



Role of ammonium ion and transition metals in the formation of secondary organic aerosol and metallo-organic complex within fog processed ambient deliquescent submicron particles collected in central part of Indo-Gangetic Plain



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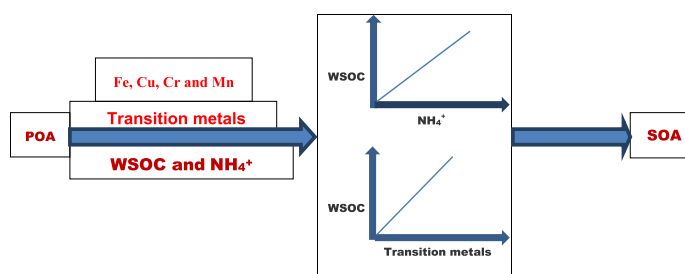
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HIGHLIGHTS

- Strong correlation of transition metals (Fe, Cu, Mn and Cr) with WSOC found upto ($\sim R^2 = 0.87$).
- Fe and Cu key Fenton species show good correlation with WSOC.
- A good correlation of WSOC with NH_4^+ was found ($R^2 = 0.71$).
- Role of NH_4^+ in neutralization, stabilization and production of WSOC.
- Aqueous phase production and oxidation of organic aerosol.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study we observed the role of ammonium ion (NH_4^+) and transition metals (Fe, Mn, Cr, and Cu) present in ambient submicron particles in stabilizing and enhancing the yield of water soluble organic carbon (WSOC). A good correlation of WSOC with transition metals and NH_4^+ was found ($R^2 = 0.87$ and 0.71), respectively within foggy episode collected ambient PM_{10} (particles having aerodynamic diameter $\leq 1.0 \mu\text{m}$) suggesting plausibility of alternate oxidation (primarily various carbonyls into their respective organic acids, esters and other derivatives.) and aging mechanisms. Molar concentration of ammonium ion was observed to be exceeded over and above to require in neutralizing the sulphate and nitrate which further hints its role in the neutralization, stabilization and enhancement of subset of WSOC such as water soluble organic acids. Transition metals were further apportioned using enrichment factor analysis. The source of Fe, Mn, and Cr was found to be crustal and Cu was tagged to anthropogenic origin. This study also described the plausible role of significant predictors (Fe and Cu) in the secondary organic aerosol (SOA) formation through effect of Fenton chemistry. Mass-to-charge ratio of identified oxalic acid from our published recent field study (carried out from same sampling location) was used for understanding the possible metallo-organic complex with Fe supports the substantial role of Fe in SOA formation in the deliquescent submicron particles facilitated by aqueous-phase chemistry.

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1. Introduction

Organic aerosol comprises of about 20–90% of submicron

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aerosol mass and it plays an important role in influencing Earth's climate primarily by two ways the first one is directly by absorbing and scattering solar radiation and the second one is indirectly by acting as cloud condensation nuclei (Jimenez et al., 2009). At the global scale chemical secondary organic aerosol formation (SOA) could be at least 50% of the primary organic aerosol emissions (Kanakidou et al., 2005). A study carried out by Rajput et al. (2017) in the central part of Indo-Gangetic Plain (IGP), they reported that bioaerosols, organic carbon and ambient particulate matter play a significant role in influencing climate and human health. Deshmukh et al. (2016) were reported that dicarboxylic acid and related compounds had strong correlations with levoglucosan and K^+ in fine mode of size-segregated aerosols collected from central India, their correlations imply a substantial contribution of primary emission from biomass burning and secondary formation from biomass burning-derived precursors.

Organic compounds form a major portion of airborne particulate matters and thus it is important to measure and identify the organic pollutants such as the polycyclic aromatic hydrocarbons and SOA fraction emitted primarily from the different combustion sources (Gupta and Singh, 2016). Rajput et al. (2015) reported that fossil-fuel based activities accountable for loading of primary and secondary aerosols contribute nearby 80%. Nevertheless, the biomass burning emissions add only to nearly 20%. They observed that secondary sources are contributing 40% of PM_{10} (particles having aerodynamic diameter $\leq 1.0 \mu m$) loading which are primarily formed from vehicular emission sources (fossil-fuel combustion). Thus, their study also highlights the high concentration of PM_{10} loading and atmospheric fog predominant throughout wintertime in the IGP can have adverse effect over the human health.

Organic aerosols adversely affect on human health and air quality. However, various types of ambiguities exist in determining true nature, the quantification of these organic aerosols and their adverse effect on health and climate. This is primarily attributed to the existence of a fairly wide and complex set of organic aerosol species in the ambient atmosphere (Poschl, 2005; Hallquist et al., 2009).

Metals speciation have an intense effect on their biological accessibility as they affect their aqueous and tissue level solubility and have serious consequences on the target organ (Okochi and Brimblecombe, 2002). It has been reported that the uptake of gaseous polar organic compounds augmented by metals and organic complex and also they enhance the solubility of metals in both atmospheric water and aerosols. (Okochi and Brimblecombe, 2002). The catalytic ability of transition metals were found to be enhanced by complex formation of metal ions with organic compounds (Spokes et al., 1996). In atmospheric aerosols and liquid water iron (Fe) manganese (Mn) and copper (Cu) were found to be the most abundant transition metals and it was observed that these metal ions are passed through aerosols into liquid phase which contain oxides and oxo-hydroxides of metal and particles of silicate. By the process of photochemical and thermal processes the metal oxide can convert into soluble metals at the surface of the particulate matter (Zuo and Hoigne, 1992; Erel et al., 1993). The complex transition metals redox chemistry in atmospheric liquid was first attempted by Deguillaume et al. (2004) and Graedel et al. (1986). Their results point out that (Cu^+ and Cu^{2+}), (Fe^{2+} and Fe^{3+}) and (Mn^{2+} and Mn^{3+}) plays an important role in aqueous phase facilitated by radical chemistry. They also predicted that Fe^{3+} -complexes photolysis should be crucial in cloud sources of hydroxyl radicals and that transitions metals should be the sinks for HO_2/O_2^- radicals in clouds. Fe^{2+} is generated through Fe^{3+} hydroxide photolysis and Fe^{3+} -oxalate complexes photolysis and also by of HO_2/O_2^- radical or Cu^+ reactions with Fe^{3+} -hydroxo

complexes (Zuo and Hoigne, 1992; Faust and Zepp, 1993). In addition to water soluble substances present in atmospheric particulate matter, various potential organic compounds have been determined (Saxena and Hildemann, 1996; Pun et al., 1999). Decesari et al. (2000) observed 77% of WSOC as polyols/polyethers, mono/dicarboxylic acids and fulvic/humic acid derived from fog water samples analyzed by using 1H NMR and TOC analyses.

Noziere et al. (2009) suggested that ammonium-catalysed reaction with carbonyls such as glyoxal occurs within aerosol particles supports SOA formation. They also reported that reactions of glyoxal with OH radicals play a substantial role to the sink of glyoxal during daytime. Ammonium catalysis has an important role in the formation of oligomers and heterocycle containing carbon-oxygen/carbon-nitrogen bond via formation of iminium intermediate within atmospheric aerosols (Noziere et al., 2009).

The accurate mechanism of secondary organic aerosol (SOA) formation is still not completely implicit but it is largely ascribed gas to particle phase conversion and oxidation of reactive organic gases (Gupta and Singh, 2016). Carboxylic acids particularly dicarboxylic acid such as oxalic acid are common in water droplets suspended in ambient atmosphere (Zuo and Zhan, 2005). These chemical compounds (primarily carbonyls and their derivatives) are produced by ozonolysis, incomplete combustion and hydrocarbons oxidation in the presence of sunlight in the atmospheric liquids or in gas phase. Due to polar nature, the carbonyl compounds are specially changed to the liquid phase.

Oxalic acid perform as a coordinate ligand for Fe, they have a substantial impact on the speciation and reactivity of Fe^{3+} and Fe^{2+} in acidic atmospheric aqueous phase and form stable complexes. Catalytic activity of metal ions strongly depends on the concentration level of oxidants (e.g. HO_2/O_2^- , H_2O_2 , O_3 , OH^- and O_2) and reductants ($Cu(I)$ and $S(IV)$) as well as the complexing agents (organic ligands like oxalate, formate etc.), pH mostly on the oxidation state of the metal ions (Zuo and Zhan, 2005). It is also possible that once metals get attached to ligands in the aqueous phase it may result in stronger bonding and uptake of various organic compounds present in the gas phase. This has very important implications in context to metal toxicity and related interference with normal functioning of human endocrine system.

This paper presents a good correlation of WSOC with NH_4^+ and transition metals and hints towards their underlying significant role in ambient aerosol aqueous oxidation by Fenton reaction during foggy episode. This study also explains the plausible role of transition metals primarily Fe and Cu in Secondary Organic Aerosol (SOA) formation. This may be over and above the typical photochemical oxidation as evident in the excess production of SOA from our past field studies (Singh and Gupta, 2016a; Kaul et al., 2011). In this paper, the data obtained from our previous studies Singh et al. (2014) and Singh and Gupta (2016a) have been reconsidered to investigate the correlation of WSOC with NH_4^+ and transition metals and to explore their role in ambient aerosol aqueous oxidation. Mass to charge ratio of oxalic acid, their derivatives and levoglucosan was reconsidered for understanding the metallo-organic complex of Fe with oxalic acid. However, the methods and analyses performed in previous studies have been described here briefly for the convenience of the reader.

2. Materials and methods

2.1. Description of sampling site

PM_{10} samples were collected on the roof top of a 12 m high building (Western Laboratory Extension) in Indian Institute of Technology (IIT) Kanpur campus (lat: 26.308N; long: 80.138E; 142 m above mean sea level) during fog-dominated period

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