Chemosphere 153 (2016) 332–339

Contents lists available at ScienceDirect

Chemosphere

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

Non-polar organic compounds in marine aerosols over the northern South China Sea: Influence of continental outflow

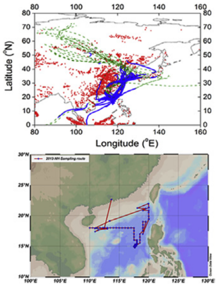
Yan Zhao [a], Yingyi Zhang [a, **], Pingqing Fu [b], Steven Sai Hang Ho [c, d], Kin Fai Ho [e], Fobang Liu [f], Shichun Zou [g], Shan Wang [a], Senchao Lai [a, f, *]

[a] *Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control, School of Environment and Energy, South China University of Technology, Guangzhou, China*
[b] *State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China*
[c] *State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China*
[d] *Division of Atmospheric Sciences, Desert Research Institute, 2215 Raggio Pathway, Reno, NV, United States*
[e] *The Jockey Club School of Public Health and Primary Care, The Chinese University of Hong Kong, Shatin, Hong Kong*
[f] *Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany*
[g] *School of Marine Sciences, Sun Yat-Sen University, Guangzhou, China*

HIGHLIGHTS

- A total of 115 NPOCs were detected in the marine aerosols over the northern South China Sea.
- Biomass burning in southern/southeastern China was the major source for NPOCs in marine aerosols in the open sea area.
- Fossil fuel combustion was the considerable source of NPOCs in marine aerosol samples with strong continental influence.
- Terrestrial plant contributed to the higher molecular weight *n*-alkanes in marine aerosols.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 February 2016
Received in revised form
13 March 2016
Accepted 15 March 2016

Handling Editor: Ralf Ebinghaus

Keywords:
Northern South China Sea
n-Alkanes
PAHs

ABSTRACT

Filter samples of total suspended particle (TSP) collected during a cruise campaign over the northern South China Sea (SCS) from September to October 2013 were analyzed for non-polar organic compounds (NPOCs) as well as organic carbon (OC), elemental carbon (EC) and water-soluble ions. A total of 115 NPOCs species in groups of *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs), iso-/antiso-alkanes, hopanes, steranes, methylalkanes, branched alkanes, cycloalkanes, alkenes and phthalates were detected. The characteristics of NPOCs in marine TSP samples were investigated to understand the sources from the Asian continent and other regions. The concentrations of total NPOCs ranged from 19.8 to 288.2 ng/m^3 with an average of 87.9 ng/m^3, which accounted for 0.8–1.7% (average 1.0%) of organic matter (OM). *n*-Alkanes was the predominant group, accounting for 43.1–79.5%, followed by PAHs (5.5–44.4%) and hopanes (1.6–11.4%). We found that primary combustion (biomass burning/fossil fuel combustion) was the dominant source for the majority of NPOCs (89.1%). Biomass burning in southern/southeastern China via long-range transport was proposed to be a major contributor of NPOCs in marine aerosols over the

---

* Corresponding author. School of Environment and Energy, South China University of Technology, Guangzhou, China.
** Corresponding author.
E-mail addresses: zhyy@scut.edu.cn (Y. Zhang), sclai@scut.edu.cn (S. Lai).

http://dx.doi.org/10.1016/j.chemosphere.2016.03.069

northern SCS, suggested by the significant correlations between nss-K$^+$ and NPOCs groups as well as the analysis of air mass back-trajectory and fire spots. For the samples with strong continental influence, the strong enhancement in concentrations of n-alkanes, PAHs, hopanes and steranes were attributed to fossil fuel (coal/petroleum) combustion. In addition, terrestrial plants waxes were another contributor to NPOCs.

Hopanes
Biomass burning
Long-range transport

1. Introduction

Marine aerosol is one of the most important natural aerosol systems globally (O'Dowd and De Leeuw, 2007). It has been reported that marine aerosol can play an important role in global and regional climate directly by back scattering solar irradiation and indirectly via forming cloud condensation nuclei (CCN) (Meskhidze and Nenes, 2006). Generally, aerosol is not only the main route for marine species transferring to the continent but also a major channel for terrestrial species transporting to the ocean (Duce et al., 1991). Hawkins et al. (2010) highlighted that the aerosols in the marine boundary layer were mostly mixtures of local primary (e.g., sea salt and organic compounds from sea spray), local secondary (e.g., sulfate from dimethyl sulfide oxidation), and long-range transport products. In recent years, the strong influence of continental emissions (both natural and anthropogenic) in the atmospheres of coastal and open ocean areas has been observed (Ding et al., 2007, 2013; Fu et al., 2011; Kunwar and Kawamura, 2014). Measurements of organic tracers can support more accurate source apportionment. Non-polar organic compounds (NPOCs) such as n-alkanes, polycyclic aromatic hydrocarbons (PAHs) and hopanes are organic compounds of special interest because they are ubiquitous in the terrestrial atmosphere and emitted from well-known sources including anthropogenic (e.g., fossil fuel combustion, petroleum residues and biomass burning) and biogenic emissions (e.g., higher plant leaf waxes) (Simoneit, 1989, 2002; Simoneit et al., 1991). Therefore, the variation and composition of NPOCs could be used to trace the contribution of different sources and to understand the influence of how much continental emissions could influence marine aerosols.

The South China Sea (SCS) is a marginal sea surrounded by fast-developing regions. Anthropogenic pollutants and natural products could be introduced into the atmosphere over the SCS through long-range transport (Zhang et al., 2007; Lai et al., 2010). Their chemical compositions including water-soluble ions, elements and organophosphate in airborne particles have been studied (Hsu et al., 2007; Zhang et al., 2007; Lai et al., 2015). However, with the exception of one study which reported the results of NPOCs in a sample collected in a round-the-world cruise passing through the SCS (Fu et al., 2011), very little research has been conducted to study NPOCs in marine aerosol particles in this region.

Here we present the results of NPOCs in total suspended particle (TSP) samples collected over the northern SCS during a cruise campaign. With this dataset we demonstrate that biomass burning in southern/southeastern China can influence marine aerosols over the SCS via long range transport in the open sea samples while other continental sources are also discussed.

2. Method

2.1. Sample collection

TSP samples ($n = 10$) were collected in the northern SCS during a 20-d cruise campaign from September to October 2013 (Fig. A1). A high volume aerosol sampler (~1 m^3/min, Tisch, USA) was placed in the upper deck of the research vessel. One filed blank filter was obtained. All samples were collected onto pre-baked (550 °C) quartz fiber filters (8 × 10 inches, Pall MI, USA). After sampling, the filters were sealed with prebaked aluminum foil and stored in a freezer at −20 °C.

2.2. Chemical analysis

2.2.1. Non-polar organic compounds

An in-injection port thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) method was used to determine NPOCs including n-alkanes, iso-/antiso-alkanes, methylalkanes, branched alkanes, cycloalkanes, alkenes, PAHs (parent, alkylated- and oxy-PAHs), hopanes, steranes and phthalates. This method has less contamination from solvent impurities and higher sensitivity compared to solvent extraction (SE) followed by GC/MS. The detailed description of this method has been presented in previous publications (Ho et al., 2008, 2011). Briefly, for each sample, a filter aliquot (1.0 cm^2) was cut into pieces and inserted into the TD glass tubes for placement into the split/splitless injector liner of an Agilent 6890 GC/5975 MS detector (Santa Clara, CA, USA). The temperature of the injector port was set at 50 °C before analysis and then manually raised to 275 °C for desorption in a splitless mode. During this period, the temperature in GC oven was kept at 30 °C. After the injector temperature reached the set point, the oven temperature program started. The limits of detection (LODs) for the TD-GC/MS method are listed in Table A1.

2.2.2. Carbonaceous fractions and water-soluble ions

Organic carbon (OC) and elemental carbon (EC) were analyzed (punch of 1.0 cm^2) using the thermo-optical transmittance (TOT) method (NIOSH protocol) (Sunset, OR, USA) (Birch and Cary, 1996).

Water-soluble ions were detected (punch of 4.0 cm^2) by ion chromatography (Dionex ICS3000, Thermo Fisher, MA, USA). Briefly, the cut portion was extracted in 3 mL ultra-pure water. A CS12 column (4 × 250 nm) with 20 mM methanesulfonic acid (MSA) eluent and AS11-HC column (4 × 250 nm) with 30 mM NaOH eluent were used for the determination of 5 cations (i.e. Na$^+$, NH$_4^+$, K$^+$, Mg^{2+} and Ca^{2+}) and 5 anions (i.e. MSA$^-$, Cl$^-$, SO$_4^{2-}$, C$_2$O$_4^{2-}$ and NO$_3^-$), respectively. The LODs are shown in Table A2.

2.3. Quality assurance/quality control (QA/QC)

Contamination from the ship exhaust was prevented by manually shutting off the sampling pump when the ship stopped or was under unfavorable wind conditions. The contamination from the ship exhaust is confirmed to be negligible based on the previous publication (Lai et al., 2015). All the data reported here were corrected for the field blank.

2.4. Air mass back-trajectory and fire spot analysis

Air mass back-trajectory analysis was preformed along the sampling route using NOAA's HYSPLIT model at a height of 200 m and with a backward tracing of 72 h. Fire spots were obtained from the Fire Information for Resource Management System (FIRMS) operated by National Aeronautics and Space Administration (NASA) of the United States (https://earthdata.nasa.gov/data/near-real-time-data/firms).

3. Results and discussion

3.1. NPOCs and other chemical components

Concentrations of OC and EC were 4.6 μg/m^3 (1.1–15.5 μg/m^3) and 1.1 μg/m^3 (0.2–4.7 μg/m^3), respectively. The fraction of organic matter (OM) could therefore be estimated as 9.6 μg/m^3 using an OC multiplying factor of 2.1 for aged aerosols (Turpin and Lim, 2001). A total of 115 NPOCs were quantified in the TSP samples. These NPOCs are grouped into ten classes, including *n*-alkanes, PAHs, iso-/antiso-alkanes, hopanes, steranes, methylalkanes, branched alkanes, cycloalkanes, alkenes and phthalates. The concentrations of NPOCs are summarized in Table 1 and Table A3. The total concentrations of NPOCs (ΣNPOCs) ranged from 19.8 to 288.2 ng/m^3 with an average of 87.9 ng/m^3. ΣNPOCs accounted for 0.8–1.7% (average 1.0%) in OM. Water-soluble ions (WSI) were the major faction of TSP with the average concentration of 26.1 μg/m^3 (ΣWSI). SO_4^{2-}, Cl^- and Na^+ were the most abundant ions accounting for 50.0%, 11.6% and 16.4% of ΣWSI, respectively. The high abundances of Cl^- and Na^+ indicate the direct contribution of sea salt spray during the cruise campaign (O'Dowd and De Leeuw, 2007).

The relative abundances of NPOCs over the northern SCS are shown in Fig. A2. *n*-Alkanes were the most abundant NPOCs group, accounting from 43.1% to 79.5% for ΣNPOCs (average 62.6%). Similar abundance variation trends were observed for both ΣPAHs (5.5–44.4%) and hopanes (1.6–11.4%). PAHs are related to incomplete combustion processes of most fuels such as fossil fuels and biofuels which are more dominant in the continent rather than in oceans though they could also be produced in maritime transportation (Alves, 2008; Liu et al., 2013). Hopanes are specific biomarkers of petroleum and coal (Oros and Simoneit, 2000). Therefore, the higher abundance of PAHs and hopanes can be regarded as the indicators of continental influence. In addition, other NPOCs accounted for relatively minor fractions of ΣNPOCs (≤5%).

3.2. Variation of NPOCs

Variations of NPOCs along the cruise track are shown in Fig. 1. The top two highest ΣNPOCs concentrations were observed in the samples, Q01 (288.2 ng/m^3) and Q04 (168.7 ng/m^3). These two samples are expected to be highly influenced by the continental emissions as Q01 was collected when the ship departed from Guangzhou and Q04 was taken on the way to Hainan Island. Interestingly, not all samples collected in the coastal area showed an elevation of the ΣNPOCs concentration. For example, Q05 was collected when the ship was sailing to the open ocean area and leaving Hainan Island after a stopover. It was taken in a close coastal area with Q04, but had a much lower (about 75%) ΣNPOCs concentration (40.4 ng/m^3) compared with that of Q04. The differences could be attributed to the influences of continental and oceanic sources via long-range transport (suggested by the back-trajectory analysis, see Fig. A3). The rest of the samples were collected in the open ocean area and the concentrations of ΣNPOCs ranged from 19.8 to 84.5 ng/m^3.

In order to estimate the influences of continental and oceanic emissions, we have applied sea salt ($Cl^- + 1.47 \times Na^+$) as the oceanic tracer and hopanes and PAHs as the continental tracers. The samples can be classified into three groups: continental-, oceanic- and mixed-influenced. As shown in Fig. 2, the differences could be clearly demonstrated between the continental- and oceanic-influenced samples with higher hopanes and PAHs concentrations but lower sea salt concentrations in continental-influenced

Table 1
Mass concentrations of investigated non-polar organic compounds (NPOCs) in aerosol samples collected over the northern South China Sea in 2013 (ng/m^3).

NPOCs	Continental-influenced		Oceanic-influenced				Mixed-influenced			
	Q01	Q04	Q05	Q02	Q03	Q06	Q07	Q09	Q10	Q11
n-Alkanes										
LMW (C_{15} ~ C_{24})	41.9	9.6	11.8	6.1	6.4	16.3	8.6	20.9	19.3	20.3
HMW (C_{25} ~ C_{38})	82.3	68.5	16.0	9.6	12.3	14.9	26.8	27.0	30.3	24.8
Subtotal	124.2	78.1	27.7	15.7	18.7	31.1	35.4	47.8	49.6	45.1
C_{max}	C_{25}	C_{27}	C_{29}	C_{29}	C_{29}	C_{25}	C_{25}	C_{25}	C_{25}	C_{29}
CPI[a]	1.2	1.4	2.2	1.8	2.7	1.5	1.5	1.5	1.3	1.6
PAHs										
Parent PAHs	118.6	51.0	2.5	1.0	1.3	2.0	2.5	6.5	8.8	7.1
Alkylated-PAHs	4.5	3.7	0.2	0.2	0.5	0.4	0.7	0.6	0.3	1.0
Oxy-PAHs	4.8	3.0	0.3	0.2	0.2	0.3	0.3	0.5	0.5	0.7
Subtotal	127.9	57.6	3.0	1.5	1.9	2.7	3.4	7.5	9.6	8.8
Fla/(Fla + Pyr)[b]	0.5	0.6	0.6	0.6	0.5	0.6	0.5	0.5	0.6	0.5
Ant/(Ant + Phe)[c]	0.5	0.5	0.4	0.3	0.3	0.4	0.4	0.4	0.5	0.4
BeP/BaP[d]	1.2	1.6	3.5	4.7	3.2	2.7	2.9	1.8	2.3	1.8
Hopanes	19.6	19.0	1.6	0.4	0.4	2.5	5.3	9.6	4.7	8.3
Steranes	3.6	3.5	0.4	0.1	0.2	0.7	1.2	2.2	1.0	1.9
Branched alkanes	1.6	1.0	2.0	0.7	0.9	3.0	1.0	4.2	1.8	4.4
Cycloalkanes	2.5	2.2	3.4	0.6	1.5	5.5	2.4	6.1	1.4	4.9
Iso-/antiso-alkanes	7.8	5.9	1.3	0.2	0.2	1.4	3.5	4.7	1.9	3.4
Methylalkanes	0.2	0.1	0.6	0.2	0.4	0.9	0.2	1.2	0.2	1.1
Phthalates	0.2	0.1	0.1	0.02	0.1	0.2	0.04	0.9	0.03	0.5
Alkenes	0.7	1.2	0.3	0.3	0.7	0.9	1.1	0.2	0.4	0.4
Total NPOCs	288.2	168.7	40.4	19.8	25.2	49.0	53.5	84.5	70.6	78.6

[a] CPI, carbon preference index: $(C_{21} + C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35} + C_{37})/(C_{22} + C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34} + C_{36} + C_{38})$.

[b] Fla, Fluoranthene; Pyr, Pyrene.

[c] Ant, Anthracene; Phe, Phenanthrene.

[d] BeP, Benzo[*e*]pyrene; BaP, Benzo[*a*]pyrene.

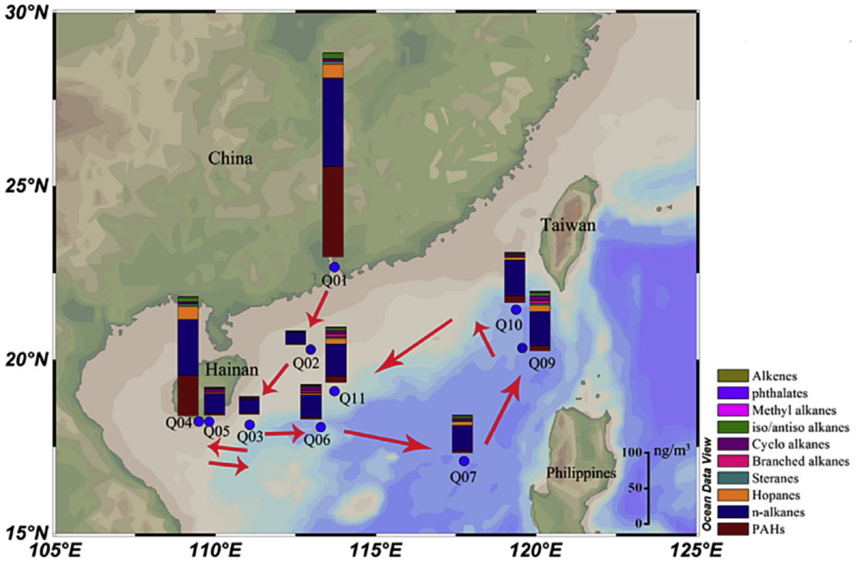


Fig. 1. Variation of non-polar organic compounds in marine aerosols along the cruising track in the northern South China Sea.

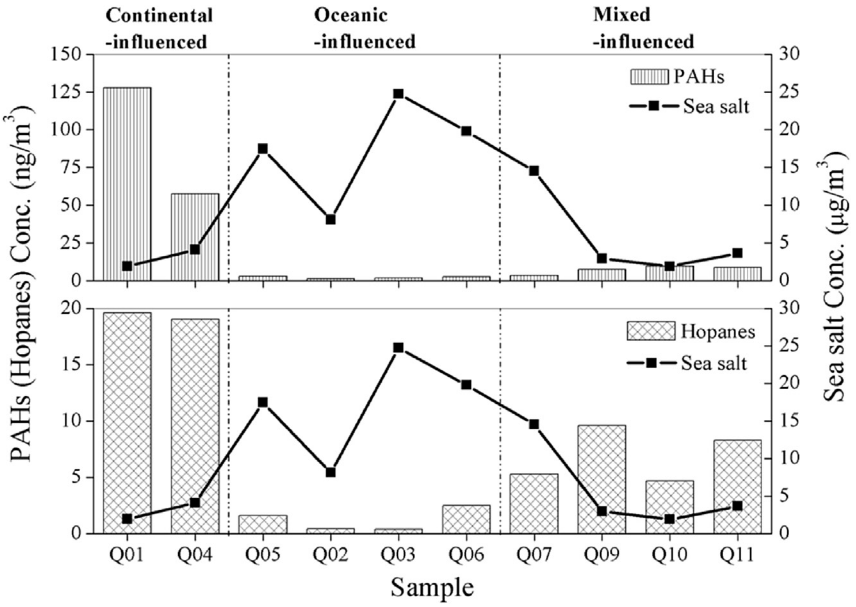


Fig. 2. Variations of PAHs, hopanes and sea salt in TSP samples over the northern South China Sea.

samples (Q01 and Q04) and vice versa in the oceanic-influenced samples (Q02, Q03, Q05 and Q06). The rest of the samples (Q07, Q09, Q10 and Q11) were characterized for mixed-influenced samples. The classification was further confirmed by the air mass back-trajectory analysis (Fig. A3). The big difference of NPOCs concentrations between Q04 and Q05 could then be explained by the influence of different air masses.

The homologous *n*-alkanes (C_{15}–C_{38}) were the most abundant group of NPOCs ranging from 15.7 to 124.2 ng/m^3 (average 47.3 ng/m^3). Other minor groups of iso-/antiso-alkanes, methylalkanes, branched alkanes and cycloalkanes had much lower concentrations than that of *n*-alkanes (Table 1). In addition, two alkenes that were quantified in the aerosols ranged from 0.2 to 1.2 ng/m^3 with an average of 0.6 ng/m^3.

The highest concentrations of *n*-alkanes were observed in continental-influenced samples (average 101.2 ng/m^3), followed by the mixed-influenced (average 44.5 ng/m^3) and oceanic-influenced samples (average 23.3 ng/m^3). The concentration range of *n*-alkanes in oceanic-influenced samples (15.7–31.1 ng/m^3) was comparable with that measured in the western North Pacific (1.3–30.5 ng/m^3), while the levels in the mixed- (35.4–49.6 ng/m^3) and continental-influenced samples (78.1–124.2 ng/m^3) were close to those observed in Sapporo Island (31.45–87.3 ng/m^3) and Gosan, Jeju Island (9.61–150.3 ng/m^3), respectively (Simoneit, 2004). However, much lower concentrations of *n*-alkanes were reported in Chichi-Jima Island (0.17–14 ng/m^3, average 1.7 ng/m^3) in which *n*-alkanes were mainly derived from terrestrial higher plant waxes and in Okinawa Island which has insignificant anthropogenic activities (average 7.9 ± 6.1 ng/m^3) (Kawamura et al., 2003; Wang et al., 2009). The results suggest the anthropogenic influences on marine aerosols over the northern SCS.

The carbon number distributions were characterized by weak odd-carbon-numbered predominance (carbon preference index, CPI, ranging from 1.2 to 2.7) with carbon number maxima (C_{max}) at C_{25}, C_{29} or C_{27}. The CPIs were close to unity, more consistent with *n*-alkanes derived from non-biogenic sources (Simoneit et al., 1991). CPIs can reach around 10 with the predominant contribution of terrestrial higher plant waxes (Simoneit, 1989).

Twenty-two parent PAHs (3–7 rings), seven alkylated-PAHs and four oxy-PAHs were determined in the TSP samples (Table A3). The ΣPAHs concentration ranged from 1.5 to 127.9 ng/m^3 (average 22.4 ng/m^3). Parent PAHs ranged from 1.0 to 118.6 ng/m^3, accounting for 80.7% of ΣPAHs, followed by alkylated-PAHs (11.5%) and oxy-PAHs (7.7%). The parent PAHs concentrations in oceanic-influenced (1.0–2.5 ng/m^3) and mixed-influenced samples (2.5–8.8 ng/m^3) were similar to those reported in the western North Pacific (0.3–2.4 ng/m^3) and Gosan, Jeju Island (0.005–7.78 ng/m^3), respectively (Simoneit, 2004). Differences in ΣPAHs concentrations were observed among the continental-influenced (average 92.8 ng/m^3), mixed-influenced (average 7.4 ng/m^3) and oceanic-influenced samples (average 2.3 ng/m^3), indicating an overwhelming contribution by the continental outflow to continental-influenced samples.

A series of hopanes (C_{27}–C_{35} without C_{28}) were detected with the predominance of $C_{29}\alpha\beta$ or $C_{30}\alpha\beta$. Again, the same descending order of concentration levels were observed in the three groups of samples: continental-influenced (average 19.3 ng/m^3) > mixed-influenced (average 7.0 ng/m^3) > oceanic-influenced samples (average 1.2 ng/m^3). Similar patterns were also found for steranes.

Phthalates are widely used in plasticizers as well as in cosmetics, lubricants, and other products (Thuren and Larsson, 1990). Five phthalates were detected in the samples, with the total concentrations ranging from 0.02 to 0.9 ng/m^3 (average 0.2 ng/m^3). Previous studies showed that phthalates were ubiquitous in vapour or in the particle phase in the marine atmosphere (Simoneit, 2004; Xie et al., 2005; Fu et al., 2013). However, the sources for outdoor phthalates are not well defined and their levels can be greatly affected by their equilibrium partition between the gas and particle phases, which may be determined by the temperature difference of the sampling period (Xie et al., 2005).

3.3. *Terrestrial plant emissions*

n-Alkanes derived from marine microbial and algae are abundant in lower carbon number (<C_{20}) with C_{max} in C_{15}, C_{17} or C_{19} (Simoneit, 1989). Therefore, the contribution of marine emissions to *n*-alkanes was minor as C_{max} was observed at higher molecular weight *n*-alkanes (HMW, ≥C_{25}) in our study.

Terrestrial plant emissions are major sources for HMW *n*-alkanes (Eglinton and Hamilton, 1967). The ratios of HMW/LMW ranged from 0.9 to 7.2, suggesting the importance of terrestrial plant emissions (Table 1). The highest concentrations of HMW *n*-alkanes were observed in the continental-influenced samples (Q01: 82.3 ng/m^3 and Q04: 68.5 ng/m^3), which were much higher than those in mixed- (average 27.2 ng/m^3) and oceanic-influenced samples (average 13.2 ng/m^3). Particularly for Q04, the ratio of HMW/LMW was 7.2 and the C_{max} was C_{27} (vs C_{25} for Q01), showing the important contribution of terrestrial plant emissions. Q04 was collected in the coastal area of Hainan Island where tourism has developed in the past decades instead of other conventional industries. HMW *n*-alkanes such as C_{29} and C_{31} contributed a major fraction to *n*-alkanes in the oceanic-influenced samples. For example, Q02, Q03 and Q05 had a C_{max} of C_{29}, suggesting an input of terrestrial plant emissions to *n*-alkanes via long-range transport.

Terrestrial plant emissions can be demonstrated by higher plant wax *n*-alkanes. They were calculated as:

$$Wax\ C_n = C_n - (C_{n+1} + C_{n-1}) \times 0.5$$

where negative values are taken as zero, wax C_n is the concentration of plant wax *n*-alkanes (Simoneit et al., 1991). The concentrations of wax *n*-alkanes were higher in the continental-influenced (average 11.1 ng/m^3) than those in mixed-influenced (average 6.0 ng/m^3) and oceanic-influenced (average 5.3 ng/m^3) samples (Fig. 3). The contributions of terrestrial plant emissions to Σ*n*-alkanes were more significant in oceanic-influenced (14.8–34.1%, average 23.5%) rather than those in mixed-influenced (9.9–19.1%, average 13.8%) and continental-influenced (7.8–16.1%, average 11.9%) samples.

3.4. *The importance of biomass burning*

We observed significant correlations between EC and PAHs, *n*-alkanes, iso-/antiso-alkanes, hopanes and steranes (Table A4). These compounds account for 89.1% of ΣNPOCs. It suggests that the majority of NPOCs were highly related to the sources of EC. EC is regarded as a tracer for primary combustion including both fossil fuels and biomass burning (Ho et al., 2002).

The diagnostic ratios of atmospheric PAHs are often used to evaluate source contributions (Yunker et al., 2002). A plot of Fla/(Fla + Pyr) against Ant/(Ant + Phe) (Fig. A4) indicates a predominant pyrogenic source of grass, wood and coal combustion for PAHs. It supports our conclusion that biomass burning is an important source for the samples. Furthermore, the ratios of BeP/BaP are used to distinguish local and transport sources (Grimmer et al., 1983). As BaP is more reactive than its isomer (BeP), the ratio of Bep/BaP (>1) indicates strong photochemical oxidation and/or aging processes during long-range transport, while the ratio being close to 1 suggests the local emissions. In our study, BeP/BaP ratios were higher in oceanic-influenced (2.7–4.7) samples than those in other samples, pointing to the contribution of long-range transport. Fresher and more local emissions might have an effect on the continental-influenced samples with lower ratios (Q01:1.2, Q04:1.6). However, the diagnostic ratios of PAHs could not efficiently distinguish the relative contributions of fossil fuel combustion and biomass burning.

Water-soluble potassium (K^+) has long been considered as a tracer for biomass burning (Andreae, 1983) but it can also be derived from sea salt in a marine environment (Riley and Chester, 1971). To avoid the influence of sea salt, we used non-sea-salt K^+ (nss-K^+ = K^+ − 0.037 × Na^+) as a marker of biomass burning (Kunwar and Kawamura, 2014). In oceanic-influenced samples (i.e. Q03 and Q05) K^+ was found to be mostly derived from sea salt. Variable levels of nss-K^+ (0.02–0.69 μg/m^3) were obtained in other samples. The levels of nss-K^+ in the continental-influenced (average 0.63 μg/m^3) and mixed-influenced (average 0.42 μg/m^3) samples were relatively higher than those reported (average 0.16 μg/m^3) in Cape Hedo, Okinawa in winter when biomass burning was an important contributor (Kunwar and Kawamura, 2014).

We observed a fair correlation between nss-K^+ and EC ($R^2 = 0.44$). However, a good correlation was found for the data set consisting only of mixed- and oceanic-influenced samples ($R^2 = 0.74$), showing that biomass burning is the major primary combustion source (Andreae, 1983). It is also confirmed by the good correlations between nss-K^+ and other NPOC groups of *n*-alkanes ($R^2 = 0.84$), PAHs ($R^2 = 0.86$), hopanes ($R^2 = 0.53$) and steranes ($R^2 = 0.46$) after excluding the continental-influenced samples. The different patterns were expected for Q01 and Q04 since they were more directly influenced by continental sources (both anthropogenic and natural) (see detail discussion in Section 3.5). Air mass

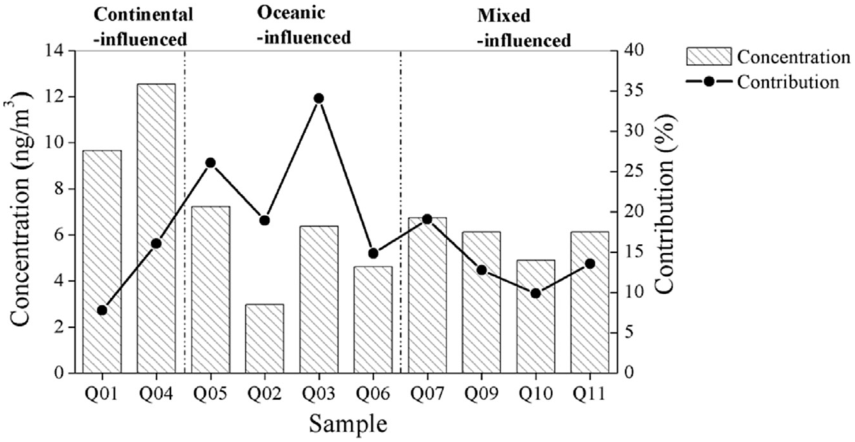


Fig. 3. Concentrations of wax *n*-alkanes and contributions to Σ*n*-alkanes in TSP samples over the northern South China Sea.

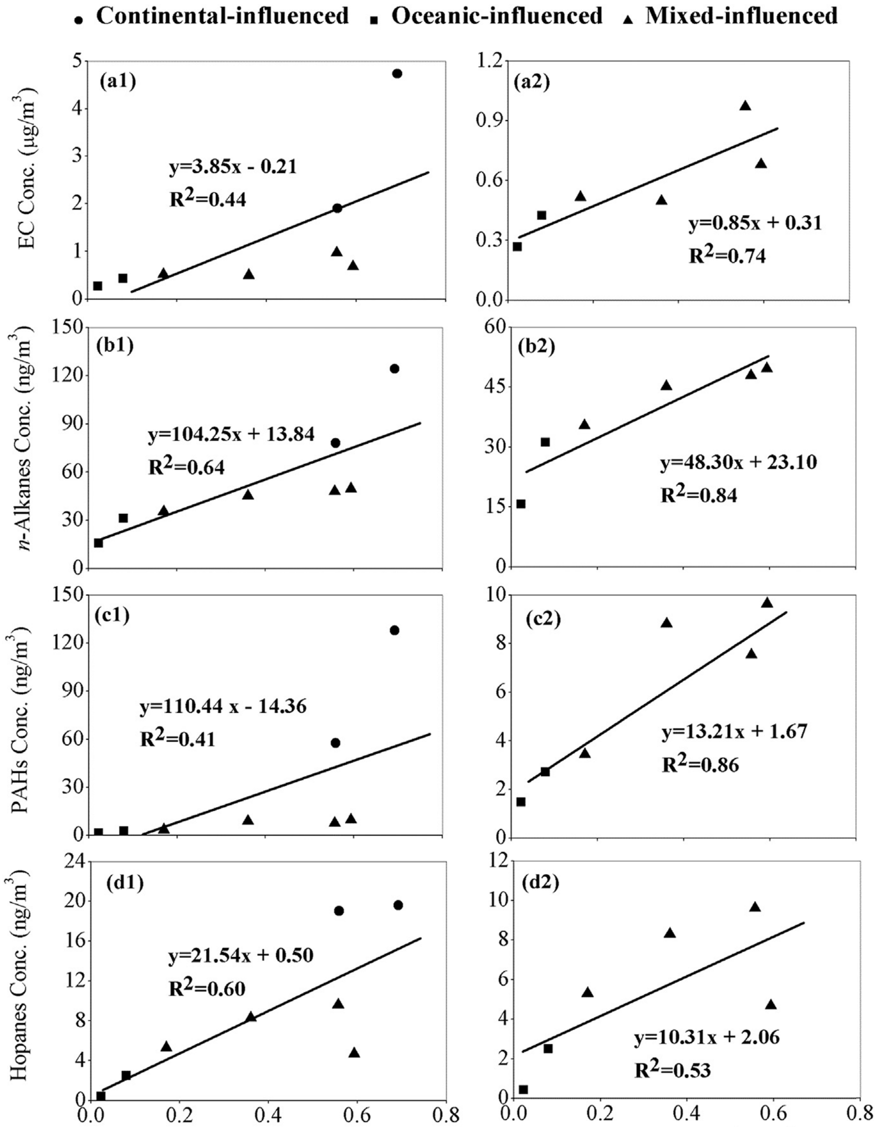


Fig. 4. Correlations between EC and nss-K^+ (a1, a2), *n*-alkanes and nss-K^+ (b1, b2), PAHs and nss-K^+ (c1, c2), hopanes and nss-K^+ (d1, d2). Data points of continental-influenced samples are included in the figures on the left side but they are excluded in those on the right side.

back-trajectories and fire spots were used to confirm the influences of biomass burning (Fig. 5a–d).

Here we further present the case study for the samples with the high nss-K^+ concentrations including Q01 (0.69 μg/m^3), Q10 (0.59 μg/m^3), Q04 and Q09 (both 0.56 μg/m^3). When these samples were collected, the air masses passed through the low altitude atmosphere over the southern or southeastern China, where relatively high numbers of fire spots were observed. It suggests that the emission of biomass burning in southern/southeastern China via long-range transport was a major contributor for NPOCs in marine aerosols over the SCS.

3.5. *Excessive NPOCs in strong continental-influenced cases*

Based on the discussion above, biomass burning was the dominant source for the NPOCs in the oceanic- and mixed-influenced samples. Therefore, we assume that they represent the source of aerosol samples over the northern SCS without strong input of continental outflow including both anthropogenic and natural sources. The excessive levels of NPOCs were then estimated in the continental-influenced samples (i.e. Q01 and Q04) based on the correlations between nss-K^+ and NPOCs. The enhanced emissions of the NPOCs were reflected in *n*-alkanes, hopanes and steranes with one-fold increase in both Q01 and Q04, pointing to the large contribution of the continental sources.

The main sources of PAHs are fossil fuel combustion and biomass burning. As shown in Fig. 4c1 and c2, a relatively poor correlation between nss-K^+ and PAHs was obtained ($R^2_{\text{oceanic + mixed + continental}} = 0.41$ vs $R^2_{\text{oceanic + mixed}} = 0.86$). It suggested that the PAHs in the continental-influenced samples were mainly derived from fossil fuel combustion rather than biomass burning. The elevated portions of PAHs were 11- and 5-fold higher than those derived from biomass burning in Q01 and Q04, respectively. The results indicate that the contribution by fossil fuel combustion should not be neglected in the strongly continental-influenced samples. In addition, the minor contribution from fossil fuel combustion observed in Q04 compared to Q01 could be due to less emissions (e.g., from heavy industries and power plants) in Hainan Island than in the Pearl River Delta region (Xing et al., 2011).

4. Conclusions

NPOCs, as well as carbonaceous fractions and water-soluble ions, were investigated in the aerosol samples collected over the northern SCS during a cruise campaign. Based on the contributions of continental and oceanic emissions, the samples were categorized into three groups: continental-, oceanic- and mixed-influenced samples. The correlations among NPOCs and EC ($R = 0.82–0.99$) show that primary combustion (biomass burning/fossil fuel combustion) was the predominant source for 89.1% of ΣNPOCs. For oceanic- and mixed-influenced samples, biomass burning in the southern/southeastern China via long-range transport was suggested to be a major source for NPOCs in marine aerosols. In contrast, for continental-influenced samples, the contribution of fossil fuel (coal/petroleum) combustion should not be ignored as it results in the strong enhancement of PAHs. Terrestrial plant emissions, characterized by wax *n*-alkanes, were suggested to be another contributor to NPOCs. This study shows that NPOCs could serve as the tracers to indicate the influence of continental outflow on marine aerosols. We expect that NPOCs in marine aerosols could be further studied to understand the interaction between continental and oceanic air masses in the coastal and open ocean areas of the SCS.

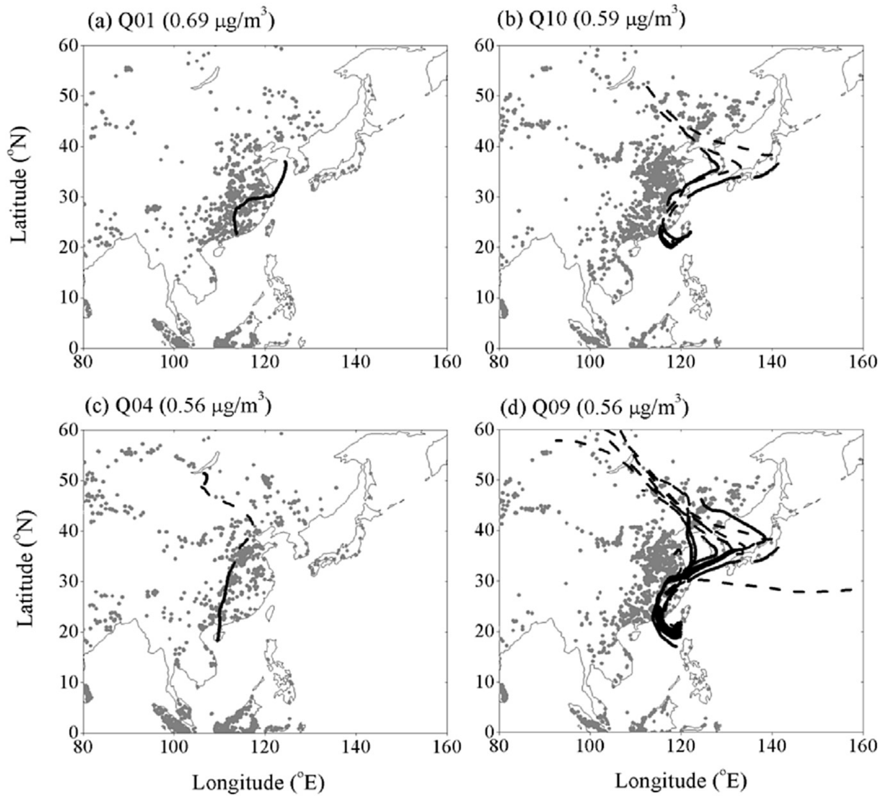


Fig. 5. 7-day back-trajectories and fire spots for the samples with high nss-K^+ concentrations: (a) Q01 (September 14–22), (b) Q10 (October 01–09), (c) Q04 (September 20–28), and (d) Q09 (September 30–October 08). Solid line for back-trajectories at 200–500 m; dash line for those above 500 m; dots for satellite-retrieved open fire.

Acknowledgment

This work is supported by the National Natural Scientific Foundation of China (Grant No. 41575115, 41275130 and 41105083) and the Fundamental Research Funds for the Central Universities (2014ZZ0054). The authors thank Mr. Jinhu Peng from Sun Yat-sen University for his help in sample collection and Dr. Pascale Lakey (Max Planck Institute for Chemistry) for the manuscript improvement. Senchao Lai and Fobang Liu thank the support of the Chinese Scholarship Council (CSC).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.03.069.

References

Alves, C.A., 2008. Characterisation of solvent extractable organic constituents in atmospheric particulate matter: an overview. An. Acad. Bras. Cienc. 80, 21–82.

Andreae, M.O., 1983. Soot carbon and excess fine potassium: long-range transport of combustion-derived aerosols. Science 220, 1148–1151.

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for occupational monitoring of particulate diesel exhaust: methodology and exposure issues. Analyst 121, 1183–1190.

Ding, X., Wang, X.-M., Xie, Z.-Q., Xiang, C.-H., Mai, B.-X., Sun, L.-G., Zheng, M., Sheng, G.-Y., Fu, J.-M., Pöschl, U., 2007. Atmospheric polycyclic aromatic hydrocarbons observed over the North Pacific Ocean and the Arctic area: spatial distribution and source identification. Atmos. Environ. 41, 2061–2072.

Ding, X., Wang, X., Xie, Z., Zhang, Z., Sun, L., 2013. Impacts of Siberian biomass burning on organic aerosols over the North Pacific Ocean and the Arctic: primary and secondary organic tracers. Environ. Sci. Technol. 47, 3149–3157.

Duce, R., Liss, P., Merrill, J., Atlas, E., Buat-Menard, P., Hicks, B., Miller, J., Prospero, J., Arimoto, R., Church, T., 1991. The atmospheric input of trace species to the world ocean. Glob. Biogeochem. Cycles 5, 193–259.

Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. Science 156, 1322–1335.

Fu, P., Kawamura, K., Miura, K., 2011. Molecular characterization of marine organic aerosols collected during a round-the-world cruise. J. Geophys. Res. 116.

Fu, P., Kawamura, K., Chen, J., Charrière, B., Sempéré, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. Biogeosciences 10, 653–667.

Grimmer, G., Jacob, J., Naujack, K.-W., 1983. Profile of the polycyclic aromatic compounds from crude oils. Fresenius Z. Anal. Chem. 314, 29–36.

Hawkins, L., Russell, L., Covert, D., Quinn, P., Bates, T., 2010. Carboxylic acids, sulfates, and organosulfates in processed continental organic aerosol over the southeast Pacific Ocean during VOCALS-REx 2008. J. Geophys. Res. 115.

Ho, K., Lee, S., Jimmy, C.Y., Zou, S., Fung, K., 2002. Carbonaceous characteristics of atmospheric particulate matter in. Hong Kong. Sci. Total Environ. 300, 59–67.

Ho, S.S.H., Chow, J.C., Watson, J.G., Ng, L.P.T., Kwok, Y., Ho, K.F., Cao, J.J., 2011. Precautions for in-injection port thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) as applied to aerosol filter samples. Atmos. Environ. 45, 1491–1496.

Ho, S.S.H., Yu, J.Z., Chow, J.C., Zielinska, B., Watson, J.G., Sit, E.H.L., Schauer, J.J., 2008. Evaluation of an in-injection port thermal desorption-gas chromatography/mass spectrometry method for analysis of non-polar organic compounds in ambient aerosol samples. J. Chromatogr. A 1200, 217–227.

Hsu, S.-C., Liu, S.C., Kao, S.-J., Jeng, W.-L., Huang, Y.-T., Tseng, C.-M., Tsai, F., Tu, J.-Y., Yang, Y., 2007. Water-soluble species in the marine aerosol from the northern South China Sea: high chloride depletion related to air pollution. J. Geophys. Res. 112.

Kawamura, K., Ishimura, Y., Yamazaki, K., 2003. Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific. Glob. Biogeochem. Cycles 17, 3-1-3-19.

Kunwar, B., Kawamura, K., 2014. One-year observations of carbonaceous and nitrogenous components and major ions in the aerosols from subtropical Okinawa Island, an outflow region of Asian dusts. Atmos. Chem. Phys. 14, 1819–1836.

Lai, S., Baker, A., Schuck, T., Velthoven, P.v., Oram, D., Zahn, A., Hermann, M., Weigelt, A., Slemr, F., Brenninkmeijer, C., 2010. Pollution events observed during CARIBIC flights in the upper troposphere between South China and the Philippines. Atmos. Chem. Phys. 10, 1649–1660.

Lai, S., Xie, Z., Song, T., Tang, J., Zhang, Y., Mi, W., Peng, J., Zhao, Y., Zou, S., Ebinghaus, R., 2015. Occurrence and dry deposition of organophosphate esters in atmospheric particles over the northern South China Sea. Chemosphere 127, 195–200.

Liu, F., Xu, Y., Liu, J., Liu, D., Li, J., Zhang, G., Li, X., Zou, S., Lai, S., 2013. Atmospheric deposition of polycyclic aromatic hydrocarbons (PAHs) to a coastal site of Hong Kong, South China. Atmos. Environ. 69, 265–272.

Meskhidze, N., Nenes, A., 2006. Phytoplankton and cloudiness in the Southern Ocean. Science 314, 1419–1423.

O'Dowd, C.D., De Leeuw, G., 2007. Marine aerosol production: a review of the current knowledge. Philos. Trans. R. Soc. A 365, 1753–1774.

Oros, D., Simoneit, B., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. Fuel 79, 515–536.

Riley, J.P., Chester, R., 1971. Introduction to Marine Chemistry. Academic Press, London and New York.

Simoneit, B.R., 1989. Organic matter of the troposphere—V: application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. J. Atmos. Chem. 8, 251–275.

Simoneit, B.R., 2002. Biomass burning—a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. 17, 129–162.

Simoneit, B.R., Sheng, G., Chen, X., Fu, J., Zhang, J., Xu, Y., 1991. Molecular marker study of extractable organic matter in aerosols from urban areas of China. Atmos. Environ. 25, 2111–2129.

Simoneit, B.R.T., 2004. Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign. J. Geophys. Res. 109.

Thuren, A., Larsson, P., 1990. Phthalate esters in the Swedish atmosphere. Environ. Sci. Technol. 24, 554–559.

Turpin, B.J., Lim, H.J., 2001. Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Sci. Technol. 35, 602–610.

Wang, G., Kawamura, K., Xie, M., Hu, S., Gao, S., Cao, J., An, Z., Wang, Z., 2009. Size-distributions of n-alkanes, PAHs and hopanes and their sources in the urban, mountain and marine atmospheres over East Asia. Atmos. Chem. Phys. 9, 8869–8882.

Xie, Z., Ebinghaus, R., Temme, C., Caba, A., Ruck, W., 2005. Atmospheric concentrations and air-sea exchanges of phthalates in the North Sea (German Bight). Atmos. Environ. 39, 3209–3219.

Xing, J., Wang, S.X., Chatani, S., Zhang, C.Y., Wei, W., Hao, J.M., Klimont, Z., Cofala, J., Amann, M., 2011. Projections of air pollutant emissions and its impacts on regional air quality in China in 2020. Atmos. Chem. Phys. 11, 3119–3136.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33, 489–515.

Zhang, X., Zhuang, G., Guo, J., Yin, K., Zhang, P., 2007. Characterization of aerosol over the Northern South China Sea during two cruises in 2003. Atmos. Environ. 41, 7821–7836.