



Characterization of Humic Acid-like Substances Extracted from Atmospheric Falling Dust Using Py-GC-MS

Jinping Zhao^{1,2*}, Ping'an Peng², Jianzhong Song², Shexia Ma², Guoying Sheng², Jiamo Fu², Dongxing Yuan³

¹ Guangdong Environmental Monitoring Center, Guangzhou 510308, China

² State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510604, China

³ State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361004, China

ABSTRACT

Humic acid-like substances (HALS) are heterogeneous macromolecules having a range of physicochemical properties and exhibiting different reactivities in environmental systems. However, to study the HALS that were isolated from atmospheric falling dust is seldom compared to which were extracted from soils and sediments. To better understand the chemical composition and heterogeneous property of HALS, which were obtained in the present work by multiple extraction of atmospheric falling dust, and their chemical composition was characterized using pyrolytic gas chromatography mass spectrometry (Py-GC-MS). This quick and effective procedure provides an insight into the structure and source of HALS. The results indicated that polysaccharides, lignin, protein/amino acid and aromatics are the main sources of this macromolecule organic fraction. Higher content of aromatic compounds which reached 67.42% suggested that aromatic structure is an important unit for HALS. Lignin-derived aromatic compounds are also major components of pyrolysates, while compounds derived from proteins and carbohydrates at higher concentrations were also detected. Compared with HALS fraction from dust in different sampling sites, it was suggested that biological emission and anthropogenic activity were the main contributors in suburban area of the university town and anthropogenic pollution was the main sources in urban area of the Wushan. The relative contents of pyrolysates in different seasons at the same sampling site indicated that meteorology is also an important factor to influence composition of HALS.

Keywords: Atmospheric falling dust; Humic acid-like substances; Py-GC-MS; Source.

INTRODUCTION

Humic acid-like substances (HALS) are heterogeneous macromolecules and among the major organic constituents actively participating in the global carbon cycle and controlling fate of organic and inorganic pollutants in surface aquatic environments (Li, 2006). It has been shown that HALS are mainly composed of aromatic cores bridged by aliphatic and functional groups (Song *et al.*, 2002; Li *et al.*, 2004), which are factors governing their chemical and biological reactivity in the environment. For example, the aliphatic portion of HALS generally absorbs more hydrophobic pollutants than polar components do (Salloum *et al.*, 2002). Therefore, many scientists are interested in elucidation of the characterization of HALS. However, the

main scopes of HALS were that extracted from soils, sediments and water (Thurman and Malcom, 1981; Song *et al.*, 2002; Campitelli *et al.*, 2006). Few researches have been conducted on HALS that is isolated from atmospheric falling dust (Mukai and Ambe, 1986; Zappoli *et al.*, 1999; Zhao *et al.*, 2009). Therefore, the detailed composition study of organic macromolecules in dust is certainly of scientific importance.

Several physical and chemical methods have been used to characterize structural and molecular properties of HALS, such as infrared spectroscopy, ¹H and/or ¹³C nuclear magnetic resonance spectroscopy, fluorescence spectroscopy, scanning electron microscopy, as well as chemical and thermal degradation techniques (Stevenson, 1994; Li *et al.*, 2006). Those methods normally only bulk information on molecular structures of HALS, because of the compositional complexity for HALS. In comparison, thermal degradation techniques, such as pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), yield a large number of structure components resulting in more detailed molecular information

* Corresponding author.

E-mail address: ynh7935@sina.com

on the various compositional features of HALS (Subbalakshmi *et al.*, 2000; Falkovich and Rudich, 2001; Fabbri *et al.*, 2002; Chow *et al.*, 2007). Py-GC-MS methods has notable advantages, such as its fast, sensitive, one-step procedure, only submilligram sample required, and it is capable to identify many structurally related compounds owing to the high separation efficiency of GC and the strong identification power of MS; Therefore, It has been successfully used to study the structure of complex organic macromolecular material such as lignin, humic acid and kerogen (Fu and Qing, 1995; Chefetz *et al.*, 2002; Fahmi *et al.*, 2007), although the limitation of incomplete pyrolysis, thermal degradation, secondary reactions and cyclization in this technique (Saiz-Jimenez, 1994).

This study aims at elucidate the structural and compositive characteristics of HALS extracted from dust. Py-GC-MS methods was used to decompose macromolecules into small detectable molecules to better elucidate structural differences at the molecular level and assess possible biological and artificial sources of detectable compounds in HALS. The results would provide new data may help us to better understand the chemical composition, geochemical behavior, origin and structure of HALS that were isolated from dust by a chemical procedure. Moreover, chemical characterization of dust would increase our knowledge of aerosol.

EXPERIMENT

Preparation of the Samples

Dust samples were collected from two sites in Guangzhou city, PR China: Wushan (WS) in Tianhe district and the university town (UT) in Panyu district. Falling dust was collected at intervals of 2 months at WS and the UT between April 2006 and May 2007. Samplings lasted one year and in total 12 samples were collected.

WS represents an urban area and is surrounded by highways, schools, residential and office buildings, and industrial factories. The main sources of air pollution at this site are thought to be anthropogenic. Samples were collected on the roof of a library building that is 18 m above the ground.

UT represents a suburban area located at the boundary between urban and rural areas and is surrounded by several universities. The main sources of air pollution at this site are a mixture of anthropogenic and biological. Samples were collected on the roof of a five-story building in South China Normal University at 23 m above the ground.

Roofs selected for sampling sites were cleaned before sampling. Neither site received any rain, but allowed atmospheric dust to fall to the ground under its own gravitation. The sampling sites were high enough to avoid contamination by secondary dust raised from the ground. The sampling sites were cleaned after individual sampling periods, prior to collection of the next sample. Sampled dust was pre-cleaned by 0.28 mm sieve and then stored in a brown bottle within desiccators before use.

Extraction of HA

The isolation protocol of HALS was based on that of International Humic Substances (IHSS) and Song *et al.*

(2002).

A predetermined amount of dust sample was placed in a centrifuged bottle and 0.1 M of NaOH was added under a nitrogen atmosphere. In this step, N₂ gas was purged into aqueous solutions of NaOH. After extraction for 12 h on a shaker, the content of the bottle was centrifuged at 4500 rev./min for 30 min, and the supernatant was transferred to another bottle. The extraction was repeated 5 times or more until the supernatant became colorless. The extracts from different batches were combined and acidified to pH 1 using concentrated HCl acid (6 M) to precipitate the HALS.

After 24 h stagnant precipitation, the acidified solution was centrifuged at 4500 rev./min for 30 min, and the supernatant, i.e., the fulvic acid fraction, was transferred to another bottle. The residue, i.e., the HALS fraction, was purified by a dissolution and precipitation processes with 0.1 M KOH/0.2 M KCl and 0.1 M HCl/0.3 M HF, respectively. This procedure was repeated two or three times. HA precipitate was transferred to a Visking dialysis tube by slurrying with water and dialyzed against distilled water until the dialysis water gave a negative Cl⁻ test with silver nitrate (AgNO₃). HALS was freeze dried and stored in a refrigerator until use.

Py-GC-MS

The Py-GC-MS analysis was performed on a pyrolysis injector (CDS-2000, CDS Analytical Inc., Oxford, PA) interfaced directly with a GC/MS (Voyager, Thermo Finnigan, Chester, UK). During analysis, approximately 1 mg of particulate material (HALS sample) was placed in a quartz tube, which was introduced into a Pt-coil pyroprobe. The probe was inserted into the injector and heated from 250°C to 650°C at 5 °C/ms and held at 650°C for 10 s. A helium carrier gas of 20 mL/min flow rate purged the pyrolysis chamber and held at 250°C. Split mode (1:20, V/V) was applied at the GC inlet for the introduction of products from the pyrolysis chamber into the GC column. A standard solution of *d*-C₂₄ *n*-alkane (100 mg/L) was injected into the samples before heating for quantification of pyrolysates.

The Py products were directly analyzed by GC/MS on a fused silica column (CP-SIL5 CB, 30 m × 0.32 mm × 0.25 μm, length × ID × film thickness). Helium (1.4 mL/min) was used as the carrier gas to flush pyrolytic compounds into the GC/MS system. The column temperature was initially set at 35°C for 3 min, then increased at 3 °C/min to 300°C and held for 15 min. The mass spectrometer was operated at ionization energy of 70 eV (EI) with a mass detection range (*m/z*) 50–700. Compounds were identified by comparing the mass spectra obtained with commercially available MS libraries (Wiley, NIST and LIBTX) and literature MS data.

RESULTS AND DISCUSSION

Characterization and Source Contributions for HALS

All 12 HALS fractions exhibited very similar total ion chromatograms (TICs). Fig. 1 presents two pyrogram obtained for UT0610 and WS0610, which show about 63 identifiable peaks. Due to the vast number of identified compounds, it is not possible to label all peaks in the pyrogram and therefore, only some important and major

compounds are indicated in the Fig. 1. The assignments of major peaks, excluding *n*-alkane/alkene doublets, are listed in Table 1. Such pyrolysates have been reported in previous pyrolysis studies for HALS of soil and/or sediment (Lu *et al.*, 2000, Chefetz *et al.*, 2002) and not of atmosphere falling dust.

Furfuran Compounds

Derivatives of furan and benzofuran (Fig. 1, peak 11, 43)

have been detected in HALS, which normally believed that these compounds originated from biodegradation of polysaccharide fraction in plants (Hayes *et al.*, 1989). These results indicated that polysaccharides maybe play an important role in formative processes of HALS. More furfuran compounds have been found in UT HALS fractions suggested that HALS in UT samples contained more easily decomposed components, which related to the biological surroundings in UT.

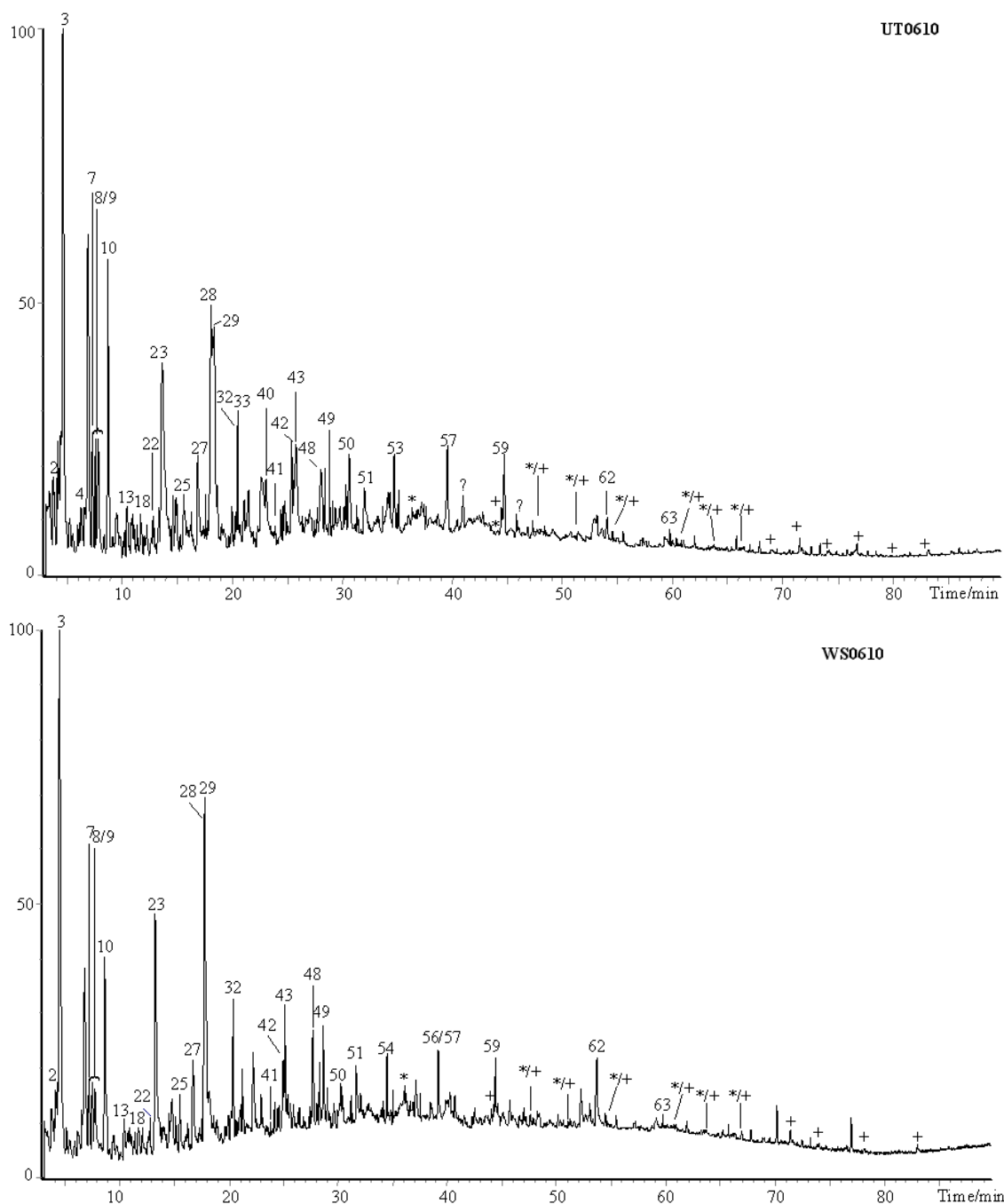


Fig. 1 Total ion chromatogram (TIC) and specific ion chromatograms ($m/z = 57 + 55$) of the pyrolysates of HALS that were extracted from summer UT and WS dust.

Note: Samples were named according to the sampling site (UT, WS) and sampling time (year and month). For example, UT0610 means that the sample was collected in UT in October, 2006.

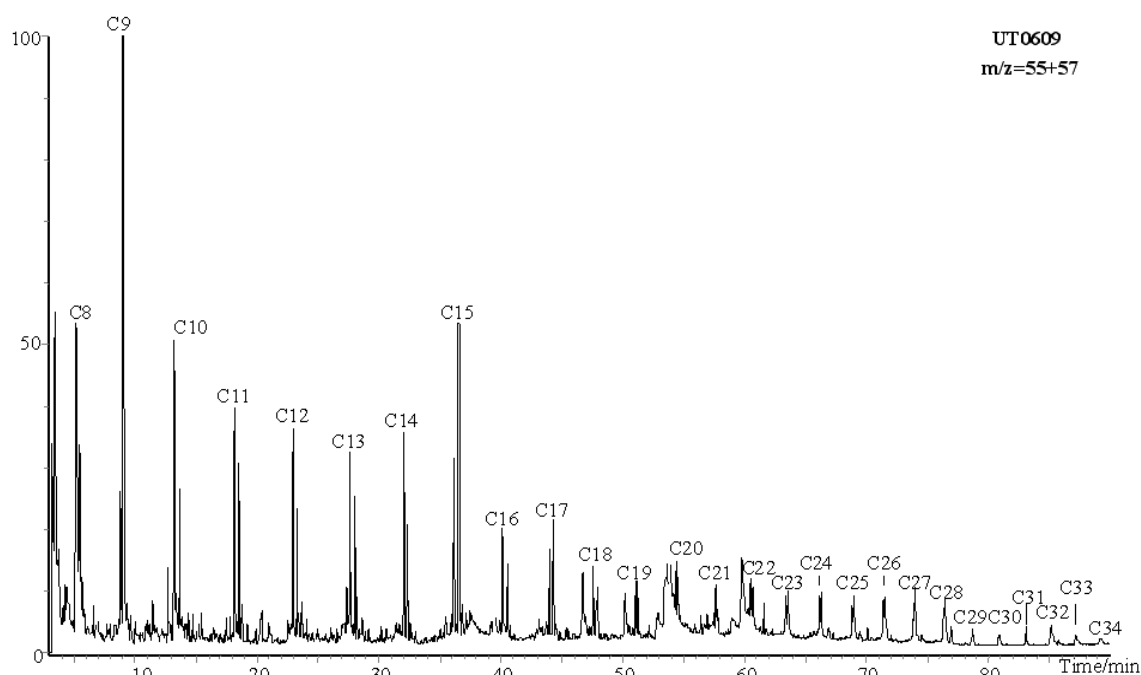


Fig. 1. (continued).

Nitrogenous Compounds

N-Containing compounds such as pyrazole, pyrrole, pyridine, pyrimidines, benzonitrile, and so on (Fig. 1, peaks 1, 2, 4, 5, 7, 12, 13, 14, 15 and 22) were thought to be released from protein/amino acid by pyrolysis (Chiavari and Galletti, 1992; Hendrick *et al.*, 1998). The abundance of N-containing compounds in HALS were higher in UT samples than that in WS samples, which indicated that HA in UT samples were contained more easily decomposed structures of protein, and which was opposite in WS samples.

Phenolic Compounds

The information presented in Fig. 1 shows that phenolic compounds were the predominant products in the pyrogram. Prominent peaks 28, 40, 46, 50, 53 and 59 on the pyrogram (Fig. 1) represent guaiacol, 2-methoxy-4-mentyl-phenol, 4-ethyl-2-methoxy-phenol, 3,4-dimethoxy-phenol, 4-propenyl-2-methoxy-phenol and 4-allyl-2,6-dimethoxy-phenol, which are indicators of lignin material (gymnosperms, angiosperms, herbaceous). Because different sources of lignin could reflect different composition of HALS (Li *et al.*, 2003), and therefore different compounds indicate their origins. The semiquantitative abundance of HALS based on *d*-C₂₄ *n*-alkane, it was showed that the abundance of phenolic compounds in UT HALS fractions were higher than that in WS HALS fractions, which implied that HALS in WS contained structures of phenolic compounds was lower than that in UT. Based on these analysis, it would be easily found that lignin in UT was originated both from sources of woody plants and herbaceous plant. Lignin in WS, however, was mainly contributed by land-woody plants.

Phenol and alkyl-phenol were involved in pyrolysates of HALS (Fig. 1, peaks 23, 26, 29, 31, 35 and 36), which were the common pyrolysates of natural organic matter. It can be

thought that they originated from decomposed lignin of trunk (Saiz-Jimenez and De Leeuw, 1987; Martin *et al.*, 1979), and also maybe derived from other biology, such as protein, polycarboxylic acid (Bracewell *et al.*, 1980), and polysaccharide (Wilson *et al.*, 1983). However, the relatively higher content of phenol and methoxy-phenol illustrated that these classes of compounds mainly originated from biodegradation of lignin.

n-alkane/alkene

All specific ion chromatograms ($m/z = 57 + 55$) of HA fractions showed a series of *n*-alkane/alkene doublets ranging from C₈ to C₃₃ (Fig. 1). The multi-modals distribution and variation in carbon preferences indicate the complexity of the *n*-alkane sources (Fig. 2). Usually, ester-bound fatty acids yield pyrolytic *n*-alkanes/*n*-alkenes with one C atom less than the parental fatty acid moiety, whereas ether-bound compounds result in the corresponding *n*-alkane/*n*-alkene with the same chain length as the parent compound (van de Meent *et al.*, 1980). Whereas, aliphatic pyrolysates were normally thought to be decomposed from poly-fatty hydrocarbon in organic fraction by pyrolysis, which originated from the polymer of fatty hydrocarbon in biology (Tegelaar *et al.*, 1989; Almendros *et al.*, 1996).

The main carbon numbers is C₁₂-C₂₇ that can be found from Fig. 2, which have partly odd-even predominance. From Fig. 2, the *n*-alkanes distribution observed was trimodal, although there main peaks have some differences. The main peaks of alkane in UT organic fraction was C₁₃, C₁₆ and a relative high peak C₂₉ which was only appeared in sample December, 2006, as well as C₁₅, C₁₈, C₂₁ and C₂₃ were the main peaks of alkane in WS organic matter, which indicated that fatty hydrocarbon in UT HALS was originated from both low aquatic organisms and micro-

Table 1. Pyrolysates of HALS fractions in UT and WS dust.

Number	Compounds	Sources	Number	Compounds	Sources
1	1,3-dimethylpyrazole	Pr	33	1-vinyl-3-ethyl-benzene	Aromatic
2	pyridine	Pr	34	1-methyl-indene	Aromatic
3	toluene	Pp/Pr	35	3-ethyl-phenol	Pp/Lg
4	2-methyl-pyridine	Pr	36	3,5-dimethyl-phenol	Pp/Lg
5	5-methyl-pyrimidine	Pr	37	.alpha.-methyl- phenylacetone	Aromatic
6	3-methyl-pyrazol	Pr	38	3'-methyl- acetophenone	Aromatic
7	3-methyl-pyrrole	Pr	39	naphthalene	Aromatic
8	1,3-dimethyl-benzene	Uc	40	2-methoxyl-4-methyl-phenol	Lg
9	1,4-dimethyl-benzene	Uc	41	benzothiazole	Aromatic
10	styrene	Pp/Uc	42	3-phenyl-propionitrile	Uc
11	2,4-dimethyl-furan	Ps	43	2,3-dihydro-benzofuran	Ps
12	2-ethyl-pyridine	Pr	44	quinoline	Pr
13	2,3-dimethyl-pyrrol	Pr	45	1-acetal-1H-indene	Aromatic
14	2-vinyl-pyridine	Pr	46	4-ethyl-2-methoxyl-phenol	Lg
15	2,4-dimethyl-pyrrole	Pr	47	2-methyl-naphthalene	Aromatic
16	propenylbenzene	Aromatic	48	indole	Pr
17	propylbenzene	Aromatic	49	2-methyl-4-hydroxyl-acetophenone	Aromatic
18	benzaldehyde	Aromatic	50	3,4-dimethoxyl-phenol	Lg
19	1-ethyl- 3-methyl-benzene	Aromatic	51	4-methyl- indolizine	Uc
20	5-methyl-2-furfural	Ch	52	N-methyl- phthalimide	Pr/Uc
21	.alpha.-methyl-styrene	Aromatic	53	2-methoxyl-4-propenyl-phenol	Lg
22	benzonitrile	Pr	54	(E)-2-methoxyl-4-propenyl-phenol	Lg
23	phenol	Lg	55	1,1-diphenyl-ethane	Aromatic
24	o-methyl-styrene	Aromatic	56	4-methyl-2,5-dimethoxyl-benzaldehyde	Aromatic
25	1-ethynyl-4-methyl-benzene	Aromatic	57	3,5-dimethoxyl-acetophenone	Aromatic
26	2-methyl-phenol	Pp/Lg/Pr	58	diphenyl ketone	Aromatic
27	acetophenone	Aromatic	59	4-allyl-2,6-dimethoxyl-phenol	Lg
28	2-methoxyl-phenol	Lg	60	myristic acid	Lp
29	4-methyl-phenol	Pp/Lg/Pr	61	pentadecanoic acid	Lp
30	2,3-dihydro-1H-indole	Pr	62	Hexadecanoic acid	Lp
31	3,5-dimethyl-phenol	Lg/Pp	63	octadecanoic	Lp
32	phenyl-acetonitrile	Aromatic			
*	n-alkene	Lp	+	n-alkane	Lp

Note: Ps: polysaccharides; Pp: polyphenoles; Ch: Carbohydrate; Pr: proteins/amino acids; Lg: Lignin; Lp: Lipids; Uc: unassigned compounds.

organisms and terrestrial herb (Zhao *et al.*, 2009), whereas, fossil fuel and higher plant were the main sources of fatty hydrocarbon in WS HALS.

Fatty Acids

Fatty acids were found in all HALS fractions, ranging from myristic acid to octadecanoic acid (Fig.1, peaks 60, 61, 62 and 63) with a pronounced even-carbon-number preference. Hexadecanoic was the main fatty acids in these fatty acids. Even-carbon predominance indicated that these fatty acids were strongly sequestered in the macromolecules as a free phase (Saiz-Jimenez 1995; Gobè *et al.*, 2000; Grasset *et al.*, 2002; Li *et al.*, 2003). Because polycarboxylic acids would react by decarboxylation under pyrolysis and consequently get alkanes, alkenes, phenol and alcohol (Martin *et al.*, 1994; Saiz-Jimenez 1995). The organic matter in the dust sample clearly indicated the presence of aliphatic components, which in agreement with results of Subbalakshmi *et al.* (2000).

Other Compounds

Many aromatic compounds were detected in the samples, including polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and their alkyl-substituted compounds (Table 1, peaks 39 and 47). Although only a few PAHs were detected and their abundances also were low, their presence indicated pollution that was caused by anthropogenic activity in these areas. Styrene (peak 10) also has been founds in these compounds. Some researchers thought it was the result of contamination, such as polystyrene pollutants was inputted into environment by human (Peulve *et al.*, 1996). Other researchers believed that styrene was the pyrolysate of peat pyrolysis, which can be considered as the marker of degradation of lignin. Nierop *et al.* (2005) was thought that styrene originated from polyphenols when he was studied volcanic soil in Azores. Therefore, styrene has been detected in all HALS in our study, which implied its importance of organic composition in HALS. In addition, benzonitrile (peak 22) as a special kind of nitrogenous compounds also have been found, which was considered a pyrolysis product of protein (Nierop *et al.*, 2001).

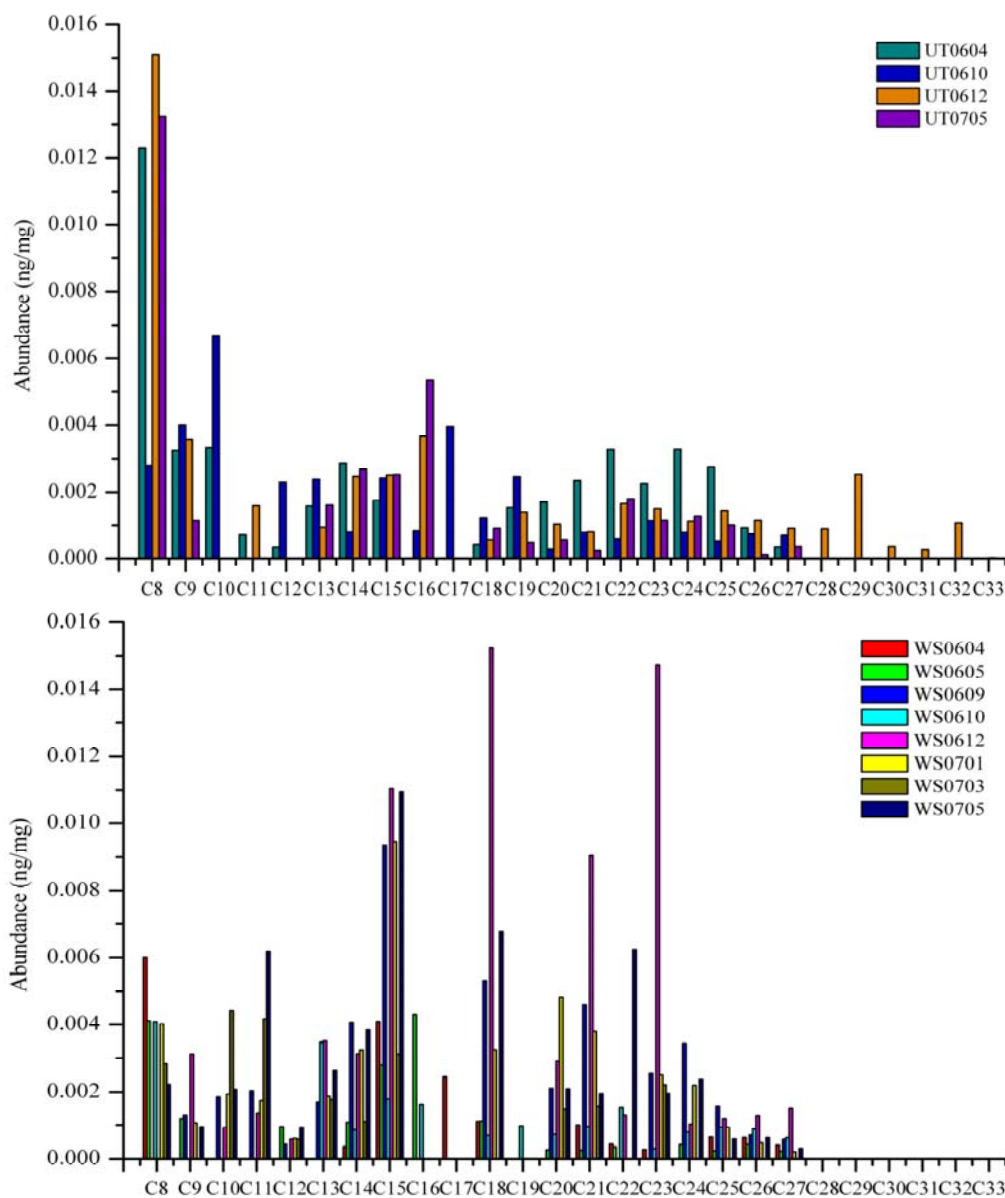


Fig. 2. Distribution of *n*-alkane in HALS fractions.

Comparison of HALS in Suburban (UT) and Urban (WS) during Different Seasons

To compare and discuss the relative content of the pyrolysates in different seasons, pyrolysates have been grouped into six classes: *n*-alkanes/alkenes, fatty acids, aromatic compounds, N-containing compounds, and other compounds. Fig. 3 showed the relative content of five classes' compounds for HALS fractions in different months at WS and UT, respectively. It was obviously found that the relative content of the five classes compounds were variation in different seasons.

Aromatic compounds and nitrogenous compounds in HA were presented their preference in all pyrolysates and accounted for 80% in five classes compounds. The content of *n*-alkanes/alkenes in UT and WS HALS were ranged from 8.08% to 13.80% and 4.06% to 15.07%, respectively. Although contents of fatty acids only reached 0.60%–4.58% and 1.16%–8.37% in UT and WS, respectively,

which were important pyrolysates in HALS. According to the seasonal variation in five classes' pyrolysates, we can see that the variation of these organic compounds was not consistent with seasons' change. However, when we divided the content of five classes' compounds into summer (including May, June, September and October) and winter season (including December, January, and March), the changes of contents for pyrolysates in summer and winter would appear clearly.

The contents of *n*-alkane/alkene were higher in winter samples than that in summer samples both in UT and WS. The reason for this difference may be due to the low level photochemical degradation and limited mixture layers which lead to an increase *n*-alkane/alkene in winter. On the other hand, frequent temperature inversion and haze days in the winter in Guangzhou also provided atmospheric conditions for cumulative *n*-alkane/alkene in Guangzhou, whereas opposite meteorologic factor and frequent rain

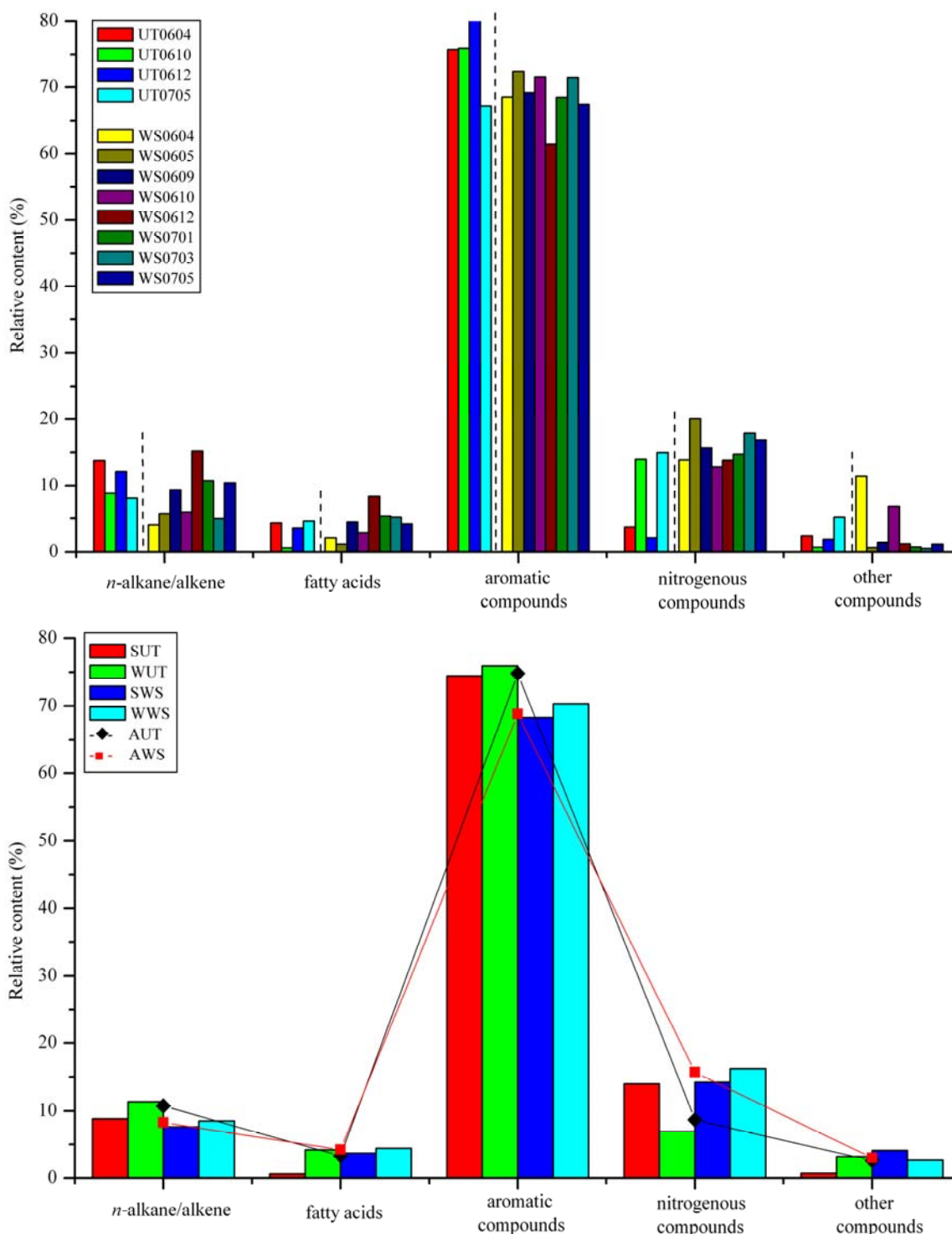


Fig. 3. Relative content of five classes compounds for HALS in different month and average content in winter and summer season.

Note: SUT, WUT, SWS, WWS, AUT, AWS are the abbreviation of organic fraction HA that was extracted from summer UT samples, winter UT samples, summer WS samples, winter WS samples, average relative content of UT and average content of WS.

summer decreased *n*-alkane/alkene pollution. From Fig. 3, it was clearly showed that the average levels of *n*-alkane/alkene in WS samples were slightly lower than that in UT samples, which may be related to mixture sources of traffic

and plant in UT, especially dead leaves would release more plant wax in winter (Guo et al., 2003; Oliveira et al., 2007).

There were presented slight differences of average contents for fatty acids in different sampling site during

winter and summer (Fig. 3), which showed lower content in summer. In this study, myristic acid to octadecanoic acid was less than 20 carbon number and the prominent peaks were hexadecanoic and octadecanoic acids. Simoneit *et al.* (1982) was thought that carbon number of fatty acids less than 20 originated from microorganism. Other researches demonstrated that smaller size particles in aerosol maybe also released fatty acids, such as cooking (Rogge *et al.*, 1991; Schauer *et al.*, 2002), vehicle exhaust gas (Rogge *et al.*, 1993; Schauer *et al.*, 2002) and fossil fuel (Rogge *et al.*, 1997). Therefore, anthropogenic activity, such as vehicle emissions, was the main sources to WS pollution, which was proved the reason that difference of content for fatty acids between summer and winter in WS was limited. The obviously higher average content of fatty acid in winter in UT samples, one reason was summer vacation would be decreased fatty acid that emitted from cooking of refectory in UT, moreover, frequent rain in summer was also not favor to accumulate higher content of fatty acid. On the other hand, long time calm wind in winter would be resulted in enrichment of fatty acids.

In addition, HALS extracted from UT dust was not enough in some samples, in order to analysis its composition, some HALS samples of different month have been mixed, such as UTHA0604 and UTHA0612 (UTHA0604 was the sample that was extracted from mixed samples of April, June and September dust; UTHA0612 was the sample that was extracted from mixed samples of December 2006, January and March 2007 dust), may be also the reason to explain lower content of fatty acid in summer and higher of that in winter.

Aromatic compounds as an important pyrolysates showed higher relative contents in HALS during winter than that in summer. From the view of whole year, however, the average content of fatty acids in UT samples showed higher level than that in WS, which may relative to the high levels of photochemical degradation and high emissions of plants in UT (Guo *et al.*, 2003; Oliveria *et al.*, 2007), whereas only vehicle emission contributed to WS and resulted in insignificant change between summer and winter.

For nitrogenous compounds, which were pyrolysed from UT samples, the relative content was higher in summer than that in winter. The reason related to the agriculture activity which would release more NH₃ by frequent management of fertilization during summer in suburban (Gilliland *et al.*, 2006; Wu *et al.*, 2008), while the fallow duration and few farmland activities in winter lead to lower nitrogenous compounds. Higher content of nitrogenous compounds in WS during winter, which was results of frequent temperature inversion and haze days, and therefore these factors supplied condition of NO_x to form secondary pollution by transformation and enrichment (Ma *et al.*, 2010).

It can be easily found from Fig. 3 that there was much more difference of various pyrolysates in HALS that was isolated from dust. The main pyrolysates of HALS fraction were aromatic compounds and nitrogenous compounds, which the relative content reached to 67.42% and 14.93%, respectively. Based on this analysis, it can be implied that the main structure of HA fraction was aromatic ring structure.

CONCLUSIONS

Multiple extractions were required to obtain a representative HALS of atmospheric falling dust. The analyses of HA fractions allowed a better assessment of macromolecule characterization in aerosol. The Py-GC/MS techniques provide a comprehensive assessment of humic macromolecules on a molecular level, significantly expanding knowledge on the source and reliability of the inferred structural data of HA in dust.

Detail identification of pyrolysates of the HALS suggests that aromatic compounds is an important unit in the humic structures. Aromatic compounds and nitrogenous compounds were presented their preference and accounted for 80% in all pyrolysates. The series of long chain *n*-alkenes/alkanes doublets in pyrolysis showed evidence for the presence of aliphatic biopolymers of both low aquatic organisms and micro-organisms and terrestrial herb in UT and only fossil fuel affect contents *n*-alkenes/alkanes in WS.

The difference of relative contents for pyrolysates was showed the different sources in UT and WS, which were controlled by the seasonal and spacial variation. The mixed sources in UT were biology emission and anthropogenic activity, the main source in WS, however, was anthropogenic pollution. The relative contents of pyrolysates in different seasons at the same sampling site suggested that meteorology was also an important factor to influence composition of HALS.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 41005082; No. 40505026) and the MEL Young Scientist Visiting Fellowship Program (MELRS1017). The authors would like to thank Yanting Chen for her help during experiments. Anonymous reviewer is thanked for the comments.

REFERENCES

- Almendros, G., Guadalix, M.E., González-Vila, F.J. and Martin, F. (1996). Preservation of Aliphatic Macromolecules in Soil Humans. *Org. Geochem.* 24: 651–659.
- Bracewell, J.M., Robertson, G.W. and Robertson, D.I. (1980). Polycarboxylic Acids as the Origin of some Pyrolysis Products Characteristic of Soil Organic Matter. *J. Anal. Appl. Pyrol.* 2: 239–248.
- Campitelli, P.A., Velasco, M.I. and Ceppi, S.B. (2006). Chemical and Physicochemical Characteristics of Humic Acids Extracted from Compost, Soil and Amended Soil. *Talanta* 69: 1234–1239.
- Chefetz, B., Salloum, M.J., Deshmukh, A.P. and Hatcher, P.G. (2002). Structure Components of Humic Acids as Determined by Chemical Modifications and Carbon-13 NMR, Pyrolysis- and Thermochemolysis-gas Chromatography/Mass Spectrometry. *Soil Sci. Soc. Am. J.* 66: 1159–1171.
- Chiavari, G. and Galletti, G.C. (1992). Pyrolysis-gas Chromatography/Mass Spectrometry of Amino Acid. *J.*

- Anal. Appl. Pyrol.* 24: 123–137.
- Chow, J.C., Yu, J.Z., Watson, J.G., Hang, H.S.S., Bohannon, T.L., Hays, M.D. and Fung, K.K. (2007). The Application of Thermal Methods for Determining Chemical Composition of Carbonaceous Aerosols: A Review. *J. Environ. Sci. Health., Part A* 42: 1521–1541.
- Fabbri, D., Prati, S. and Vassura, I. (2002). Molecular Characterisation of Organic Material in Air Fine Particles (PM₁₀) Using Conventional and Reactive Pyrolysis-gas Chromatography-mass Spectrometry. *J. Environ. Monit.* 4: 210–215.
- Fahmi, R., Bridgwater, A.V., Thain, S.C., Donnison, I.S., Morris, P.M. and Yates, N. (2007). Prediction of Klason Lignin and Lignin Thermal Degradation Products by Py-GC/MS in a Collection of Lolium and Festuca Grasses. *J. Anal. Appl. Pyrol.* 80: 16–23.
- Falkovich, A. and Rudich, Y. (2001). Analysis of Semivolatile Organic Compounds in Atmospheric Aerosols by Direct Sample Introduction Thermal Desorption GC/MS. *Environ. Sci. Technol.* 35: 2326–2333.
- Fu, J.M. and Qing, K.Z. (1995). The Geochemistry of Kerogen. Guangzhou: Guangdong Science and Technology Press, 171–182, 297–358, 376.
- Gilliland, A.B., Appel, K.W., Pinder, R.W. and Dennis, R.L. (2006). Seasonal NH₃ Emissions for the Continental United States: Inverse Model Estimation and Evaluation. *Atmos. Environ.* 40: 4986–4998.
- Gobè, V., Lemée, L. and Amblès, A. (2000). Structure Elucidation of Soil Macromolecular Lipids by Preparative Pyrolysis and Thermochemistry. *Org. Geochem.* 31: 409–419.
- Grasset, L., Guignard, C. and Amblès, A. (2002). Free and Esterified Aliphatic Carboxylic Acids in Humin and Humic acids from a Peat Sample As Revealed by Pyrolysis with Tetramethylammonium Hydroxide or Tetraethylammonium Acetate. *Org. Geochem.* 33: 181–188.
- Guo, Z.G., Sheng, L.F., Feng, J.L. and Fang, M. (2003). Seasonal Variation of Solvent Extractable Organic Compounds in the Aerosols in Qingdao, China. *Atmos. Environ.* 37: 1825–1834.
- Hayes, M.H.B., MacCarthy, P. and Malcolm, R.L. (1998). Humic Substances II, In *Search of Structure*, New York: John Wiley & Sons Ltd, Chichester (Vol.II).
- Hendricker, A.D. and Voorhees, K.J. (1998). Amino Acid and Oligopeptide Analysis Using Curie-point Pyrolysis Mass Spectrometry with in-situ Thermal Hydrolysis and Methylation: Mechanistic Considerations. *J. Anal. Appl. Pyrol.* 48: 17–33.
- Li, L., Huang, W.L., Peng, P.A., Sheng, G.Y. and Fu, J.M. (2003). Chemical and Molecular Heterogeneity of Humic Acids Repetitively Extracted from a Peat. *Soil Sci. Soc. Am. J.* 67: 740–746.
- Li, L., Jia, W.L., Peng, P.A., Sheng, G.Y., Fu, J.M., Huang, W.L. (2006). Compositional and Source Characterization of Base Progressively Extracted Humic Acids Using Pyrolytic Gas Chromatography Mass Spectrometry. *Appl. Geochem.* 21: 1455–1468.
- Li, L., Zhao, Z.Y., Huang, W.L., Peng, P.A., Sheng, G.Y. and Fu, J.M. (2004). Characterization of Humic Acids Fractionated by Ultrafiltration. *Org. Geochem.* 35: 1025–1037.
- Ma, S.X., Peng, P.A., Song, J.Z., Bi, X.H., Zhao, J.P., He, L.L., Sheng, G.Y. and Fu, J.M. (2010). Seasonal and Spatial Changes of Free and Bond Organic Acids in Total Suspended Particles in Guangzhou, China. *Atmos. Environ.* 44: 5460–5467.
- Martin, F., González-Vila, F.J., del Rio, J.C. and Verdejo, T. (1994). Pyrolysis Derivatization of Humic Substances I. Pyrolysis of Fulvic Acids in the Presence of Tetramethylammonium Hydroxide. *J. Anal. Appl. Pyrol.* 28: 71–80.
- Martin, F., Saiz-Jimenez, C. and González-Vila, F.J. (1979). Pyrolysis-gas Chromatography-mass Spectrometry of Lignins. *Holzforschung* 33: 210–212.
- Mukai, A. and Ambe, Y. (1986). Characterization of Humic Acid-like Brown Substance in Airborne Particulate Matter and Tentative Identification of its Origin. *Atmos. Environ.* 20: 813–819.
- Nierop, K.G.J., van Bergen, P.F., Buurman, P. and van Lagen, B. (2005). NaOH and Na₄P₂O₇ Extractable Organic Matter in Two Allophonic Volcanic Ash Soils of the Azores Islands—a Pyrolysis GC/MS Study. *Geoderma* 127: 36–51.
- Nierop, K.G.J., Pulleman, M.M. and Marinissen, J.C.Y. (2001). Management Induced Organic Matter Differentiation in Grassland and Arable Soil: A Study Using Pyrolysis Techniques. *Soil Biol. Biochem.* 33: 755–764.
- Oliveira, C., Pio, C., Alves, C., Evtugina, M., Santos, P., Goncalves, V., Nunes, T., Silvestre, A.J.D., Palmgren, F., Wahlin, P. and Harrad, S. (2007). Seasonal Distribution of Polar Organic Compounds in the Urban Atmosphere of Two Large Cities from the North and South of Europe. *Atmos. Environ.* 41: 5555–5570.
- Peulve, S., Sicre, M.A., Baas, M. and Saliot, A. (1996). Characterization of Macromolecular Organic Matter in Sediment Traps from the Northwestern Mediterranean Sea. *Geochim. Cosmochim. Acta* 60: 1239–1259.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. (1991). Sources of Fine Organic Aerosol. 1. Charbroilers and Meat Cooking Operations. *Environ. Sci. Technol.* 25: 1112–1125.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. (1997). Sources of Fine Organic Aerosol. 8. Boilers Burning No.2 Distillate Fuel Oil. *Environ. Sci. Technol.* 31: 2731–2737.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T. (1993). Source of Fine Organic Aerosol. 2. Non-catalyst and Catalyst-equipped Automobiles and Heavy Duty Diesel Trucks. *Environ. Sci. Technol.* 27: 636–651.
- Saiz-Jimenez, C. (1994). Analytical Pyrolysis of Humic Substances: Pitfalls, Limitations and Possible Solutions. *Environ. Sci. Technol.* 28, 1773–1780.
- Saiz-Jimenez, C. (1995). Reactivity of the Aliphatic Humic Moiety in Analytical Pyrolysis. *Org. Geochem.* 23: 955–961.
- Saiz-Jimenez, C. and De Leeuw, J.W. (1987). Chemical

- Structure of a Soil Humic Acid as Revealed by Analytical Pyrolysis. *J. Anal. Appl. Pyrol.* 11: 367–376.
- Salloum, M.J., Chefetz, B. and Hatcher, P.G. (2002). Phenanthrene Sorption by Aliphatic-rich Natural Organic Matter. *Environ. Sci. Technol.* 36: 1953–1958.
- Schauer, J.J., Kleeman, M.J., Cass, G.R. and Simoneit, B.R.T. (2002). Measurement of Emissions from Air Pollution Sources. 5. C1–C32 Organic Compounds from Gasoline-powered Motor Vehicles. *Environ. Sci. Technol.* 36: 1169–1180.
- Simoneit, B.R.T. and Mazurek, M. (1982). Organic matter of the troposphere II. Nature background of biogenic lipid matter in aerosols over the rural western United States. *Atmos. Environ.* 16: 2139–2159.
- Song, J.Z., Peng, P.A. and Huang, W.L. (2002). Black Carbon and Kerogen in Soils and Sediments. 1. Quantification and Characterization. *Environ. Sci. Technol.* 36: 3960–3967.
- Stevenson, F.J. (1994). *Humus Chemistry: Genesis, Composition, Reactions*, 2nd ed. John Wiley & Sons, New York.
- Subbalakshmi, Y., Patti, A.F., Lee, G.S.H. and Hooper, M.A. (2000). Structural Characterisation of Macromolecular Organic Material in Air Particulate Matter Using Py-GC-MS and Solid State ¹³C-NMR. *J. Environ. Monit.* 6: 561–565.
- Tegelaar, E.W., de Leeuw, J.W. and Saiz-Jimenez, C. (1989). Possible Origin of Aliphatic Moieties in Humic Substances. *Sci. Total Environ.* 81/82: 1–17.
- Thurman, E.M. and Malcolm, R.L. (1981). Preparative Isolation of Aquatic Humic Substances. *Environ. Sci. Technol.* 15: 463–466.
- Van de Meent, D., Brown, S.C., Philp, R.P. and Simoneit, B.R.T. (1980). Pyrolysis-high Resolution Gas Chromatography and Pyrolysis Gas Chromatography–mass Spectrometry of Kerogens and Kerogens Precursors. *Geochim. Cosmochim. Acta* 44: 999–1013.
- Wilson, M.A., Gillam, A.H. and Collin, P.J. (1983). Analysis of the Structure of Dissolved Marine Humic Substances and their Phytoplanktonic Precursors Using ¹H and ¹³C NMR. *Chem. Geol.* 40:187–201.
- Wu, S.Y., Hu, J.L., Zhang, Y. and Aneja, V.P. (2008). Modeling Atmospheric Transport and Fate of Ammonia in North Carolina-Part II: Effect of Ammonia Emissions on Fine Particulate Matter Formation. *Atmos. Environ.* 42: 3437–3451.
- Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M.C., Gelencser, A., Kiss, G., Krivacsy, A., Molnar, A., Meszaros, E., Hansson, H.C., Rosman, K. and Zebuhr, Y. (1999). Inorganic, Organic and Macromolecular Components of Fine Aerosol in Different Areas of Europe in Relation to their Water Solubility. *Atmos. Environ.* 33: 2733–2743.
- Zhao, J.P., Peng, P.A., Song, J.Z., Ma, S.X., Sheng, G.Y. and Fu, J.M. (2009). Characterization of Organic Matter in Total Suspended Particles by Thermodesorption and Pyrolysis-gas Chromatography-mass Spectrometry. *J. Environ. Sci.* 21:1658–1666.

Received for review, June 18, 2011

Accepted, October 10, 2011