Dual isotope (^{13}C-^{14}C) Studies of

Water-Soluble Organic Carbon (WSOC) Aerosols

in South and East Asia

Elena N. Kirillova

Doctoral Thesis

Department of Applied Environmental Science

Stockholm University

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Cover: Yellow Sea from Jeju Island, South Korea, March 2011

Abstract

Atmospheric aerosols may be emitted directly as particles (primary) or formed from gaseous precursors (secondary) from different natural and anthropogenic sources. The highly populated South and East Asia regions are currently in a phase of rapid economic growth to which high emissions of carbonaceous aerosols are coupled. This leads to generally poor air quality and a substantial impact of anthropogenic aerosols on the regional climate. However, the emissions of different carbon aerosol components are still poorly constrained. Water-soluble organic carbon (WSOC) is a large (20-80%) component of carbonaceous aerosols that can absorb solar light and enhance cloud formation, influencing both the direct and indirect climate effects of the aerosols.

A novel method for carbon isotope-based studies, including source apportionment, of the WSOC component of ambient aerosols was developed and tested for recovery efficiency and the risk of contamination using both synthetic test substances and ambient aerosols (**paper I**). The application of this method for the source apportionment of aerosols in South and East Asia shows that fossil fuel input to WSOC is significant in both South Asia (about 17-23%) highly impacted by biomass combustion practices and in East Asia (up to 50%) dominated by fossil energy sources (**papers II, III, IV**). Fossil fraction in WSOC in the outflow from northern China is considerably larger than what has been measured in South Asia, Europe and USA (**paper IV**). A trend of enrichment in heavy stable carbon isotopes in WSOC with distance the particles have been transported from the source is observed in the South Asian region (**papers II, III**). Dual-isotope ($\Delta^{14}C$ and $\delta^{13}C$) analysis demonstrates that WSOC is highly influenced by atmospheric aging processes.

List of abbreviations

AAE	Ångström absorption exponent
ABC	Atmospheric Brown Clouds
AMS	Accelerator mass spectrometer
BC	Black carbon
BTs	Back-trajectories
BVOCs	Biogenic volatile organic compounds
CCN	Cloud condensation nuclei
DOC	Dissolved organic carbon
EC	Elemental carbon
KIE	Kinetic isotope effect
MAC	Mass absorption coefficient
OC	Organic carbon
OA	Organic aerosols
POA	Primary organic aerosols
QFF	Quartz fiber filter
SC	Soot carbon
SOA	Secondary organic aerosols
TC	Total carbon
TOC	Total organic carbon
TSP	Total suspended particulates
VOCs	Volatile organic compounds
WINSOC	Water-insoluble organic carbon
WS-BrC	Water-soluble brown carbon
WSOC	Water-soluble organic carbon

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List of papers

Paper I

Natural abundance ^{13}C and ^{14}C analysis of water soluble organic carbon (WSOC) in atmospheric aerosols.

Kirillova, E. N., R. J. Sheesley, A. Andersson, and Ö. Gustafsson (2010), *Analytical Chemistry, 82,* 7973–7978.

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Paper II

^{13}C- and ^{14}C-based study of sources and atmospheric processing of water-soluble organic carbon (WSOC) in South Asian aerosols.

Kirillova E. N., A. Andersson, R. J. Sheesley, M. Krusa, P. S. Praveen, K. Budhavant, P. D. Safai, P. S. P. Rao and Ö. Gustafsson (2013), *Journal of Geophysical Research - Atmospheres, 118,* 614–626, doi:10.1002/jgrd.50130.

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Paper III

Water-soluble organic carbon aerosols during a full New Delhi winter: Isotope-based source apportionment and optical properties.

Kirillova, E.N., A. Andersson, S. Tiwari, A.K Shrivastava, D.S. Bisht and Ö. Gustafsson

Manuscript

Paper IV

Sources and light absorption of water-soluble brown carbon aerosols in the outflow from northern China.

Kirillova, E.N., A. Andersson, J. Han, M. Lee and Ö. Gustafsson

Submitted

Statement

I, Elena N. Kirillova, contributed to the papers included in the thesis as follows:

Paper I. I developed and tested the method for the isolation of water-soluble organic carbon (WSOC) from atmospheric aerosol samples and its preparation for carbon isotope analysis. I collected the samples used for method validation and wrote the paper with substantial support from co-authors.

Paper II. The sampling campaign in 2008-2009 was planned and performed by others. I carried out all the laboratory analysis and performed data interpretation in collaboration with the co-authors. I had the main role in the writing of the paper.

Paper III. The sampling campaign in 2010-2011 was planned and performed by others. I performed all the laboratory analysis and took a leading role in the paper writing.

Paper IV. I actively participated in the planning of the Gosan Pollution Experiment (GoPoEx) campaign in March 2011 and had a leading role in the sample collection. I did all the laboratory analysis and took a leading role in the paper writing. The data interpretation was done in close collaboration with the co-authors.

Objectives of the thesis

The overall objective of this thesis was to investigate the sources and characteristics of water-soluble organic carbon (WSOC) in the highly polluted South and East Asian regions using dual-carbon isotope data. By performing the measurements of natural abundance radiocarbon and stable carbon isotopes, we were able to derive insights on the sources and atmospheric processing of WSOC in ambient aerosols.

The specific objectives for each paper were:

Paper I:

To develop and test a method for dual-carbon isotope-based source apportionment of water-soluble organic carbon (WSOC) component of atmospheric aerosols.

Paper II:

To perform a dual isotopic apportionment of the sources and study of processing of particulate WSOC over South Asia based on a 15-month continuous aerosol sampling campaign at two regional receptor sites: the Indian Ocean site at the Maldives Climate Observatory – Hanimaadhoo island (MCOH) and West India (Sinhagad; SINH).

Paper III:

To perform a carbon isotope-based investigation of WSOC aerosol sources collected in the source region of megacity New Delhi, India during the dry winter season.

Paper IV:

To perform carbon isotope-constrained source apportionment of WSOC and assessment of its light absorption properties in the outflow from northern China collected during the Gosan Pollution Experiment (GoPoEx), performed at the Korea Climate Observatory at Gosan (KCOG), Jeju Island, SE Yellow Sea in March 2011.

1. Introduction

1.1. *Atmospheric aerosols*

Atmospheric aerosols consist of a mixture of liquid and solid particles suspended in air with natural or anthropogenic origin that range in size from few nanometers to hundreds of micrometers in diameter (Raes et al, 2000, Seinfeld and Pandis, 2006). Aerosol particles introduce the largest uncertainty to the climate models as they impact the radiation balance of the Earth directly by absorbing and scattering sunlight and indirectly acting as cloud condensation nuclei (CCN) and, therefore, affecting cloud albedo (IPCC, 2007). Moreover, aerosols affect human health by penetrating to the lungs and causing different adverse effects (Downs et al, 2007, Nel, 2005).

Particles can be emitted to the atmosphere directly as primary aerosols, and represent different natural sources like sea spray, terrestrial dust, volcano ash emissions, bacteria, microscopic fungi, spores and pollen, emissions from forest fires etc. (Seinfeld and Pandis, 2006). Fossil fuel and biomass/biofuel combustion processes are significant sources of anthropogenic primary aerosol particles (e.g., Andreae and Merlet, 2001; Reddy and Venkataraman, 2002a,b). Secondary particles are formed in the atmosphere by transformation of anthropogenic and natural gaseous emissions such as sulfur oxides, nitrogen oxides, and volatile organic compounds (VOCs) into less volatile species and their further nucleation and growth or condensation on the pre-existing particles (Odum et al, 1996; Raes et al, 2000; Song et al, 2005). VOCs can be emitted by land vegetation and marine phytoplankton (Claeys et al, 2004; Kamens et al, 1999; Kavouras et al, 1998; Miyazaki et al, 2011), or generated during the combustion of biomass and fossil fuels, as well as emitted during other anthropogenic activities (various industrial processes, cooking, etc.) (Piccot et al, 1992; Volkamer et al, 2006). Organic aerosols (OA) are a significant component of ambient particle mass, which constitute about 20-50% of fine aerosols at continental mid-latitudes and up to 90% in tropical forests (Kanakidou et al., 2005).

In the atmosphere, primary and secondary aerosols undergo aging processes. Physical processes include particle coagulation and aggregation, structural rearrangement, phase transition, growth/shrinkage by condensation/evaporation of semi-volatile components, adsorption/absorption of volatile components (Fuzzi et al, 2006; Pöschl, 2005). Aerosol

chemical ageing of organic aerosols, e.g. by reactions with the hydroxyl radical, involves processes of oxidation, nitration, hydrolysis, and photolysis leading to functionalization, fragmentation and condensation/oligomerization (Fuzzi et al, 2006; Kroll et al., 2011; Pöschl, 2005).

Aerosols residence time in the atmosphere is relatively short (~ 1–2 weeks) due to their removal by dry and wet deposition processes (e.g., Seinfeld and Pandis, 2006). The size of the particles influences their atmospheric lifetime and the distance they can be transported. While the nucleation mode of submicron particles (<10nm) may survive only few hours due to coagulation and growth, the coarse fraction (>2.5μm) is influenced by gravity and undergo the dry deposition (e.g., Laakso et al., 2003). The residence time is also dependent on the chemical properties of the particles: hygroscopic aerosols can act as CCN and can be easier scavenged by wet deposition, while hydrophobic soot carbon (SC) particles have longer lifetime (Granat et al, 2010).

1.2. Water-soluble organic carbon

Water-soluble organic carbon (WSOC) component is a large fraction (20-80%) of total carbonaceous aerosols (e.g., Feng et al, 2006; Mayol-Bracero et al, 2002; Saxena and Hildemann, 1996). In ambient aerosols, it consists of a large variety of chemical species: anhydrosugars, sugars, alcohols, aliphatic and aromatic acids, amino acids and aliphatic amines, etc, as well as large complicated molecules as Humic-Like Substances (HULIS) (e.g., Graber and Rudich, 2006; Graham et al, 2002; Mader et al, 2004).

WSOC may influence regional climate contributing to direct and indirect climate effects of aerosols. It has recently been found that WSOC exhibits light-absorbing ("brown carbon" BrC) properties (Cheng et al., 2011; Zhang et al., 2011). Therefore, WS-BrC contributes to a direct climate forcing by heating the atmosphere (Bahadur et al, 2012; Chung et al, 2012; Jacobson, 2012). An indirect effect of WSOC is determined by its contribution to the particle's hygroscopicity and hence the ability of aerosol particles to act as cloud condensation nuclei (CCN) (e.g., Asa-Awuku et al., 2008, 2011; Charlson et al., 2001; Facchini et al, 1999; Svenningsson et al., 2006). It is found that organic containing CCN form smaller cloud droplets than inorganic containing CCN (Feng and Möller, 2004), which can affect cloud properties and alter cloud lifetime (Ramanathan et al, 2001). Moreover, absorptive properties

of WS-BrC also contribute to an absorption-indirect climate effect through heating and evaporation of clouds (Jacobson, 2012).

WSOC may affect human health. It has been demonstrated that in mammals WSOC catalyze the reduction of oxygen and, therefore, contributes to the formation of reactive oxygen species that have toxic effect (Biswas et al, 2009; Verma et al, 2009, 2012).

The particulate WSOC can have a primary or a secondary nature (Mayol-Bracero et al, 2002; Miyazaki et al, 2009; Volkamer et al, 2006). Although, primary organic aerosols (POA) are typically less soluble in water (Miyazaki et al., 2006), aging processes usually increase the water solubility of the particulate organic carbon (De Gouw et al, 2008). In order to propose mitigation strategies for the climate and health issues related to WSOC it is important to monitor its ambient concentrations and to examine its main sources.

1.3. Aerosol source studies

Different approaches can be applied in order to determine the carbonaceous aerosol sources. One method is using certain ion or molecular markers indicating primary emissions (elemental carbon, mannitol, arabitol, K^+), secondary aerosol formation (e.g., SO_4^{2-}) or biomass burning (K+ and levoglucosan) (e.g., Kumagai et al., 2009; Miyazaki et al., 2009; Novakov et al., 2000). The application of this method is restricted due to variability of emission factors and the limited stability of the tracers in the atmosphere.

Source apportionment of organic aerosols can also based on the advanced source-receptor techniques, like the chemical mass balance (CMB) and the positive matrix factorization (PMF), applying mathematical models using information of the chemical tracers and emission profiles for the known sources in order to describe the observations (e.g., Kim et al., 2004; Lanz et al., 2008; Ulbrich et al., 2009). However, these methods are developed mainly for the near source studies and may not be applicable for remote background stations.

Another approach involves the analysis of carbon isotopes to distinguish between the aerosol sources (Fig. 1). Radiocarbon isotopes (^{14}C) allows distinguishing between modern and fossil sources and since the 1950s (Clayton et al., 1955) it is applied for different components of organic aerosols (e.g., Gustafsson et al., 2009; Szidat et al., 2004; Weber et al, 2006; Wozniak et al., 2008, 2012a,b Zencak et al 2007b etc) and even for compound-specific radiocarbon analysis (e.g., Mandalakis et al., 2005; Sheesley et al., 2011; Zencak et al., 2007a). The

measured $\Delta^{14}C$ values allow for determining the contributions of contemporary biomass/biogenic sources and radiocarbon-extinct fossil fuel sources based on the isotopic mass balance equation:

$$\Delta^{14}C_{sample} = \Delta^{14}C_{biomass}f_{biomass} + \Delta^{14}C_{fossil}(1-f_{biomass}) \qquad (1)$$

where $f_{biomass}$ is fraction of biomass/biogenic contribution, $\Delta^{14}C_{sample}$ is the measured radiocarbon content of a sample and $\Delta^{14}C_{fossil}$ is -1000‰. The $\Delta^{14}C_{biomass}$ end-member is between +50‰ (contemporary CO_2) and +225‰ (wood logged in the 1990s) values (Graven et al, 2012; Klinedinst and Currie, 1999; Levin et al, 2010; Zencak et al., 2007b).
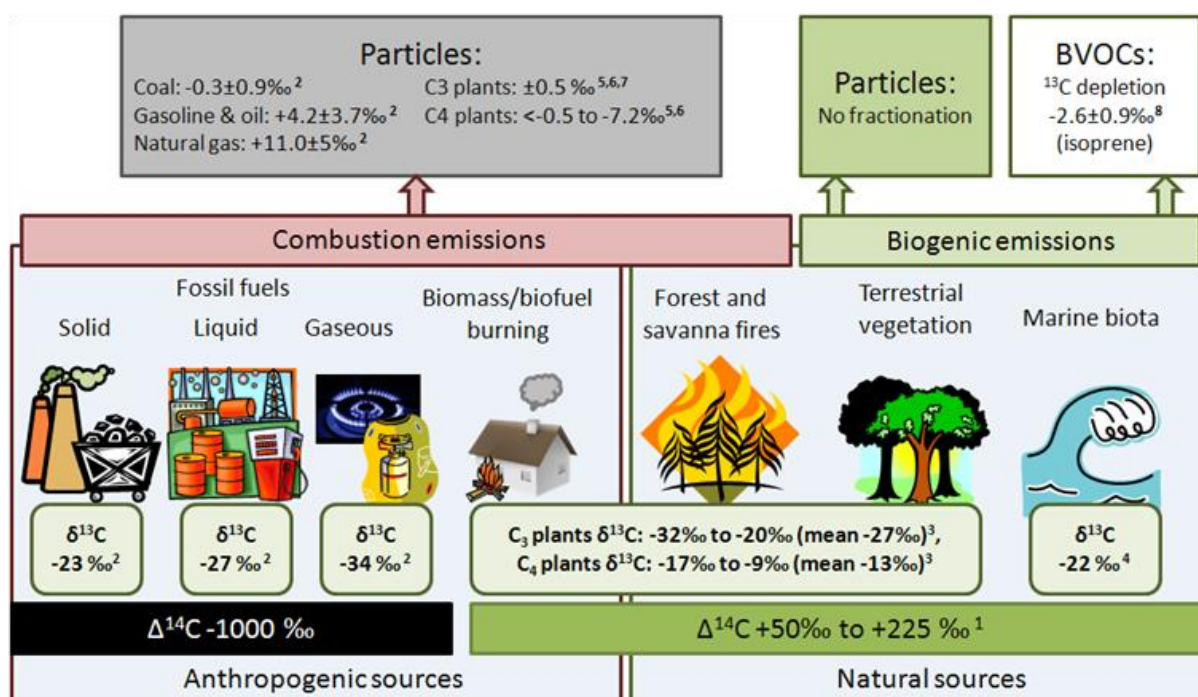
Figure 1. Summarized data of carbon isotope (^{13}C and ^{14}C) signatures for different sources of ambient aerosols and fractionation processes during the emissions. This figure is based on the following literature: [1] Levin et al., 2010, Graven et al., 2012, Zencak et al., 2007b, Klinedinst and Currie, 1999; [2] Widory, 2006; [3] Smith and Epstein, 1971; [4] Miyazaki et al, 2011; [5] Turekian et al, 1998; [6] Das et al, 2010; [7] Currie et al, 1999; [8] Rudolph et al, 2003.

Different aerosol sources also have specific ranges of stable carbon (^{13}C/^{12}C) isotope ratios (Fig. 1). [13]C isotope abundance in vegetation is determined by the photosynthesis pathway. Plants with C_3 and C_4 pathways have different ^{13}C isotope ratios: -32‰ to -20‰ (mean -27‰) and -17‰ to -9‰ (mean -13‰), respectively (Smith and Epstein, 1971). Marine organic aerosol sources, like phytoplankton, typically have mean ^{13}C isotope signature of -22‰ (Miyazaki et al, 2011). Liquid fossil fuel isotope composition is similar to C_3 plants (-28‰ to -24‰), solid fuels such as coal are enriched in $\delta^{13}C$ (e.g., -24 to -21‰) and gaseous fossil

fuels are strongly depleted (-40 to -28 ‰) (Agnihotri at al., 2011; Huang et al., 2006; Lopez-Veneroni, 2009; Kawashima and Haneishi, 2012; Widory, 2006).

Although, some fractionation of stable carbon is observed in the particles produced during combustion processes compared to the initial combusted material (Fig.1). Fractionation in the particles emitted during fossil fuel combustion differs: -0.3 ±0.9‰ (coal), 4.2 ±3.7‰ (gasoline and fuel oil), 11.0±5‰ (natural gas) and depends on combustion conditions (Widory, 2006). Biomass combustion of C_4 plants results in ^{13}C depletion (<0.5 to 7.2‰) in the combustion derived aerosols (Das et al., 2010; Turekian et al., 1998). While the particles produced during C_3 plant combustion demonstrate no significant fractionation compared to plant material (Currie et al., 1999; Das et al., 2010; Turekian et al., 1998).

Also in the atmosphere the formation of secondary organic aerosols (SOA) and the transformation processes of POA can contribute to fractionation of ^{13}C in the particles due to kinetic isotope effect (KIE). KIE describes the ability of molecules with different isotope composition to react with different rates. It is easier to break the bonds of molecules that contain the lightest isotopes, because the vibrational frequency of such bonds will tend to be higher, then the lighter isotopes will be preferentially incorporated in the products of incomplete reactions, while the heavy isotopes will become enriched in the unreacted residue (Criss, 1999).

Photochemical transformation reactions of VOCs result in the formation of oxidized less volatile compounds forming SOA (e.g., Virtanen et al., 2010). Chamber studies show that during photooxidation of both aromatic and aliphatic VOCs the products forming SOA are depleted in ^{13}C compared to the gaseous reactants (e.g., Anderson et al., 2004a,b, Iannone et al., 2010; Irei et al., 2006, 2011). Hence, SOA formation is expected to cause the depletion of the bulk organic aerosols.

Chemical transformations of POA and SOA during aging can also alter the isotopic signature in the bulk OA as well as in either WSOC or water-insoluble carbon (WINSOC) pools. During *functionalization* hydrocarbons are transformed into multifunctional hydrocarbon derivatives with higher oxidation state of carbon atoms, higher polarity, therefore, increased solubility in water (Kroll et al., 2011; Pöschl, 2005;). In these processes isotope composition of total organic carbon (TOC) fraction will not be changed, however, the molecules with more reactive lighter isotopes may be transformed easier and move to WSOC pool. Although, the studies of such processes in the atmospheric aerosols are still lacking.

Condensation (oligomerization/polimerization) reactions lead to covalent association of the organic molecules and can occur during the whole aerosol lifetime (Kalberer et al., 2004; Kroll et al., 2011; Nguyen et al., 2011; Rudich et al., 2007). Large amounts of SOA undergo such processes on the particulate surface (Hung et al., 2005; Jang et al, 2003; Kalberer et al, 2004; Zahardis et al., 2006;). Such polymers/large molecules are less hygroscopic (Kalberer et al., 2004; Rudich et al., 2007) and, therefore, can contribute to the WINSOC component of the particles depleting it in ^{13}C.

Fragmentation reactions include the cleavage of C-C bond and release of semivolatile organic compounds (SVOCs), VOCs, CO, or CO_2, which can lead to volatilization of particulate OC (Kroll et al., 2011; Pöschl, 2005; Rudich et al., 2007). Chamber experiments showed that volatilization is an efficient removal process for aliphatic particulates exposed to OH-initiated oxidation compared to more stable towards volatilization of aromatic particulates (Molina et al, 2004). Due to KIE, such fragmentation and volatilization processes cause the enrichment in ^{13}C of the resulting shorter-chain species remaining in the particulate phase (Wang and Kawamura, 2006). Hence, this group of reactions will lead to TOC enrichment in ^{13}C during the aging. Moreover, the more oxygenated aerosols the faster they fragment and volatilize (Smith et al., 2009). The WSOC component as more oxidized pool in TOC may be the most influenced by these processes.

Finally, it has been demonstrated that condensation or evaporation-related isotopic fractionation of OA components due to SVOCs partitioning between gas and particulate phases is likely insignificant (Harrington et al., 1999; Wang and Kawamura, 2006).

Taken together, compared to radiocarbon-based method it is not straightforward to apply stable carbon isotopes for the ambient aerosol source studies as they contain information not only about the potential sources and formation pathways but also about photochemical aging during the aerosols transport.

1.4. Aerosols in South and East Asia

Rapid economic development and population growth with associated increase of energy production and consumption has resulted in enhanced emissions of OA and their precursors in South and East Asian regions. These regions are influenced by the Asian monsoon systems, which differ in South and East Asia but in general determine both continental and oceanic influences on the regional climate (Carmichael et al., 1996; Hubert et al., 2003; Lawrence and

Lelieveld, 2010; Lee et al., 2003). During the summer monsoon season clean moist maritime air masses dominate in the regions reducing particulate pollution by wet precipitation. The winter season is characterized by the influence of continental dry air masses impacted by the anthropogenic activities. During this season, particulate and gaseous pollutants, to a large extent from India and China, form Atmospheric Brown Clouds (ABC), a thick haze layers that cover large areas in South and East Asia (e.g., Ramanathan and Crutzen, 2003; www.rrcap.unep.org/abc/). ABC have considerable impact on regional climate (heating the atmosphere and cooling the surface), human health, storm frequency and hydrological cycles (e.g., Bollasina et al., 2011; Evan et al., 2011; Ramanathan et al., 2005; Ramanathan and Carmichael, 2008; Shindell et al., 2012).

Fuel usage and combustion practices differ in China and India (e.g., Bond et al., 2004), therefore, the anthropogenic aerosols are expected to be more influenced by biomass/biofuel burning in India and Indian outflow and by fossil fuel (coal) combustion in China (e.g., Fu et al., 2012; Bond et al., 2004; Venkataraman et al., 2005). Several "bottom-up" and "top-down" studies have been performed in these regions to characterize the sources of carbonaceous aerosols and their different components, especially light absorbing black carbon (BC) (Bond et al., 2004; Gustafsson et al., 2009; Sheesley et al., 2011, 2012). However, the uncertainties regarding the sources of bulk OA and especially of WSOC in South and East Asia remain.
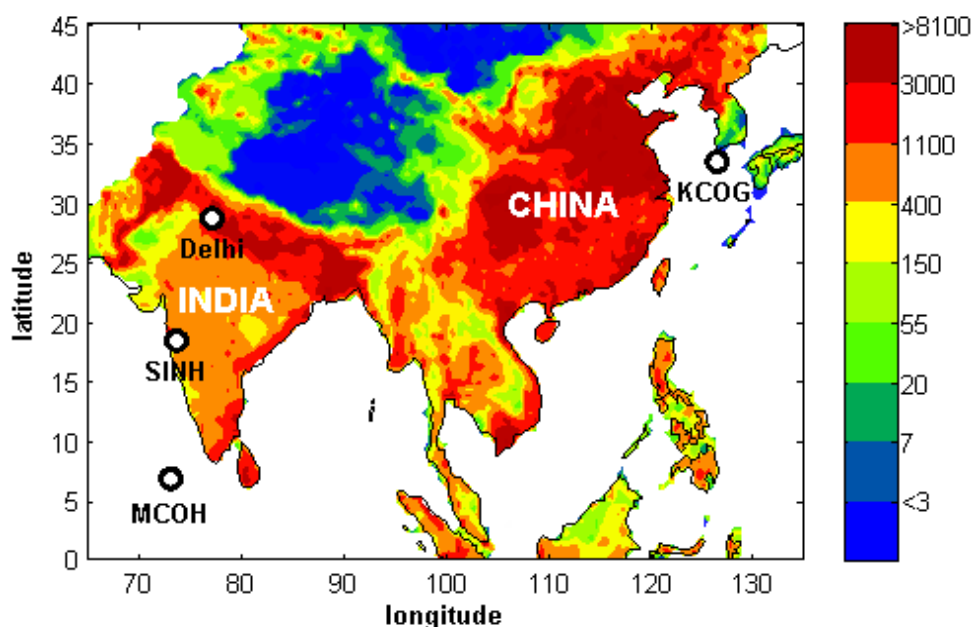
Figure 2. Map depicting emission inventory estimates of anthropogenic emissions of carbonaceous aerosols estimated as the sum of black carbon (BC) and organic carbon (OC) in tons yr^{-1} per 0.5×0.5 degree grid for Asia in year 2006 (data from Zhang et al., 2009). Locations of the study sites are marked as SINH (Sinhagad) and MCOH (Maldives Climate Observatory at Hanimaadhoo), Delhi and KCOG (Korean Climate Observatory - Gosan).

2. Methods

2.1. Field sampling

2.1.1. Stockholm

In order to test the method of WSOC quantification and preparation for isotope analysis (**paper I**), total suspended particulates (TSP) were collected during 3-day intervals from a 15 m platform on the top floor of the Geoscience building (Geohuset) at Stockholm University campus (59°21´58´´N, 18°03´29´´E), Stockholm, Sweden, 19 August - 2 October 2009. The site is located in a mixed grassland-forested area (a National park) about 120 m away from a highway.

2.1.2. Atmospheric Brown Cloud 2008-09 year-round campaign

Year-round study of WSOC component were performed during a 15-month campaign from January 2008 to April 2009 at two regional receptor sites in South Asia (**paper II**).

Sinhagad (SINH)

Sinhagad (SINH: lat 18.35N long 73.75E) is located in NW India on a hill top near Sinhagad Fort, 1300-1400 meters above sea level and is operated by the Indian Institute of Tropical Meteorology (IITM, Pune). There are no strong emission sources in the vicinity of SINH. It is a high altitude site, representing regionally mixed sources in west central India. The aerosol samples (TSP) at SINH were collected with one week intervals during the whole campaign.

The Maldives Climate Observatory at Hanimaadhoo (MCOH)

The Maldives Climate Observatory – Hanimaadhoo (MCOH: lat 6.78N long 73.18E) is located on a small (6.5 x 0.73 km) northern island in the Republic of the Maldives, isolated at the northern tip of the island of Hanimaadhoo and is operated jointly by the Government of the Maldives (currently by Environmental Protection Agency and formerly by the Department of Meteorology) and the UNEP-ABC Programme. This northern Indian Ocean site is located away from significant local sources and in the winter dry period it is located downwind of the Indian subcontinent. The ambient aerosols (TSP) at MCOH were sampled with one week intervals during the non-monsoon periods and two week intervals during monsoon season.

2.1.3. Delhi

To investigate WSOC in the source area aerosol samples were collected at the rooftop sampling site of the IITM-Pune (New Delhi Branch) in the central part of New Delhi, India (28° 35' N; 77° 12' E, 15m a.g.l.). The site is located in a small park-like sector in the central part of New Delhi, India. The sampling campaign covered the dry winter season from the end of October 2010 to the beginning of March 2011. Fine particles ($PM_{2.5}$) were collected every second day with the sampling intervals of 24 hours (**paper III**).

2.1.4. GoPoEx high-intensity campaign at Gosan

Korea Climate Observatory - Gosan (KCOG) (33.17°N, 126.10°E) is located on the western tip of Jeju Island of South Korea at the northern part of the East China Sea, about 100 km south of the Korean peninsula. The station resting at the top of a 72 m cliff and facing the East China Sea has been regarded as an ideal place to study the transport and transformation of atmospheric pollutants in northeast Asia because it has low local anthropogenic emissions and is frequently influenced by various air masses from China, Korea, Japan, and the Pacific Ocean (Kim et al, 2007, 2012). During Gosan Pollution Experiment (GoPoEx) the sampling of TSP and $PM_{2.5}$ was performed from the 8th to 27th of March 2011 (**paper IV**). Sampling intervals (4-24 hours) were synchronized with the air mass direction change.

2.1.5. Sampling equipment and routine

Total suspended particulate (TSP) samples were collected using custom-built samplers operated at 14-19 m^{-3} hr (SINH and MCOH) or 26-39 m^{-3} hr (KCOG) and collected particles on 142 mm quartz fiber filters (QFF; Millipore, Billerica, MA or Pall Gelman) in a custom built filter holder. At KCOG $PM_{2.5}$ size fraction samples were collected using a high-volume air sampler Digitel DHA-80 (Digitel Electronics GmbH, Bürs, Austria) operated at 31 m^{-3} hr and collected PM2.5 samples on 150mm QFF (Millipore). In Delhi an APM 550 aerosol sampler (Envirotech Pvt. Ltd, India) equipped with US EPA standardized impactors was operated at 1 m^3 hr^{-1} to collect $PM_{2.5}$ aerosols on 47mm QFF (Millipore).

All QFF were pre-baked at 450°C for 12 h and individually stored in aluminum foil packets in double Ziploc bags in the freezer. Field blanks were obtained by placing and removing the blank filters in the filter holder at site. All blanks were shipped, stored and processed in an identical manner as the samples.

2.2. Laboratory measurements and calculations

### 2.2.1. TOC concentration measurement and preparation for isotope analysis

Total carbon (TC) concentrations were measured with a standard thermal-optical transmission (TOT) analyzer (Sunset Laboratory, Tigard, OR, USA) using the standard NIOSH 5040 method (Birch and Cary, 1996). For the measurements of ^{13}C and ^{14}C a filter area corresponding to at least 100 μg TC was acidified by fumigation in hydrochloric acid (12M) for 24 hours to remove carbonates and subsequently dried at 60°C for 1 hour. The TOT analyzer was modified for online isolation of CO_2 produced during the combustion of a sample. The total carbon method was used on the TOT instrument to isolate the entire total organic carbon (TOC) for subsequent radiocarbon analysis. During this method a 1.5 cm^2 subsample was heated at the two ramps to 870°C in the atmosphere of helium (98%) and oxygen (2%) during 110 seconds and remained to be exposed to the temperature of 870°C for 190 seconds until all the TOC was oxidized to CO_2. Subsequently, it was cryotrapped in liquid N_2 and sealed in the glass ampoules. Carbon isotope measurements are performed at the US National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility (Woods Hole, MA, USA).

2.2.2. WSOC extraction, quantification and preparation for isotope measurements

In order to make the carbon isotope-based source apportionment of the WSOC, a reliable method for ambient aerosol WSOC extraction and preparation for isotopic analysis was developed and tested for the recovery efficiency and the risk of contamination (**paper I**). The method can be divided into three blocks (Fig. 3): extraction and purification, preparation for isotope analysis and measurements of carbon concentration and isotope ratios.

For quantification of WSOC concentration, initially, filter subsamples are *extracted* during 15 min in 15-20 mL of Milli-Q water by ultrasonication. For further *purification* from the particle suspension and pieces of the filter, the extracts are spinned in the centrifuge at 1500 rpm for 10 min and filtrated using 0.02 μm cutoff aluminum syringe filters. The concentration of the WSOC are *measured* as total dissolved organic carbon (DOC) in the filtered solutions using a high-temperature catalytic oxidation (HTCO) instrument (Shimadzu-TOC-VCPH analyzer; Shimadzu, Kyoto, Japan) following the non-purgeable organic carbon (NPOC) protocol

measuring CO_2 produced by combustion of the acidified sample. For each sample triplicate injections are done. The blank corrections are made using the measurement of WSOC on field blank filters. Finally, the blank corrected WSOC load on the whole filter area and the air volume filtered are used calculate the concentrations in the air.
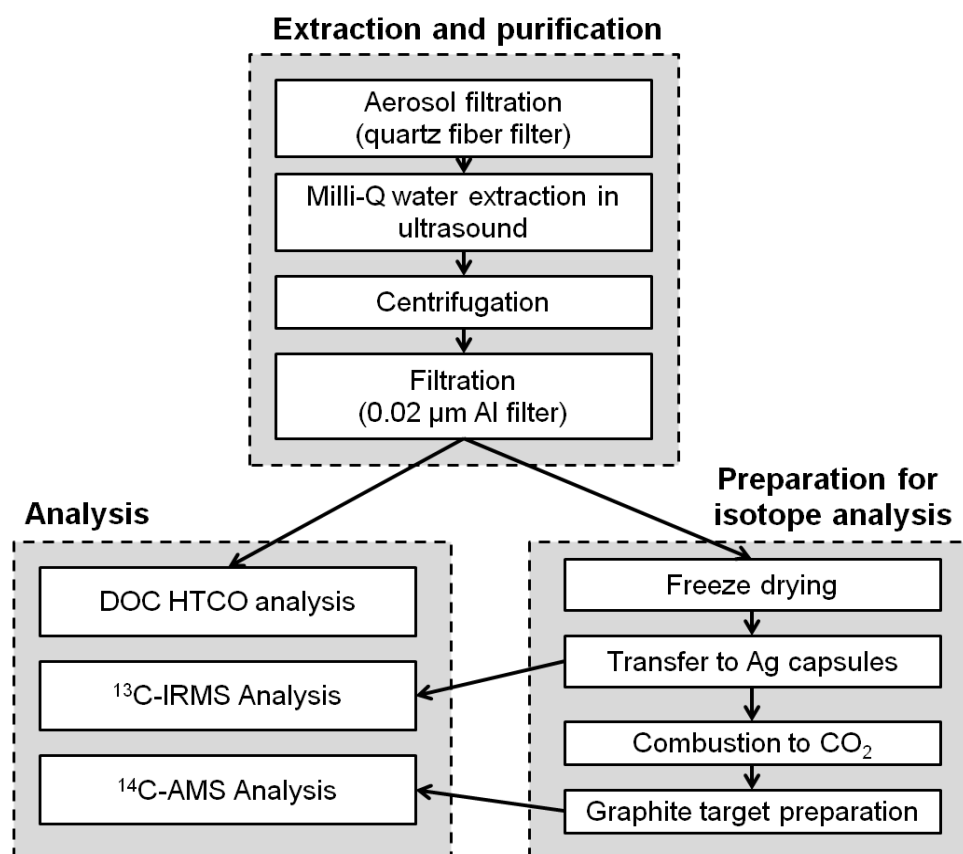
Figure 3. Flowchart of the method for stable carbon and radiocarbon isotope analysis of the WSOC component in atmospheric aerosols. The removal of inorganic carbon is performed right before the DOC high temperature catalytic oxidation (HTCO) analysis step for WSOC concentration measurement and before the Milli-Q extraction step for the radiocarbon analysis.

For isotope analysis, we estimate filter area containing about 300 μg of WSOC based on the previous WSOC concentration measurements. After carbonate removal by acid fumigation as described above for TOC, the filter subsamples are *extracted* the same way as for WSOC concentration measurements in 10 mL of Milli-Q water and *purified* in the same manner by centrifugation and filtration. Then, WSOC solutions placed into 30 ml polycarbonate vials are frozen and freeze dried. The residue material is redissolved in 300 μl of Milli-Q water and transferred into two silver capsules (one third in the capsule for stable carbon measurements and two thirds to the capsule for radiocarbon measurements). Alternatively, for smaller amount of aerosol material, 150 μg is extracted and transferred to one capsule for measurements of both carbon isotopes. Then the water from the capsules is evaporated at

60°C. The capsules are closed and sent for isotope analysis. Stable carbon isotope *measurements* are performed at the Stable Isotope Laboratory (SIL) at the Department of Geological Sciences of Stockholm University (Stockholm, Sweden). The $\Delta^{14}C$ (or both $\delta^{13}C$ and $\Delta^{14}C$) determination is performed at NOSAMS with the Accelerator Mass Spectrometry System (McNichol et al, 1992, Pearson et al, 1998).

The mass recovery, the method-induced isotope contamination and isotope fractionation after all the steps of the preparation to the isotope analysis were assessed for both few WSOC test substances (oxalic acid, cis-pinonic acid, phthalic acid and sucrose) and ambient aerosols sampled in Stockholm area (**paper I**). The average mass recovery for the WSOC test compounds was 71±20% and for the ambient aerosol samples 73±11%. Despite the mass was not completely recovered, no isotope contamination and isotope fractionation was observed.

2.2.3.   Isotope ratios

Results of the stable carbon isotope analysis are reported as $\delta^{13}C$ according to the following equation:

$$\delta^{13}C = ((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{std} - 1) \times 1000‰ \qquad (2)$$

where the standard is the Vienna Pee Dee Belemnite (VPDB).

Radiocarbon data are reported as fraction modern (F_m) calculated from the following equation:

$$F_m = (S-B)/(M-B) \qquad (3)$$

where B, S, and M represent the $^{14}C/^{12}C$ ratios of the blank, the sample, and the modern reference, respectively. The $^{14}C/^{12}C$ ratio of the modern reference is defined as 95% of the radiocarbon content of NBS Oxalic Acid I in AD 1950 normalized to $\delta^{13}C$ of -25‰.

Due to the very low load of WSOC on field blank filters there was not sufficient carbon mass for isotope measurements in the WSOC blank samples. Therefore, the blank correction for WSOC radiocarbon measurements have been done using isotope ratios of TOC blank samples. The definition of $\Delta^{14}C$ by Stuiver and Polach (1977) as the relative difference between the $^{14}C/^{12}C$ ratios of the absolute international standard (base year 1950) and sample corrected for the age of the sample is described in the following equation:

$$\Delta^{14}C = (Fm \times e^{\lambda(1950-x)} - 1) \times 1000‰ \qquad (4)$$

where λ is 1/(true mean-life) of radiocarbon (corresponding to 1/8267) and x is the year of collection. From these $\Delta^{14}C$ values, fractional contributions of contemporary biomass/biogenic sources vs radiocarbon-extinct fossil fuel sources can be determined using the isotopic mass balance equation (1).

Since the relative contributions to WSOC from biogenic SOA and from biomass burning POA and SOA are not known *a priori*, they were assumed to be of equal importance. Hence, the biogenic/biomass $\Delta^{14}C$ endmember for WSOC was set to +124‰ in S.Asia, which is the mean value of +50‰ and +199‰ calculated for biomass burning in India (Gustafsson et al., 2009), and +81 which is the mean value of +50‰ and +112‰ applied to biomass burning in China.

2.2.4. Uncertainty estimation.

The precision in the TOC and WSOC concentrations and isotopic signatures was estimated considering the precision of concentration estimation (estimates from triplicate analysis), mass contributions from field blanks, as well as precision of isotope measurements (instrument precision) and the isotope signature of the field blanks. To obtain the overall precision, these factors need to be combined using an error propagation scheme. Here, a Monte Carlo approach was employed (Andersson, 2011).

3. Main results and discussion

3.1. Radiocarbon-based source apportionment of WSOC in South and East Asia (papers II, III and IV)

In order to gain insight into the main source contributions to the WSOC component in South Asia 15-month year-round campaign was conducted at two regional receptor sites: MCOH and SINH (**paper II**), followed by a winter time study in a source region, the megacity New Delhi, located in the densely populated and industrialized northern Indo-Gangetic Plain (**paper III**). Monsoon-driven meteorology yields significant WSOC concentration differences between the dry winter season (0.94±0.43 µg m^{-3} MCOH; 3.6±2.3 µg m^{-3} SINH; 20.8±12.2 µg m^{-3} Delhi) and the summer monsoon season (0.10±0.04 µg m^{-3} MCOH and 0.35±0.21 µg m^{-3} SINH). At the SINH hilltop site the average fossil contribution to WSOC at SINH for 2008 was 23±4%, while for the Indian Ocean site (MCOH) it was lower 17±4%, showing the dominance of biomass burning/biogenic sources in the South Asian region. During the dry winter season, the fossil contribution at both sites was very similar (19-23%, Fig. 4). The air masses during this high-aerosol loading season were highly influenced by the sources in W India and N India / Ganges Valley. During the rest of the year, the fossil contribution at the continental SINH site was almost twice as large as that at the ocean receptor MCOH site (Fig.4). It can be explained by the influence from different source regions and by the relative proximity of the SINH site to large urban areas of Mumbai and Pune. Despite a higher influence of fossil aerosol sources in urban regimes (e.g., Lam et al., 2012; Ohara et al., 2007) in the near-source urban study in Delhi, the fossil contribution to WSOC in PM$_{2.5}$ size fraction was constrained to 22±4% during the dry winter season 2010-2011. It is very close to the values observed at SINH and MCOH for this season in 2008-2009 (Fig.4). In February fossil contribution in Delhi increased following the trend previously observed at the SINH site which was predominantly under the influence of air masses from N-NW India and Pakistan during this month in 2008 and 2009.

In contrast to India, a much larger fraction of anthropogenic OA in China comes from fossil fuel combustion in the industrial, domestic, and transport sectors (e.g., Ohara et al., 2007). The importance of these practices in the formation of WSOC aerosols was probed during GoPoEx campaign at KCOG station on Jeju Island, South Korea during March 2011 when it intercepted the pollution outflow from N. China (**paper IV**).
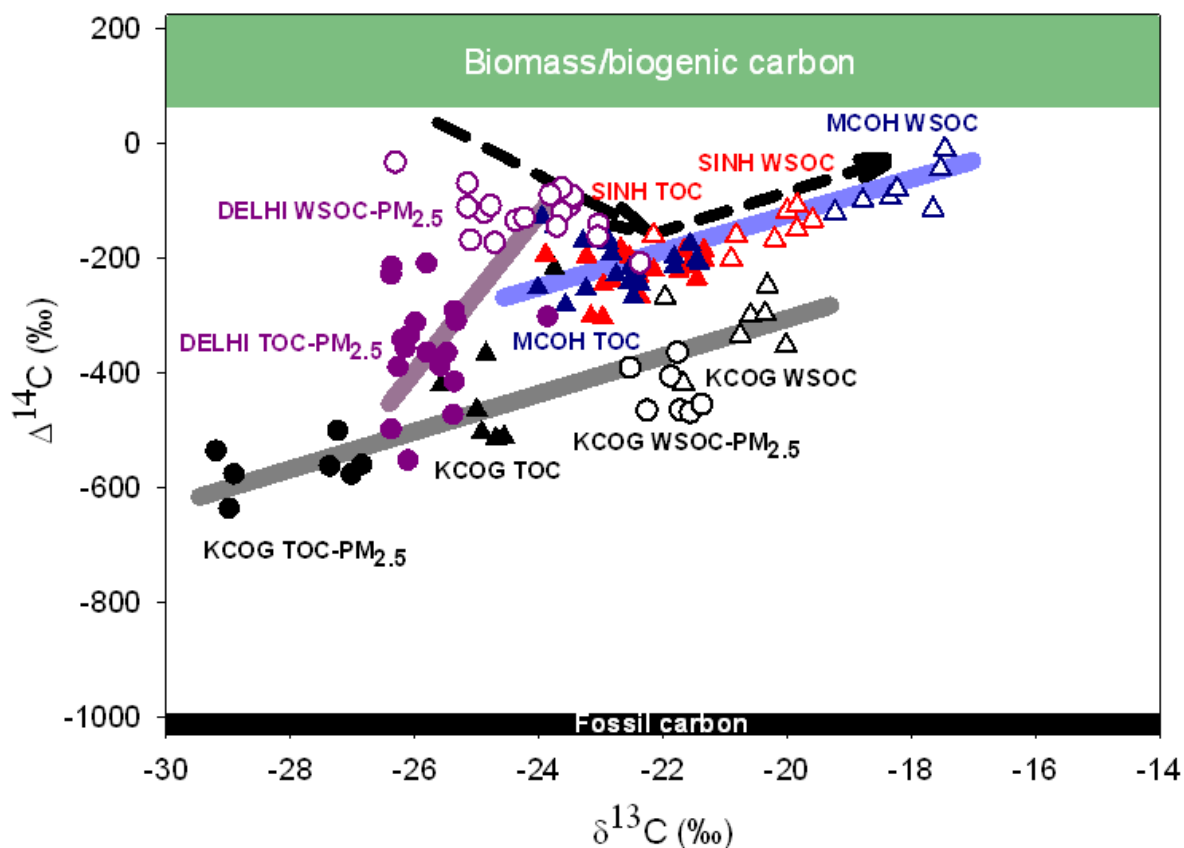
Figure 4. Radiocarbon-based estimation of fraction fossil of WSOC in ambient aerosols collected at Haminaadhoo, Maldives (MCOH) and Sinhagad, NW India during year-round campaign in 2008-2009 (**paper II**), in New Delhi, India during winter season 2010-2011 (**paper III**), and at KCOG, Jeju Island, South Korea in March 2011 (**paper IV**).

During GoPoEx about 80% of the WSOC component was found in the fine (<2.5 μm) mode (1.4±0.5 μg m^{-3} PM2.5; 1.7±0.7 μg m^{-3} TSP). Radiocarbon-based measurements showed very high variability of source contributions to WSOC (Fig. 4). The air masses represented the direct outflow from the Beijing area and Liaoning province of China and the air masses from the same origin but circulated during 3-4 days at high altitude over the Yellow Sea, had the highest fossil contribution to WSOC (30-38% in TSP and 40-49% in PM$_{2.5}$). WSOC had much lower fossil input (12-19% in TSP and 26% in PM$_{2.5}$) in the air masses that contained Asian dust. In all samples WSOC carbon isolates in PM$_{2.5}$ fraction were more fossil than in TSP pointing at more modern contribution in coarse particles, showing a difference in the sources of fine and coarse particles and a large influence from biomass/biogenic coarse mode water-soluble particles.

The radiocarbon-based source studies in South and East Asia can be compared to a limited number of radiocarbon measurements of WSOC in other regions. All of them report the

dominant contribution of biomass/biogenic sources to WSOC in different size fractions (Szidat et al., 2004; Weber et al., 2007; Wozniak et al., 2008, 2012a,b; **paper I**). Fossil contribution measured in the $PM_{2.5}$ fraction in Atlanta metropolitan area (eastern USA) was also higher (19-33%, Weber et al., 2007) than fossil content in PM10 from Zürich, Switzerland (4-24%, Szidat et al., 2004) and TSP from the rural areas of Millbrook, NY and Harcum, VA 0-25% (Wozniak et al., 2008, 2012a,b). The results of the method test on summertime Stockholm TSP samples show only 0-12% fossil consistent due to a high production of SOA from BVOC, which has previously been reported for this region (e.g., Tunved et al., 2006).

Despite biomass burning practices and/or biogenic SOA formation are major contributors to the South Asian WSOC, the fossil component is also considerable at both urban and regional background study sites (Fig. 4, **paper II, III**). East Asian aerosols representing the outflow from China demonstrate the highest fossil fraction in WSOC compared to all other reported data from Europe, USA and South Asia (**paper IV**).

3.2. *Investigation of aging/processing of WSOC compared to TOC using ^{13}C and ^{14}C isotopes (papers II, III and IV)*

The combined analysis of natural abundance radiocarbon and stable carbon isotopes allows for evaluation of both source contribution to organic aerosols and their atmospheric processing. For all sampling sites TOC and WSOC data points form clusters (Fig. 5), which follow strait lines: light blue for SINH and MCOH data, light purple for Delhi data and grey for KCOG data. These lines demonstrate the general trend observed in all studies (in TSP and $PM_{2.5}$ fractions in South and East Asia): WSOC is more modern ($\Delta^{14}C$ signal is closer to contemporary) and enriched in ^{13}C compared to TOC. It can be explained by the difference in the sources of water-soluble and water-insoluble OA components as well as by the different level and form of their processing/aging. The lines for regional receptor sites in South and East Asia are very similar, while for a source region New Delhi it differs. At source we observe higher difference in $\Delta^{14}C$ and smaller in $\delta^{13}C$ values between WSOC and TOC.

Here we expect the isotopic difference in WSOC and TOC predominantly due to the source composition and the aerosol formation paths (**paper III**). Higher WSOC/TOC ratio, which have been observed in biomass burning plumes compared to fossil fuel combustion emissions

(Andreae and Rosenfeld, 2008), may be reflected in a more modern ^{14}C signal in WSOC compared to TOC in New Delhi.
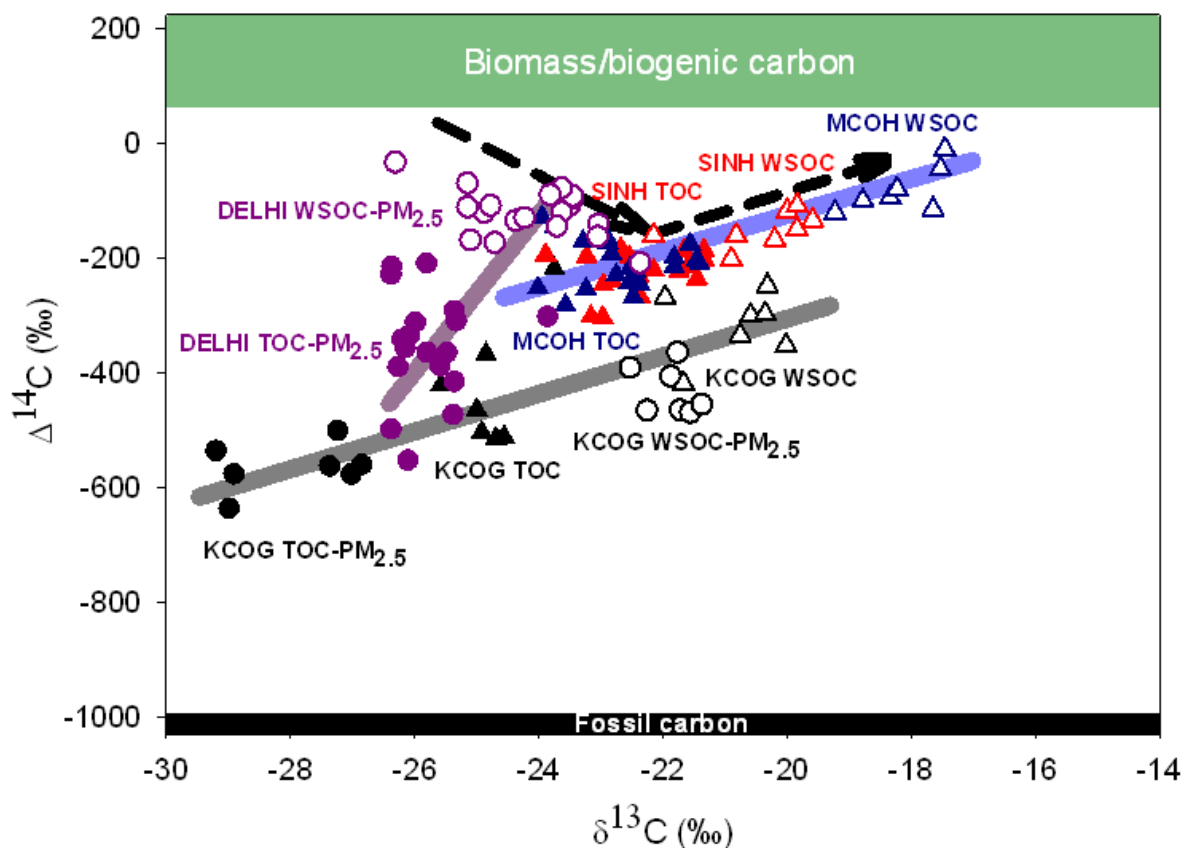
Figure 5. Two-dimensional presentation of dual-isotope (δ^{13}C vs Δ^{14}C) signals of WSOC and TOC in TSP at NW Indian site in Sinhagad (SINH) and Indian Ocean site on Hanimaadhoo Island, Maldives (MCOH) (data from Sheesley et al., 2012 and **paper II**, marine-influenced samples are excluded); in PM2.5 in New Delhi (**paper III**); in PM2.5 and TSP for GoPoEx campaign at KCOG (**paper IV**) in E Asia (dust-influenced samples are excluded). Black dashed lines represent the expected aging trend for WSOC in S. Asia.

A relative depletion in^{13}C of WSOC compared to TOC was previously observed by Fisseha et al. (2009) in the biomass-burning dominated aerosols during winter time in Switzerland and in the highly influenced by biogenic aerosols Stockholm area (**paper I**). One of the possible explanations is the preferential formation of primary WSOC during biomass combustion from parts of the plants, which are more enriched in ^{13}C (Fisseha et al., 2009; Kundu et al., 2010). TOC can also be formed from fresh SOA, which at low humidity conditions to a large extent is insoluble in water (Favez et al., 2008) but are expected to be depleted in ^{13}C (e.g., Anderson et al., 2004a,b, Irei et al., 2006, 2011, Iannone et al., 2010).

Particles undergo aging during the transport, therefore, the farther regional receptor sites are located from the sources the more particulate WSOC is influenced by aging. As demonstrated for SINH and MCOH samples (Fig 5), the aerosols transported longer distances/times away from pollution sources in India and thereby more aged, had larger differences in $\delta^{13}C$ and $\Delta^{14}C$ signature between WSOC and TOC (**paper II**). In general, $\delta^{13}C$ signals of WSOC show the enrichment with the distance from sources Delhi (-24.1±1.0‰) -> SINH (-20.4±0.8‰)-> MCOH (-18.2±0.7‰) (**papers II, III**). It would support fragmentation of molecules and volatilization of light carbon atoms as the major aging process. In contrast, SOA production, which would lead to depletion, is likely a less important process of WSOC formation during the transport in the S. Asian region. However, Delhi WSOC pool does not fit the same trend line (light blue line, Fig. 5) as WSOC at SINH and MCOH, which can be explained by the hypothesis of the loss of WSOC component during aging and building it up from WINSOC pool.

In the oxidative environment of the atmosphere, the WSOC component, being in general more polar, can be more readily involved in further functionalization and fragmentation reactions with subsequent volatilization of the produced small molecules (Kroll et al., 2011; Smith et al, 2009). Biomass-derived POA and SOA from the WSOC pool can be lost easier due to their greater propensity toward oxidation compared to the more recalcitrant fossil component (Elmquist et al., 2006). As a result, WSOC would overall become more fossil. At the same time, the enrichment in ^{13}C is expected due to 1. a preferential oxidation and evaporation of light carbon isotopes; 2. condensation reactions of several polar species into larger less soluble molecules (e.g., Jang et al., 2003; Nguyen et al., 2011; Zaharidis et al., 2006). At this stage, the WSOC pool would move towards the right and downward on the 2D-isotope plot (Fig. 5). Moreover, WSOC aerosols can be preferentially washed out by precipitation, therefore, the WSOC formed as POA and SOA at source region can be lost to a certain extent during the transport to a remote site. At the same time, functionalization of the less polar species of the WINSOC pool of TOC can transfer them into the WSOC pool (e.g., Decesari et al., 2002; Wozniak et al., 2012b), again preferentially from the biomass burning rather than the fossil combustion, which will increase the modern content of WSOC. A continued oxidation and fractionation of WSOC will enrich it in ^{13}C isotopes. At this stage, the WSOC pool would be shifted towards the right and upward direction on 2D plot (Fig. 5). Hence, the particulate WSOC at a regional receptor site may represent not WSOC at the source but the evolved water-insoluble component of TOC. Such hypothesis (summarized on Fig. 5 as

dashed black arrows) could explain why the observed isotope data points of WSOC in Delhi are not on the same line (light blue) as the data points of SINH and MCOH sites, while the isotope data points of TOC in Delhi fit to this line.

However, these data are rather limited and we should consider that isotope measurements in Delhi were performed on WSOC in $PM_{2.5}$ compared to TSP at SINH and MCOH. It is also obvious that Delhi is just one source region and measurements at SINH and MCOH sites are influenced by several source regions in India. Finally, the influence of local sources at each site should not be excluded, however, during the dry winter season the long-range transported pollution from India dominate at both SINH and MCOH (e.g., Sheesley et al., 2012).

The WSOC component in the outflow from N. China (**paper IV**) has a very similar trend line (grey line, Fig. 5) to WSOC in the outflow from India (SINH and MCOH). In general, this may reflect similar aging processes in WSOC and WINSOC components in coarse and in fine particles. In addition, East Asian dataset demonstrates that TSP is more modern and enriched in ^{13}C compared to $PM_{2.5}$ for both WSOC and TOC (Fig 5, **paper IV**). This can be explained by several reasons. Fine and coarse particles can have different sources, and while fine mode particles may better represent the emissions at source after the long-range transport, coarse fraction can be easier lost or influenced by local sources. Very low $\delta^{13}C$ values and high fossil content in TOC of $PM_{2.5}$ fraction may indicate significant contribution from SOA, which are depleted in ^{13}C compared to the combusted fuels or vegetation. A larger difference between WSOC $PM_{2.5}$ and TOC $PM_{2.5}$ clusters compared to WSOC TSP and TOC TSP pair can demonstrate that fine particles easier undergo aging due to their higher volume to surface ratio and, therefore, greater accessibility for atmospheric oxidants (e.g., hydroxyl radical, ozone).

4. Conclusions

➤ The method of extraction of non-volatile WSOC component and its preparation for the carbon isotope analysis using freeze-drying technique demonstrated no significant isotope fractionation and contamination. Combining of $\Delta^{14}C$ and $\delta^{13}C$ values of WSOC gives the possibility to examine the dual effects of source variability and atmospheric processing during a long-range transport.

➤ The radiocarbon-based source apportionment of WSOC in South Asia shows the dominance of the biogenic/biomass burning sources, however, fossil fuel input is also significant (about 17-23%) both at the source region in New Delhi and the background sites in NW India and in the Indian Ocean. The seasonal variation in the fossil contribution at the background sites depends on the air mass origins. The higher fossil input is observed in the samples impacted by the air masses from industrialized Indian areas and the lower fossil signal is found in the samples influenced by the Indian Ocean and the Arabian Sea marine sources.

➤ Radiocarbon constraints of carbonaceous aerosols in Chinese outflow show that up to about 50% (in $PM_{2.5}$) of WSOC is of fossil origin. This contribution is significantly larger than what has been observed in South Asia, Europe and USA. However, the East Asian aerosol samples containing some Asian dust have much lower fossil content (12-26%) in WSOC.

➤ Stable carbon isotope analysis revealed a trend of enrichment in heavy isotopes in particulate WSOC with the distance the particles were transported from the source in South Asia. Photochemical oxidation and fragmentation of molecules in the WSOC pool and the volatilization of cleaved light carbon atoms influences such enrichment. In contrast, SOA production, which would lead to WSOC depletion, is likely a less important process during transport in this region.

➤ Both $\Delta^{14}C$ and $\delta^{13}C$ signatures of WSOC and bulk TOC differ in TSP and $PM_{2.5}$ fractions at the East Asian background site, pointing at the different sources and different level of processing of coarse and fine particles.

5. Future perspectives

The results of our research discussed in this thesis and a limited number of isotope-based studies of WSOC in Europe and USA has revealed some trends for this aerosol component: WSOC is more modern than bulk TOC; WSOC is influenced by aging; the isotope signature of WSOC differs in different aerosol size fractions. However, it is just the first steps in the investigation of this important aerosol component using carbon isotopes. It is important in the areas with a variety of different emission sources to study the input of various activities to the different aerosol components, whereas the process of aerosol aging requires a special attention as it can help to explain the evolution of aerosol properties, their possible impact on climate and human health and source signature during the long-range transport.

Source-receptor studies of chemical and isotopic composition of WSOC and TOC can substantially improve the knowledge about aerosol aging processes. South and East Asian regions with their monsoon climate systems and high aerosol loadings are very convenient for the studies of aerosol processing at source and at the regional receptor sites on different distances from the source area. Our sampling campaigns at Delhi-SINH-MCOH sites were successful pilot studies of WSOC aging. To diminish the uncertainty of the results of these studies, the sampling campaigns during the same seasons and focused on the same size fractions at source and receptor sites should be planned for future. It would be important to focus the studies on $PM_{2.5}$ fraction due to many reasons: fine particles have more impact on human health and regional climate (as CCN); they are transported longer distances from the sources without settling by the gravitation force. However, the comparison of the aerosol sources and aging processes in different size fractions would bring additional information for this research. In our East Asian outflow study, we found that $\Delta^{14}C$ and $\delta^{13}C$ values for WSOC and TOC differ in TSP and $PM_{2.5}$. If the same trend is true also for South Asia, then TOC in $PM_{2.5}$ fraction at SINH and MCOH will probably have a very similar isotope signature as TOC in Delhi. That would indicate that bulk TOC isotope signature was not significantly affected by aging compared to WSOC and some mechanisms drove the carbon isotope composition in WSOC and WINSOC fractions in different directions. For the East Asian region, we are missing the isotope composition of WSOC at source areas in China. The analysis of $\Delta^{14}C$ and $\delta^{13}C$ in both the Beijing urban area and in the outflow from Beijing sampled at the KCOG background station would provide important data to characterize

organic aerosol aging in fossil fuel combustion dominated region. The studies of the isotopic effects of aerosol aging on WSOC and TOC may be compared in Asia with high level of anthropogenic aerosol emissions and in the other regions with high amount of natural (e.g., biogenic) aerosols.

For the interpretation of the aging processes in bulk WSOC and bulk TOC aerosols we rely on some laboratory aerosol studies (e.g., Jang et al., 2003; Nguyen et al., 2011; Smith et al., 2009; Zaharidis et al., 2006). Most of the chamber studies of aerosol aging are focused on the chemical transformation during the oxidation at different conditions. It can already be valuable information for the prediction of isotope fractionation, however, a combined investigation of aging transformation paths for different compounds and compound classes with the measurements of isotope fractionation during these reactions would give a strong support for the interpretation of the field observations.

Light-absorbing properties of WSOC have been previously observed in several studies (e.g., Hecobian et al., 2010; Zhang et al., 2011; Cheng et al., 2011). For our South and East Asian campaigns we also started to measure the absorptive properties of WSOC samples (**paper III, IV**). The results demonstrated that the absorptive radiative effect of water-soluble brown carbon (WS-BrC) may correspond to up to 49% of the effect of highly-absorptive black carbon. The source-receptor studies of WSOC absorptive properties combined with the studies of aerosol aging would help to characterize the dependence of the BrC absorptive properties and the level of atmospheric oxidation of the WSOC.

Long-term studies using quantification and carbon isotope-based source apportionment and other methods to characterize different OA fractions in rapidly developing regions like South and East Asia should be performed to investigate how the aerosol loadings, composition as well as health and climate-related properties change with the application of new technologies and pollution regulation policies.

Acknowledgments

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