerosols: Polar and non-polar organics

The sampling site (Patiala: 30.2°N, 76.3°E, 250 m above mean sea level) in Northern India is surrounded by agricultural-fields and located upwind of major industrial polluting sources in the Indo-Gangetic Plain (IGP). The details regarding sampling site and regional meteorology have been reported in an earlier publication (Rajput et al., 2011). In this study, we report on the characteristics of organic aerosols (polar and non-polar fractions) collected from two distinct biomass burning emissions. $PM_{2.5}$ samples were collected onto tissuquartz fiber filters (20 cm × 25 cm; PALLFLEX™; 2500QAT-UP) using a high-volume sampler (Thermo Scientific, calibrated flow rate: $1.2\ m^3\ min^{-1}$) during massive emissions of particulate matter from post-harvest burning of paddy-residue (with moisture content: 40–50%) in October–November and wheat-residue (moisture content <5%) burning in April–May. The aerosol samples were extracted using accelerated solvent extraction technique (ASE 200, Dionex®), sequentially in hexane followed by dichloromethane (DCM):acetone (1:1, v:v) mixture (in 30–40 mL each; Table 1). The organic carbon (OC1) and organic mass (OM1) in hexane correspond to non-polar fraction of OA; whereas the OC2 and OM2 determined in DCM:acetone extract correspond to polar fraction. Each extract was evaporated to near dryness under inert atmosphere (N_2) in an evaporator (Turbo Vap® LV II, Caliper Life Sciences, Hopkinton, USA). Subsequently, the final volume was made to 0.5 mL by adding the appropriate solvent, hexane to non-polar and acetone to polar fraction. From each of these fractions, a 20 μL aliquot was deposited onto the pre-combusted tissuquartz filter (1.5 sq. cm) for determination of OC1 and OC2, whereas a 100 μL aliquot was deposited for the gravimetric determination of OM1 and OM2. All solvents [hexane, DCM and acetone; Chromasolv® Plus, Sigma–Aldrich] used for extraction and sample preparation were HPLC grade (purity $\geqslant$95%).

2.2. Quality assurance and quality control (QA/QC) for determination of OC

The concentrations of OC1 and OC2 were determined using thermo-optical method on Carbon Analyzer (Sunset Laboratory, US) using NIOSH protocol (National Institute for Occupational Safety and Health) (Rengarajan et al., 2007). Likewise, total organic and elemental carbon (OC, EC) in composite aerosols were determined using a separate filter-punch (1.5 sq. cm) on Carbon Analyzer. The OC concentration determined in composite aerosols was used for comparison with that measured (OC1 and OC2) after solvent extraction. The OC and OM contents of polar and non-polar fractions were determined after drying the filter punches for about 24 h in an inert atmosphere (N_2) at room temperature. The complete evaporation of solvents (hexane and DCM:acetone) on filter punches was ascertained by measuring the OC content in blank filters ($n = 14$; $0.41 \pm 0.09\ \mu g\ cm^{-2}$) that were processed with solvents and compared to that in the unprocessed blank filters. Furthermore, with every batch of analysis, a 100 μL of hexane and acetone were deposited on blank filter punches (1.5 sq. cm) and left over night for drying under inert atmosphere (nitrogen purging, as discussed above). Subsequent determination of OC in these filter aliquots, also ascertain that no measurable memory effect of solvents influences the determination of OC, and hence OM in the aerosol samples.

Over 60% of the samples were analyzed in duplicate to ascertain the uncertainty in the measurements for OC and EC as ±3% and ±7%, respectively. Analytical accuracy in the determination of total carbon was assessed by analyzing known amount of potassium hydrogen phthalate (KHP) solution ($n = 22$); the average ratio of measured carbon to expected carbon is 1.03 ± 0.05 (Av ± sd).

Table 1
Extraction protocol for quantitative determination of non-polar and polar fractions of organic aerosols.

Technique	Solvent extraction (30 mL)	OC	Organic mass
ASE[a]	Hexane	Non-polar (OC1)[b]	OM1[c]
	DCM:acetone (1:1, v:v)	Polar (OC2)[b]	OM2[c]

[a] Accelerated solvent extraction [200 series, Dionex®: T: 100 °C and P: 10342 (k)Pa].

[b] OC1 and OC2 are determined on a thermo-optical (transmittance) EC–OC Analyzer using NIOSH protocol (National Institute for Occupational Safety and Health) (Rajput et al., 2011).

[c] OM1 and OM2 are assessed gravimetrically.