Characterization of organic matter in total suspended particles by thermodesorption and pyrolysis-gas chromatography-mass spectrometry

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Abstract

The organic matter in tropospheric aerosol plays an important role in atmospheric physical and chemical processes. The bulk of organic matter, representing a significant proportion of the total suspended particulate (TSP) mass, is bound to polymeric material whose structure and properties are largely unknown. Here we used thermodesorption gas chromatography/mass spectrometry (Td-GC/MS) to study organic compounds of low molecular mass and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) to characterize the chemical structure of macromolecules in TSP samples collected in different seasons from different sites in Guangzhou. *n*-Alkanes, fatty acids and nitriles were the predominant compounds in the thermodesorption products, whereas aromatics, fatty acids, nitriles and *n*-alkanes/alkenes were the major compounds in the pyrolysates. The results indicated that aromatics were main units in macromolecules. The fatty acids and nitriles formed from carboxylic ammonium salts were detected in both thermodesorption products and pyrolysates at a certain concentration, indicating the importance of these compounds in TSP formation. The TSP source mainly determined the occurrence of compounds in samples from urban, suburban and forest sites, whereas the TSP source and formation process maybe controlled the seasonal variation in compounds detected. High levels of nitriles in summer samples from suburban and forest sites coincide with the release of ammonium from the land and of fatty acids from vegetation at these sites.

Key words: thermodesorption; pyrolysis; total suspended particles; organic matter; macromolecule

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Introduction

Atmospheric particulate matter has very complex chemical composition and structure. It is a carrier of anthropogenic pollutants such as heavy metals and polyaromatic hydrocarbons and plays an important role in climate change and reducing air quality (Gill and Graedel, 1983; Posfai *et al*., 1998). In addition, bulk organic matter, a significant component of aerosols, can greatly affect global carbon cycles and control the fate of organic and inorganic pollutants in the atmosphere. These effects have sparked interest in the chemical and physical properties of particulate matter with increasing interest in its organic matter composition.

The organic matter of atmospheric particulates includes low-molecular-weight (LMW) compounds, which can be analyzed by gas chromatography (GC), and macromolecules compounds. LMW compounds in organic matter have been widely studied and their relationships to atmospheric physical and chemical processes have been discussed (Facchini *et al*., 1999), even LMW organic

matter only takes a few percentage of the total organic matter in total suspended particulate (TSP) matter (Bi *et al*., 2008). However, for organic macromolecules substances, the majority of organic matter compounds of air particulate matter, only a few studies have conducted on their nature (Mukai and Ambe, 1986; Zappoli *et al*., 1999). Macromolecules in air particulates, often described as "humic-like substances" in the literature may significantly contribute to the overall mass balance of air particulate organic matter, which has not been studied in detail owing to the limitation of the analysis methods available.

Several physical and chemical methods have been used to characterize organic macromolecules, such as X-ray diffraction (Fu and Qing, 1995; Stanmore *et al*., 2001) and solid ^{13}C nuclear magnetic resonance (Fu and Qing, 1995; Francioso *et al*., 2002). Those methods normally need milligram to gram sample, which is sometimes not possible for TSP. Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) methods is a valid technique for the analysis of macromolecules, which can yield information on chemical structure at the molecular level and its application to particulate matter in the atmosphere (Fabbri *et al*., 2002; Subbalakshmi *et al*., 2000; Falkovich and Rudich,

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2001; Chow *et al*., 2007). Py-GC/MS methods has notable advantages, such as it only requires submilligram sample 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; and has been successfully used to study the structure of complex organic macromolecular material such as lignin, humic acid and kerogen (Fahmi *et al*., 2007; Chefetz *et al*., 2002; Fu and Qing, 1995).

The objective of the present study was to characterize the chemical composition of organic matter, including LMW compounds and macromolecules, in TSP collected in Guangzhou, China using Py-GC/MS technique. The TSP samples from different sites and seasons were analyzed by two methodologies: (1) sample thermodesorption (Td); and (2) pyrolysis of samples after Td. Differences in the chemistry of particulate organic matter among different sites and differences seasons were discussed. This study provides valuable data which may help us to better understand the organic macromolecules present in TSP of Guangzhou.

1 Samples and methods

1.1 Sample collection

The TSP samples were collected at three sites in Guangzhou: Wushan in the Tianhe District, the university town in Panyu District, and Maofeng Mountain Forest Park in Baiyun District.

Wushan (denoted as 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.

The university town (denoted as UT) represents a suburban area and is located at the boundary between urban and rural areas and is surrounded by many universities. The main sources of air pollution at this site are 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.

Maofeng Mountain Forest Park (denoted as MF) represents a forest site and comprises 5362 ha of tropical and subtropical forest. This park has not been completely developed and access is difficult. Visitors and industrial factories are limited. The main sources of local air pollution are possibly only biogenic. Samples were taken on the roof of the park office, approximately 15 m above the ground.

A high-volume air sampler with a Whatman glass fiber filter (GFF, 20.3 cm × 25.4 cm) was used to collect TSP samples at a flow rate of 1.2 m^3/min (Tianhong Intelligent Instruments, Wuhan, China) for 40 h. The filters were pre-cleaned by baking in a furnace at 450°C for 15 h and then stored in aluminum foil within sealed polyethylene bags before use. TSP samples from three sites were collected during 16 June to 30 August 2006 (representing summer)

and 9 January to 20 February 2007 (representing winter), three summer and three winter TSP samples which have been chosen for analyzing.

After sampling, filters were wrapped in aluminum foil and stored in a freezer at –40°C until analysis. TSP concentrations were determined by weighing the filters before and after collection. Before weighing, filters were conditioned for 24 h in a chamber maintained at 25°C and 50% humidity.

1.2 Thermodesorption and pyrolysis

The Td-GC/MS analysis was performed on a pyrolysis injector (CDS2000, CDS Analytical Inc., Oxford, PA) interfaced directly to GC/MS (Voyager, Thermo Finnigan, Chester, UK). During analysis, approximately 2 mg of particulate material 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 to 300°C at 5°C/ms and held at 300°C for 250 s. A helium carrier gas with 20 mL/min flow rate was purged into 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-C$_{24}$ (deuterated-C$_{24}$) *n*-alkane (100 mg/L) was injected into the samples before heating for quantification of pyrolysates.

Pyrolysis of TSP after Td was carried out using the same quartz tube. The probe was heated from 250 to 650°C at 5°C/ms and held at 650°C for 10 s. Before pyrolysis, samples were heated at 250°C for 180 s under N$_2$ atmosphere to eliminate LMW compounds

1.3 GC/MS analysis

The Td and 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.

2 Results and discussion

2.1 Thermodesorption of TSP

All six TSP samples in summer and winter from WS, UT, and MF (denoted as WSS, WSW, UTS, UTW, MFS, and MFW, respectively) exhibited very similar total ion chromatograms (TICs). Figure 1 presents a Td chromatogram obtained for UTW, which shows about 62 identifiable peaks, excluding *n*-alkanes. Appendix 1 in Supporting Material lists the assignments of major peaks. The compounds were classified into six classes, including *n*-alkanes, fatty acids, aromatic compounds,
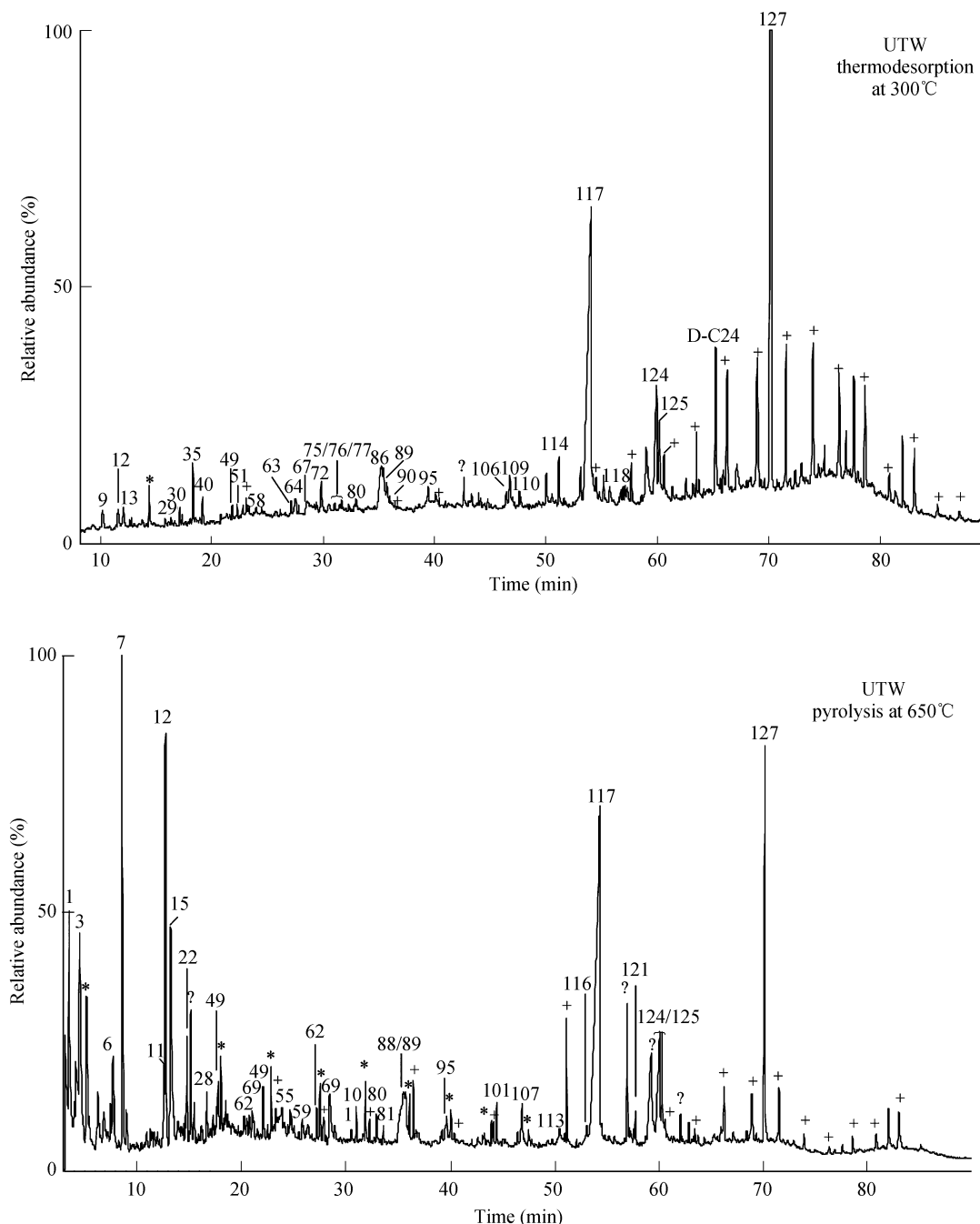
Fig. 1   Total ion chromatograms of samples collected at University Town in winter (UTW) after thermodesorption and pyrolysis. Peak numbers correspond to substance numbers listed in Appendix 1.

nitriles, non-nitrile N-containing compounds, and other compounds.

2.1.1 *n*-Alkanes

The relative abundance of *n*-alkanes in six samples is shown in Fig. 2. In general, all samples exhibited a similar carbon distribution, with high amounts of C_{19}–C_{33} *n*-alkanes and low amounts of C_{10}–C_{18} *n*-alkanes.

Slight spatial changes in *n*-alkane distribution were observed for C_{10}–C_{25} compounds. For example, C_{10} and C_{12} levels were higher in UT and WS samples, C_{19} levels were higher in WS and MF samples, and C_{25} levels were obviously higher in UTW samples. The reasons for these variations are not known, but differences in the source and formation process for different *n*-alkanes may play an important role. The winter samples contained more C_{10}–C_{32} *n*-alkanes with a pronounced odd-to-even carbon preference compared to summer samples.

C_{19}–C_{33} *n*-alkanes have been widely detected in TSP solvent extracts by GC/MS (Bi *et al*., 2005a). They were thought to be derived from epiphytes, waxes from higher fibrovascular plants and conifer leaves (Tang *et al*., 1993; Kavouras *et al*., 1999; Bi *et al*., 2005b), which are widespread in tropical and subtropical area. The nC_{19}–nC_{33} distribution (Fig. 2) observed was tri-modal, with maxima at nC_{31}, nC_{29}–nC_{27} and nC_{25}, representing inputs
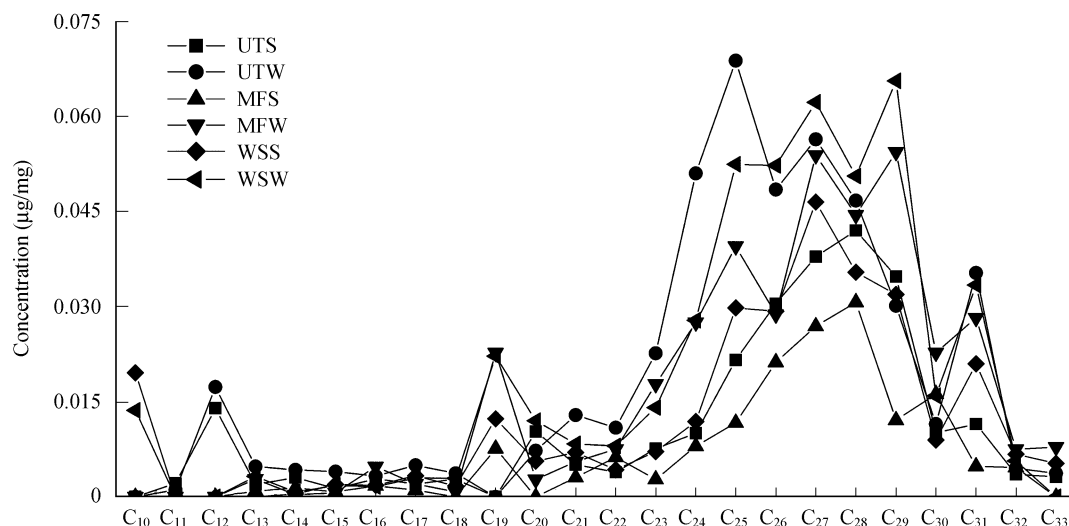
Fig. 2   *n*-Alkanes distribution (*m/z* = 57) of six TSP samples after thermodesorption at 300°C.

of *n*-alkanes from grass, wood and fungal debris, respectively (Azevedo *et al.*, 1999; Lu *et al.*, 2004; Yu *et al.*, 2007). The nC_{31}/nC_{27} ratio was similar from summer to winter, indicating that *n*-alkanes from grass and wood in MF were constant over the year. As shown in Fig. 2, it is also evident that the levels of C_{25} *n*-alkane were much higher in the UTW samples, which suggested that anthropogenic activity (e.g., vehicle exhaust), excluding biological sources (e.g., fungal debris), were another important sources for UT samples.

C_{10}–C_{18} *n*-alkanes may be derived from emissions due to fossil fuel combustion and inputs from lower organisms such as algae and bacteria. Considering the origin of the TSP samples from areas experiencing rapid economic development, fossil fuel combustion is the more likely source.

Carbon preference index (CPI) values (Table 1) also indicated the origin of the *n*-alkanes detected. CPI_1 (C_{11}–C_{33}) and CPI_2 (C_{11}–C_{24}) were approximately 1, especially in WS samples, which indicated that an origin in WS mainly was vehicle exhaust. Higher CPI_3 (C_{25}–C_{33}) values indicated that *n*-alkanes in the MF samples were predominantly from biological materials. The data shown in Table 1 also suggested that mixed sources, including anthropogenic activity and biological materials, were presented in UT sampling site.

2.1.2 Fatty acids

Fatty acids were detected in all six TSP samples, ranging from octanoic acid to octadecanoic acid (Fig. 1, peaks 52, 64, 76, 95, 107, 117, and 124), and only even-carbon acids were detected. Hexadecanoic and octadecanoic acids were the main fatty acids, which are generally associated with anthropogenic activity such as cooking (Rogge *et al.*, 1991; Schauer *et al.*, 1999), vehicle exhaust gas (Rogge *et al.*, 1993; Schauer *et al.*, 2002) and plant biogenic origin (Simoneit, 1982). In terms of sample locations, fatty acids may be derived from anthropogenic activity in WS samples, from both anthropogenic and biogenic sources in UT, and from plants in MF samples.

2.1.3 Aromatic compounds

Many aromatic compounds were detected in the samples, including polycyclic aromatic hydrocarbons (PAHs) such as naphthalene (peak 49), phenanthrene (peak 106), fluoranthene (peak 118), pyrene (peak 120) and other aromatic compounds, such as α-methyl styrene (peak 11) and 1,1′-biphenyl (peak 75) (Fig. 1). Although only a few PAHs were detected, their presence implied the different sources of pollution in these areas, such as fossil fuel combustion in WS and UT, and biology emission in MF.

2.1.4 Nitrogen compounds

Nitriles were detected in Td samples, including benzonitrile (Fig. 1, peak 12), *o/m/p*-benzenedicarbonitrile (peak

Table 1   Concentration of compounds and carbon preference index (CPI) values for *n*-alkanes in six TSP samples after thermodesorption

Compound class	WSS	WSW	UTS	UTW	MFS	MFW
n-Alkanes (μg/mg)	0.32	0.48	0.27	0.47	0.18	0.45
Fatty acids (μg/mg)	0.34	0.40	0.51	0.41	0.14	0.13
Aromatic compounds (μg/mg)	0.05	0.04	0.06	0.07	0.04	0.09
Nitriles (μg/mg)	0.03	0.04	0.16	0.09	0.19	0.06
Total N-containing compounds (μg/mg)	0.11	0.10	0.24	0.25	0.27	0.19
Other compounds (μg/mg)	0.04	0.03	0.03	0.04	0.02	0.02
CPI_1 (C_{11-33})	1.54	1.50	0.94	1.16	1.22	1.98
CPI_2 (C_{11-24})	1.22	0.99	0.42	0.52	0.58	1.86
CPI_3 (C_{25-34})	1.48	1.50	1.14	1.44	1.38	1.88

$CPI_1 = (\sum C_{11-31} + C_{13-33})/2\sum C_{12-32}$; $CPI_2 = \sum C_{11-23}/\sum C_{12-24}$; $CPI_3 = \sum(C_{25-33} + C_{27-35})/2\sum C_{26-34}$.

60) and a series of long-chain nitriles from octanenitrile to octadecanenitrile (peaks 32, 51, 63, 77, 90, 96, 109, 110, 114 and 121). These compounds only occurred in the samples collected from UT and MF and were present at higher levels in summer than in winter. Alkyl and aromatic nitriles were produced from the corresponding carboxyl ammonium or phenolic ammonium salts in samples by heating. Nucleophilic substitution reaction of NH_3 with carboxylic acids followed by dehydration was a possible pathway for nitrile formation (Chang and Novakov, 1975; Evans *et al*., 1985; Simoneit *et al*., 2003). High levels of NH_3 emission in suburban and forest areas in summer (Gilliland *et al*., 2006; Wu *et al*., 2008) explain the occurrence of nitriles in the samples.

The predominant non-nitrile N-containing compounds detected in the samples were benzothiazole (Fig. 1, peak 58), 3-(1-methyl-2-pyrrolidinyl)-pyridine (peak 72), *N*-methyl-phthalimide (peak 80), phthalimide (peak 86) and hexadecanamide (peak 125). These compounds were derived from cyclization and aromatization reactions of proteins or from intermediates in the transformation of carboxyl ammonium salts to nitriles (Chiavari and Galletti, 1992; Kögel-Knabner, 1997; Hendricker and Voorhees, 1998).

2.1.5 Oxygen compounds

2-Phenyl-furan, 3-phenyl-furan (Fig. 1, peaks 13 and 39) and dihydro-5-isopropyl-3(2H)-furanone (peak 43) were detected in samples. Lignin-related compounds such as 3,5-dimethyl-phenol (peak 8), 2-methoxy-phenol (peak 34) and 2,6-dimethoxy-phenol (peak 73) were also detected in WS and MFW samples. These compounds may be derived from carbohydrates and lignin by photochemical reaction.

2.1.6 Quantification of Td products

We used D-C_{24} *n*-alkane as a standard to measure the concentration of *n*-alkanes, fatty acids, nitriles, non-nitrile N-containing compounds and other compounds in samples. The results are showed in Table 1. Although this method did not take response factors into account and the results may not be exactly quantitative, it provides a tool for comparison of compound concentrations in samples.

n-Alkanes were the predominant compounds in Td products, at concentrations ranging from 0.18 to 0.48 μg/mg. Levels were higher in winter than in summer samples, and in urban samples than in suburban and forest samples. Low levels of photochemical degradation and limited mixture layers or the frequent formation of a temperature inversion layer in the atmosphere in Guangzhou during winter would facilitate the occurrence of high *n*-alkane concentrations in the samples. High levels of photochemical degradation and of mixture layers in the atmosphere and heavy rainfall during summer would lead to low concentrations of *n*-alkanes in samples.

The distribution of fatty acids was different to that of *n*-alkanes, and anthropogenic sources may be just as important as biogenic sources. Therefore, fatty acid concentrations were high in samples from UT and low in

samples from WS and MF. In addition, biogenic sources contribute greater amounts of fatty acids in summer because biosynthesis is high in this season. These general rules explain the seasonal variations in fatty acid concentrations in samples: high levels were detected in summer for samples from UT and MF, whereas the opposite was observed for samples from WS.

Variations in nitrile concentrations were similar to those for fatty acids, with higher levels in summer for samples from UT and MF and similar levels in summer and winter for samples from WS. As mentioned above, high levels of NH_3 emission in suburban and forest areas in summer explain the presence of nitriles in samples (Gilliland *et al*., 2006; Wu *et al*., 2008).

Non-nitrile N-containing compounds represented a mixed group. Seasonal variations in the relative abundance of these compounds were therefore complex. Further investigation is required before detailed explanation can be provided.

Although six samples are not statistically sufficient to draw conclusions about seasonal differences and need to study detailedly and deeply, it gives us some helpful information that meteorology also an important factor influencing TSP formation. This is coincident with former studies (Bi *et al*., 2005a, 2008).

2.2 Pyrolysis of TSP after Td

Figure 1 also shows a Py chromatogram of sample UTW in which 97 compounds (Appendix 1) were identified, excluding *n*-alkane/*n*-alkene doublets. All samples of Py chromatograms exhibited very similar TICs. Aromatic compounds were the most abundant in Py products.

2.2.1 Aromatic compounds

The major pyrolysates were toluene (Fig. 1, peak 3) and C_3–C_{12} alkyl-substituted benzenes (peaks 5, 6, 10, 19, 26, 47, 59, 74, 93, 100, 108 and 113). These non-lignin class aromatic compounds are commonly observed in pyrolysates of natural macromolecular materials, such as kerogen and carbon black (Boussafir *et al*., 1995; Faure *et al*., 2006). These compounds are considered from aromatic ring structures of macromolecular organic matter or from secondary cyclization and aromatization reactions during pyrolysis (Saiz-Jimenez, 1995; Almendros *et al*., 1996). Considering that our samples were TSP and contain low concentrations of long-chain compounds, cleavage of aromatic structures was the more likely source. Aromatic carbons may act as building blocks across TSP substances (Hatcher and Clifford, 1994).

Derivatives of benzofuran (Fig. 1, peaks 36, 69 and 83) were detected in the samples from MF. They are generally considered from microbial degradation of plant polysaccharides (Hayes *et al*., 1989).

Although methoxy-phenol and dimethoxy-phenol were detected in Td products, alkyl phenols were only found in Py products of samples from UT, MF and WS (Fig. 1, peaks 15, 27 and 56). Alkyl phenols are released from lignin-type organic matter (Martin *et al*., 1979; Saiz-Jimenez and de Leeuw, 1987). However, they may also be

derived from pyrolysis of polycarboxylic acids, proteins and polysaccharides (Wilson *et al.*, 1983; Bracewell *et al.*, 1980).

In addition, styrene (Fig. 1, peak 7), biphenyl (peak 75), naphthalene (peak 49), methyl-naphthalene (peaks 62 and 65), phenanthrene (peak 106), fluoranthene (peak 118), and other aromatic compounds were detected in Py products. Of these compounds, styrene is considered a pyrolysate product of polystyrene plastics (Peulve *et al.*, 1996). Sample contamination by polystyrene in the laboratory can be ruled out because we did not detect styrene in blank samples. Styrene is an alkyl benzene compound that can act as a structural moiety in TSP. Moreover, styrene and toluene are indicators of the aromaticity of organic matter.

2.2.2 Nitrogen compounds

Nitriles were also present in Py products (Fig. 1, peaks 12, 17, 31, 32, 42, 44, 60, 70, 90, 109, 114 and 121), especially alkyl-substituted nitrile compounds in samples from UT and MF. A series of alkyl-substituted nitriles, especially for higher-molecular-weight nitriles, have been detected in pyrolysates. Evans *et al.* (1985) thought that nitriles form during pyrolysis from alkanoic acids and ammonia via the amide intermediate. Therefore, these nitriles in pyrolysates have indicated the presence of ammonia in sampling sites, and also suggested that the characterization of macromolecule organic matter in TSP which was needed higher temperature to degradation.

In addition, some non-nitrile N-containing compounds, including pyridine (Fig. 1, peak 2), methylpyrrole (peak 4), benzonitrile (peak 12) and phthalimide (peak 86), were detected in Py products of all samples. Non-nitrile N-containing compounds are released from proteins and amino acid on pyrolysis (Chiavari and Galletti, 1992; Kögel-Knabner, 1997; Hendricker and Voorhees, 1998).

2.2.3 Fatty acids

Compounds detected at later elution times in Py chromatograms were a series of fatty acids (Fig. 1, peaks 64, 76, 95, 107, 111, 117 and 124) with a pronounced even-carbon-number preference. Nonanoic and decanoic acids were detected as major components of UTS and MFS Py products, but were not detected in WS samples. High concentrations in summer samples from suburban and forest areas suggest that these compounds were derived from biogenic sources (Ambls *et al.*, 1994; Grasset and Amblès, 1998). Even-carbon predominance indicated that these fatty acids were strongly sequestered in the macro-molecules as a free phase; they were not fully released by Td at 300°C. The organic matter in the air particle sample clearly indicated the presence of aliphatic components, which in agreement with results of Subbalakshmi *et al.* (2000).

2.2.4 *n*-Alkanes/alkenes

A series of *n*-alkane/*n*-alkene doublets ranging from C_8 to C_{32} was present in all chromatograms (Fig. 3). A slight odd-to-even predominance was observed for carbon numbers from C_{11} to C_{23} and an even-to-odd carbon number preference for carbon numbers from C_8 to C_{12} and from C_{24} to C_{32} (Fig. 4). The tri-modal distribution and variation in carbon preferences indicated the complexity of the *n*-alkane sources. However, the presence of *n*-alkane/*n*-alkene doublets is indeed evidence that these compounds were formed from cleavage of bound compounds. 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).
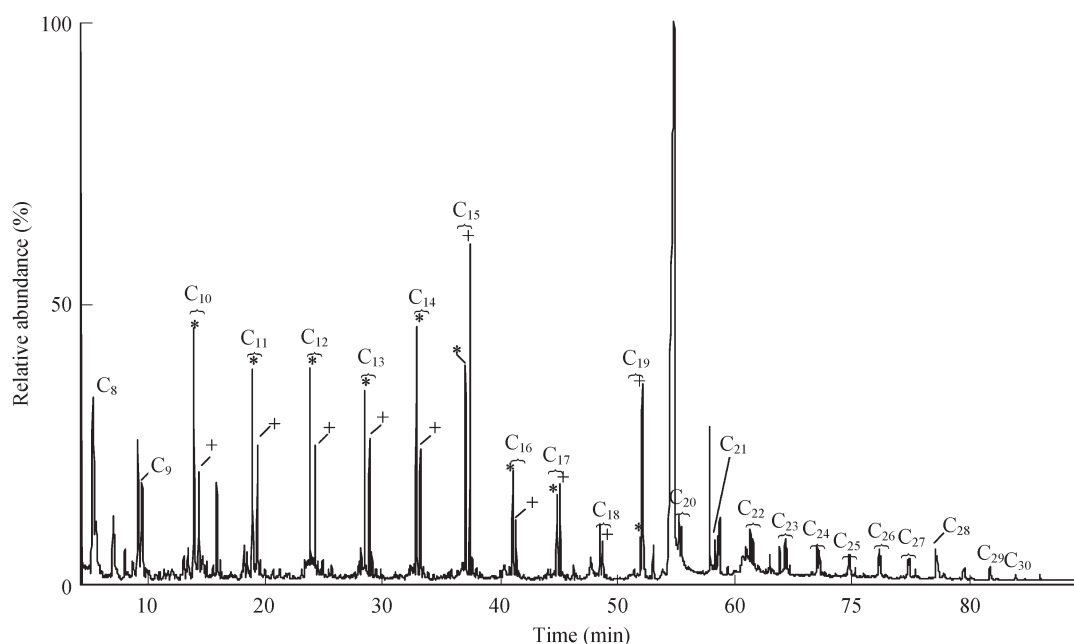

Fig. 3   Chromatrogram (*m/z* = 55 + 57) of pyrolysate of UTW sample. C_n refers to the carbon chain number of the *n*-alkane/alkene.
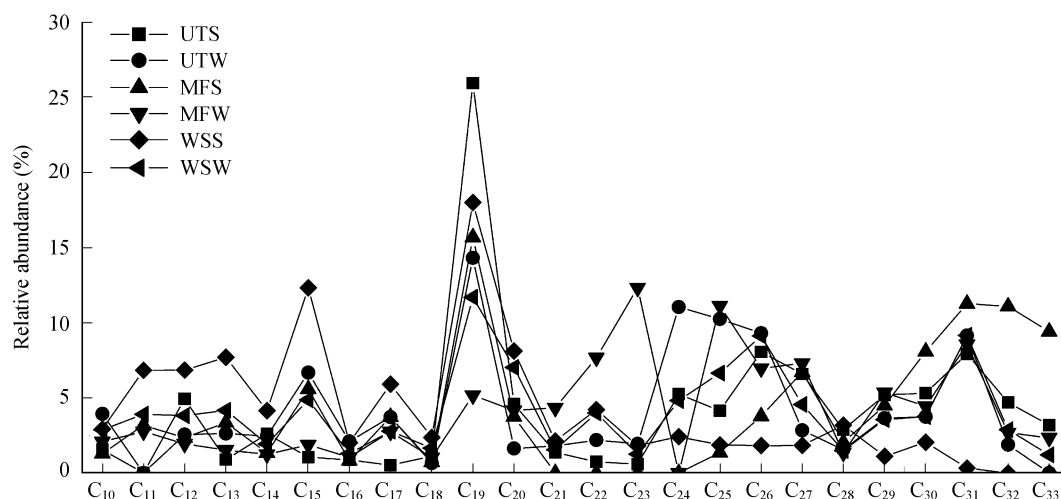
Fig. 4   *n*-Alkanes distribution (*m/z* = 57) of six samples after pyrolysis at 650°C.

2.2.5 Sulfur compounds

Some S-containing compounds such as benzothiazole (Fig. 1, peak 58) were detected in samples. The low abundance of these compounds reflects the lower possibility of SO*x* incorporation into organic matter via photochemical processes.

2.2.6 Relative abundance of compounds

To discuss the relative abundance of the compounds detected, the Py products were also divided into six classes: *n*-alkanes/alkenes, fatty acids, aromatic compounds, nitriles, non-nitrile N-containing compounds, and others. Table 2 shows the relative content of these compounds in the samples.

The data confirmed that aromatics, fatty acids and *n*-alkane/alkenes were the predominant groups of compounds in the samples. Seasonal variations for Py products were lower than for the Td products because of the thermal reaction occurred at lower temperature. The relative content of compounds at the different locations can be observed. For example, high concentrations of *n*-alkanes/alkenes and aromatics were observed in samples from MF and WS, while fatty acid concentrations were high in samples for UT (Table 2). The differences were not readily explained by the differences of source and photochemical processes may also be involved.

Nitriles accounted for 17% of the total compounds and were present at higher level than other nitrogen compounds, especially in samples from MF and UT, which indicated that ammonia was presented in these sampling sites and contained much higher in summer.

2.3 Comparison of Td and Py products

Py of the TSP samples yielded more resolved organic species in GC than that analyzed by Td. The Py products contained much more aromatics than Td products. Aromatic compounds are core units in organic macromolecules and cleavage of aromatic bonds in such macromolecules requires a high temperature. These core entities may be different in urban and forest areas, with condensed aromatics such as carbon black observed for the former and phenols derived from lignin, except for carbon black, observed for the latter.

Fatty acids were present in both Td and Py products at high relative abundance indicated that fatty acids not only occurred in TSP as a free phase, but also as a bound or chelate phase. As typical polar compounds, fatty acids may play important roles in TSP formation.

Nitriles were present in both Td and Py products. The precursors of nitriles are carboxyl ammonium salts. Similar to fatty acids, the occurrence of these salts in the bound phase highlights their importance in TSP formation.

n-Alkenes, styrene and limonene were only detected in Py products. Their absence in Td products implied that most of these compounds released by pyrolysis were presented in the samples as a polymeric phase.

3 Conclusions

Td-GC/MS and Py-GC/MS are highly sensitive and informative direct techniques for a rapid characterization of the organic component in TSP, especially for charac-

Table 2   Relative abundances of compounds in pyrolysates of six TSP samples

Compound class	WSS	WSW	UTS	UTW	MFS	MFW
n-Alkanes/alkenes (%)	31.00	26.00	19.40	17.60	30.90	31.30
Fatty acids (%)	23.21	26.30	32.10	28.40	17.80	12.50
Aromatic compounds (%)	31.21	30.03	31.30	35.10	25.30	41.50
Nitriles (%)	6.21	6.50	9.20	8.10	17.80	8.50
Total N-containing compounds (%)	10.81	11.40	10.50	12.40	24.90	14.10
Other compounds (%)	3.70	6.40	6.70	6.60	1.20	0.40

terization of macromolecule organic matter, which have provided information on a wide array of possible precursors and enhanced the reliability of the inferred structural data.

n-Alkanes, fatty acids and nitriles were the predominant compounds in Td products, whereas aromatics, fatty acids, nitriles and *n*-alkanes/alkenes were the major compounds in Py products. Aromatic compounds are main units in macromolecules. Fatty acids and nitriles formed from carboxylic ammonium salts were detected in Td products and pyrolysates, highlighting the importance of these compounds in TSP, and suggested that amides and nitriles were thermal reaction products from organic acids and ammonium nitrate coexisting in the aerosol samples. The emission sources of primary organic matter mainly determined the occurrence of compounds in samples from urban, suburban and forest sites. The sources and formation processes for TSP maybe also control the seasonal variation of compounds detected. High nitrile levels in summer samples from suburban and forest sites coincide with the release of ammonium and fatty acids in summer at these sites.

Some results of seasonal differences for six TSP samples also have been involved. Although six samples are not statistically sufficient to draw conclusions about seasonal differences, they also provide some helpful information to support that meteorology is an important factor influencing composition of organic matter in TSP.

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Appendix

Identification of compounds in the chromatograms after thermodesorption and pyrolysis of six TSP samples

Number	Compound	Fragments (*m/z*)	Remark	Number	Compound	Fragments (*m/z*)	Remark
1	(*E*)-2-Butenoic acid, methyl ester	69, 100	Py	65	1-Methyl-naphthalene	142, 141	Py
2	Pyridine	79, 52	Py	66	4′-Methyl-acetophenone	119, 91, 134	Py
3	Toluene	91, 92	Py	67	Phthalic anhydride	104, 148	Td
4	2-Methyl-pyrrole	80, 53	Py	68	1-Pentyl-2-propyl-cyclopentane	69, 83	Py
5	Ethyl-benzene	91, 106	Py	69	2,3-Dihydro-2-methyl-benzofuran	134, 119	Py
6	1,3/4-Dimethyl-benzene	91, 106	Py	70	1,4-Benzenedicarbonitrile	128, 101	Py
7	Styrene	104, 78	Py	71	1*H*-Indene-1,3(2*H*)-dione	146, 104	Both
8	3,5-Dimethyl-phenol	122, 107	Td	72	3-(1-Methyl-2-pyrrolidinyl)-pyridine	84, 133, 162	Both
9	Benzaldehyde	106, 77	Td	73	2,6-Dimethoxy-phenol	154, 139	Td
10	C₃-Benzene	91/105, 120	Py	74	Heptyl-benzene	92, 176	Py
11	α-Methyl styrene	118, 78	Both	75	1,1′-Biphenyl	154	Both
12	Benzonitrile	103, 76	Both	76	Decanoic acid	60, 73	Both
13	2-Phenyl-furan	81, 138	Td	77	Undecanenitrile	96, 110	Td
14	2-Methyl-5-(1-methylethenyl)-1,3-cyclohexadiene	91, 229, 134	Td	78	1,7-Dimethyl-naphthalene	156, 141	Py
15	Phenol	94	Py	79	1,3-Dimethyl-naphthalene	156, 141	Py
16	C₄-Benzene	119, 134	Td	80	*N*-Methyl-phthalimide	161, 104	Both
17	2/3/4-Pyridinecarbonitrile	104, 77	Py	81	5/6,7-Dimethyl-naphthalene	172, 128	Py
18	2,3,6-Trimethyl-pyridine	121, 120	Py	82	Acenaphthylene	152	Py
19	1,3,5-Trimethyl-benzene	105, 120	Py	83	2-Isopropenyl-3-methyl-benzofuran	172, 157	Py
20	1-Propenyl-benzene	117, 91	Py	84	1-Phenyl-1-hexanone	105, 77, 120	Py
21	*m*-Methyl-styrene	117, 91	Py	85	(1-Methylheptyl)-benzene	105, 190	Py
22	*D*-Limonene	68, 93	Py	86	Phthalimide	147, 104	Both
23	Indene	116	Py	87	1-Pentyl-2-propyl-cyclopentane	69, 83	Td
24	*Trans*-Tetrahydro-2,4-dimethyl-furan	85, 56, 100	Td	88	3-Methyl-biphenyl	168, 152	Py
25	Benzamide	105, 77, 121	Td	89	3-(1-Methylpyrrol-2-yl)-pyridine	158, 130	Both
26	Butyl-benzene	91, 134	Py	90	Dodecanenitrile	97, 110	Both
27	2-Methyl-phenol	108, 79	Py	91	4-Methyl-biphenyl	168, 152	Py
28	Acetophenone	105, 77, 120	Both	92	1-Naphthonitrile	153	Py
29	1,2-Dimethyl-1,3-cyclopentadiene	79, 93	Td	93	Nonyl-benzene	92, 204	Py
30	1,3-Dihydro-2*H*-Inden-2-one	104, 77, 132	Py	94	Fluorene	166	Py
31	Benzeneacetonitrile	117, 90	Py	95	Dodecanoic acid	73, 60	Both
32	Octanenitrile	82, 96	Both	96	Tridecanenitrile	96, 110	Td
33	2,6-Dimethyl-styrene	117, 132	Both	97	Benzophenone	105, 77, 182	Py
34	2-Methoxy-phenol	109, 124, 81	Td	98	Benzo[*H/C/F*]quinoline	179	Py
35	Nonanal	57, 98	Td	99	1,3-Diphenyl-propane	92, 105, 196	Py
36	2-Methyl-benzofuran	131	Py	100	Decyl-benzene	92, 218	Py
37	2,3/4/5-Dichloro-toluene	125, 160	Td	101	Benzoic acid, pentyl ester	105, 70	Py
38	1,2-Dibutyl-cyclopropane	55, 69, 83	Py	102	2,3-Dihydro-1,1,3-trimethyl-3-phenyl-1*H*-indene	221, 143, 91	Td
39	3-Pentyl-furan	82, 138	Td	103	α-Methyl-stilbene	194, 179	Py
40	2,2,3-Trimethyl-3-cyclopentene-1-acetaldehyde	108, 93	Td	104	9*H*-Fluorene-9-one	180, 152	Py
41	3,4-Dimethyl-styrene	117, 132	Py	105	Dibenzothiophene	184	Td
42	2/3/4-Methyl-benzonitrile	117, 90	Py	106	Phenanthrene	178	Both
43	Dihydro-5-isopropyl-3(2*H*)-furanone	70, 85	Td	107	Tetradecanoic acid	73, 60	Both
44	2/3/4-Chloro-benzonitrile	137	Py	108	Undecyl-benzene	92, 232	Py
45	1-Methyl-indene	130, 115	Py	109	Tetradecanenitrile	97, 110	Both
46	3′-Hydroxy-acetophenone	121, 136	Td	110	Pentadecanenitrile	97, 110	Td.
47	Pentyl-benzene	91, 148	Py	111	Pentadecanoic acid	73, 60	Py
48	2-Methoxy-6-methyl-pyrazine	125, 123, 95	Td	112	1-(Phenylmethylene)-1*H*-indene	203	Py
49	Naphthalene	128	Both	113	Dodecyl-benzene	92, 246	Py
50	3-Methyl-acetophenone	119, 91, 134	Td	114	Hexadecanenitrile	97, 110	Both
51	Nonanenitrile	96, 82	Td	115	10,13-Dimethyl-tetradecanoic acid, methyl ester	74, 87	Both
52	Octaoic acid	60, 73	Td	116	2-Phenylnaphthalene	204, 101	Py
53	*Trans*-2-Methyl-5-(1-methylethenyl)-cyclohexanone	95, 109	Td	117	Hexadecanoic acid	73, 60	Both
54	1,1-Dimethyl-1*H*-indene	129, 144	Py	118	Fluoranthene	202	Both
55	Benzoic acid	105, 122	Py	119	9-Octadecenamide	122, 136	Td
56	2,4,5-Trimethyl-phenol	121, 136	Py	120	Pyrene	202	Both
57	5-Methyl-4-undecene	55, 69, 83	Py	121	Octadecanenitrile	97, 110	Both
58	Benzothiazole	135, 108	Both	122	14-Methyl-heptadecanoic acid, methyl ester	74, 87	Py
59	Hexyl-benzene	91, 162	Py	123	*m/p*-Terphenyl	230	Py
60	1,2,3-Benzenedicarbonitrile	128, 101	Both	124	Octadecanoic acid	73, 60	Both
61	2,3-Dihydro-1*H*-indene-1-one	132, 104, 78	Py	125	Hexadecanamide	59, 72	Both
62	2-Methyl-naphthalene	142	Both	126	Octadecanoic acid, 2-propenyl ester	57, 100, 113	Py
63	Decanenitrile	96, 110	Td	127	Mono(2-ethylhexyl)phthalate (contaminant)	149, 167	Both
64	Nonanoic acid	60, 73	Both				

Py: compounds detected only after pyrolysis; Td: compounds detected only after thermodesorption; Both: compounds detected after both thermodesorption and pyrolysis.