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Composition and Source of Unknown Organic Pollutants in Atmospheric Particulates of the Xigu District, Lanzhou, People's Republic of China

H. Gao,[1] L. Zhou,[1] M.-Q. Ma,[2] X.-G. Chen,[1] Z.-D. Hu[1]

[1] Department of Chemistry, Lanzhou University, Lanzhou, 730000, People's Republic of China
[2] Lanzhou Environmental Monitoring Station, Lanzhou, 730000, People's Republic of China

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During the past decades, air pollution has become an important issue over the world due to accidental events (Nemery B et al., 2001; Firket J, 1936) and a large number of scientific studies, which prove that the air pollution has an adverse effect on health (Barnes PJ, 1994; Aunan K 1996; Dockery DW, 2001). Many epidemiological studies indicated that mortalities and morbidities could be well correlated to the levels of atmospheric particulate matter in developed and developing countries (Pope CAIII, 1996; Schwartz J, 2000). In recent years, although more and more studies recognized that the fine particulate matter (PM2.5 and PM10) has much more contributions on diseases such as cardiovascular and respiratory symptoms (Jonathan MS et al., 2000; Bert B et al., 2002), there is an increasing concern about the composition of atmospheric particulates because of the presence of copollutants. It is well known that many of the copollutants such as organic contaminants and inorganic substances are actually precursors to fine particulate matter formed in the atmosphere (Finlayson P et al., 1986). Therefore, to identify and quantify the composition of atmospheric particulate matter is significant.

Atmospheric particulate matter can adsorb a large number of toxic substances such as organic pollutants, inorganic compounds and toxic metals. Furthermore, these pollutants can react to produce second pollution and transport to the remote region even the Antarctic region (Pandis SN et al., 1992; Alessandra C et al., 2001). Many previous and recent studies mainly focused on the survey of inorganic composition and target organic pollutants (e.g. Volatile organic compounds and polycyclic aromatic hydrocarbon etc) in atmospheric particulates (Kirkitsos PD et al., 1993; Gianrico C et al., 1995; John RC et al., 1985). However, the investigation overall of unknown organic pollutants of atmospheric particulates is little available compared with these studies (Sun YZ et al., 2003).

Lanzhou is the capital city of Gansu Province and located in northwest of China, which has 13 thousand square kilometers in area and a population of nearly 3 million. It is highly industrialized, although it is not as prosperous as some of China's other major cities. Amongst its major industries, especially the oil refinery, chemical, machinery and metallurgical industry, are in the first place in China. Large quantities of industrial, traffic and domestic exhaust gas as well as its

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Correspondence to: X.-G. Chen

special geographical position and topographical conditions make it one of the most seriously air polluted cities in the world. The daily mean value of total suspended particulate matter (TSP) concentration in the city exceeds the second grade of the Ambient Air Quality standard of China throughout the year (Zhang L et al., 2000). Although the local government initiated a "Blue Sky Program" to combat air pollution, there is little improvement on air quality. In addition, relatively little data is available concerning atmospheric particulate organic composition and sources (Cheng ML et al., 2000). The Xigu District of Lanzhou city is an important petrochemical and other major industrial base and also the first place that photochemical smog occurs in China (Zhang L et al., 2000). So the investigation of organic pollutants of the atmospheric particulates in the Xigu District of Lanzhou city can reveal the sources of pollution and gives guideline of air pollution control. The aim of this work is to develop a procedure for extraction, isolation and analysis of unknown organic pollutants in atmospheric particulate matter without each standard material. Furthermore, it is to examine the concentrations and sources of n-alkane and polycyclic aromatic hydrocarbon (PAHs) and the type of other polar pollutants. In addition, it is also a contribution that partly fills the lack of data on atmospheric unknown organic pollutants and source of total suspended particulates in Xigu district of Lanzhou city, China. Due to it is believed that the composition and source of unknown organic pollutants in atmospheric particulates were first whole reported in the past twenty years.

MATERIALS AND METHODS

TSP samples were acquired from the Lanyuan hotel of Xigu district in Lanzhou city (National control monitoring site). A high-volume air sampler (TH-1000C, Tianhong Intelligent Instrument Plant of Wuhan, China) fitted with glass fiber filter ($20\times25cm^2$) was used to collected atmospheric particulate matter at a flow rate of $0.8m^3/min$. The glass fiber filters were annealed for 12 h at 450℃ prior to sampling in order to remove organic contaminants. In March 2003, six samples were obtained and each sample was collected during a 24h periods.

Two filters were extracted using an ultrasonic bath for 3 times with redistilled dichloromethane for which 130ml were used at first time and 50ml at second and last time. Each extraction lasted 25min. The organic extract of six filters was combined, filtered and concentrated to volumes of approximately 2ml by a Büchi Rotary evaporator (bath temperature < 30℃) and then added a small amount of silica gel (200mesh) and further concentrated to dryness. Above extracts powder were isolated into three fractions by silica gel column chromatography (dimensions of column 30cm large, 3cm diameter, packed with 200mesh silica gel) with redistilled 130ml hexane (the aliphatic hydrocarbons fraction), 400ml benzene (the aromatic hydrocarbons fraction) and 300ml methanol (the polar compounds fraction) as elute solvents. These elutes were concentrated to volumes of approximately 3ml on rotary evaporator and then transferred to a glass vial which was weigh prior to use. Then the samples were reduced to dryness under a gentle stream of ultra pure nitrogen and then weigh again. The difference of twice weighing was the extract yields of separated fraction. The separated fractions were then redissolved with 100μl respective solvents for instrument analysis. A same procedure blank was also concentrated and analyzed in order to monitor the background. No significant amounts of n-alkanes or PAHs were found except for small amounts of phthalates.

Qualitative analysis was tentatively identified by gas chromatography-mass spectrometry (TRACE GC-MS^{TM}, Finnigan, USA) equipped with a SE-54 fused-silica capillary column (30 m×0.25 mm i.d, 0.25-μm film thickness). The following temperature program was used: the initial column temperature was 50°C and programmed at 8°C/min to 150°C, then at 3°C/min to280°C held for 5 min. The injector and detector temperatures were set at 280°C and 300°C respectively. Helium was the carrier gas at a flow-rate of 1.0 ml/min. 1.0-μl sample extracts was injected in split mode at a ratio of 20:1. The electron impact (EI) ionization conditions were: ion energy 70 eV and mass range (m/z) 15.00-431.00 in the full scan mode. The n-alkanes and aromatic hydrocarbons compounds partly were confirmed by standards.

The aliphatic and aromatic fractions were quantified by gas chromatography (GC) with flame ionization detection (FID) (VarianCP-3800, USA) equipped with the same type of column as that used for the GC-MS analysis. Nitrogen as a carrier gas at a flow rate of 1.4ml/L and 1.0-μl sample extracts was injected in split mode at a ratio of 20:1.The injector and detector were maintained at 280°C and 300°C. The column temperature program began with 50°C followed by a 8°C/min ramp to 150°C and then a 3°C/min ramp to280°C held for 30 min. A new calculation method with the FID relative carbon weight response factors of hydrocarbons for FID quantitative analysis was used in order to resolve the lack of standards (Huang YR et al., 1990). All analysis was carried out on triplicate.

RESULTS AND DISCUSSION

The individual concentrations of aliphatic fraction and aromatic fraction were the average values of triplicate experiment. Relative standard deviations ranged from 0.1% to 13.7%. The aliphatic fraction total concentration reached 2.76 μ g/m^3 and consisted primarily of n-alkanes and other minor amounts of isomeric alkanes, isoprenoids, cycloparaffin and halogenation alkanes. The n-alkanes range from C_{10} to C_{30} were found at concentrations in the range of 1.9-179 ng/m^3 and were no an odd carbon number predominance above C_{25} (Fig.1, Fig.2). So the homologs ranging between C_{25} and C_{30} were believed to be derived chiefly from plant waxes while n-C_{27} $\geqq$ n-C_{29} also indicated a mixed origin from forest and grassland (Cranwell PA, 1973). Other some indexes were also calculated to estimate the sources of n-alkanes (Juan CC et al., 1989). The carbon preference index (CPI) was 1.0 showed that n-alkanes were mainly from anthropogenic activities. 11 as the n-C-$_{16}$ ratio (the sum of all n-alkanes/n-C-$_{16}$) indicated the presence of the petrogenic origin in the TSP. Meanwhile, C_{17}/Pr (n-C_{17}/pristine) and C_{18}/Ph (n-C_{18}/phytane) were 2.7 and 1.2 and greater than 1 indicated the presence of high hydrocarbon levels and fresh oil input. The ratio of low/high molecular weight hydrocarbons (the sum of n-alkanes $\leqq$ n-C_{20}/ the sum of n-alkanes $\geqq$ n-C_{21}) is

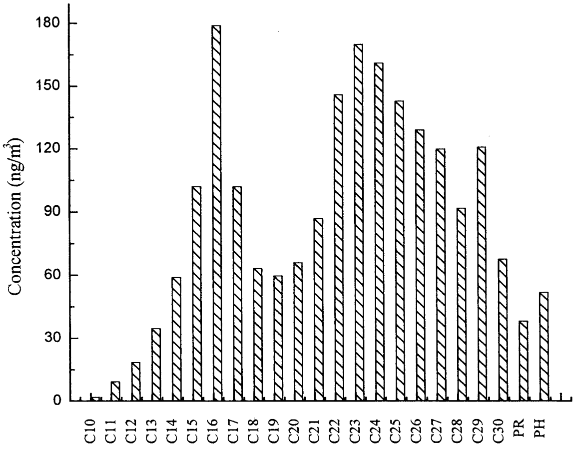

Figure 1. The content of n-alkanes and two isoprenoids in the TSP

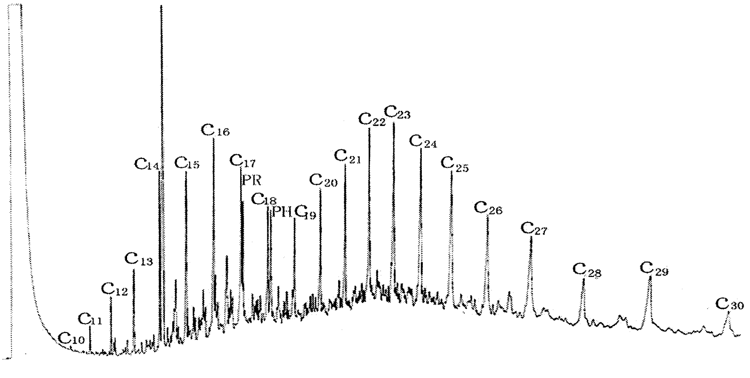

Figure 2. GC trace of the aliphatic fraction

usually close to 1.0 in algae and crude oil while lower values in higher plants and marine animals. This index in our study was 0.6, in addition, the $2(C_{27}+C_{29})/(C_{26}+2C_{28}+C_{30})$ ratio, another CPI index was obtained as 1.3 (petrogenic hydrocarbons show values around 1, plants range from 3 to 6), which further confirmed the major petrogenic sources and part plants sources of n-alkanes.

In aromatic fraction, more than one hundred and seventy components mainly including benzene derivatives and PAHs were found, and their total content was 7.23 μ g/m^3 (Fig. 3, peak number from 1 to 40 in left column and from 41 to 80 in

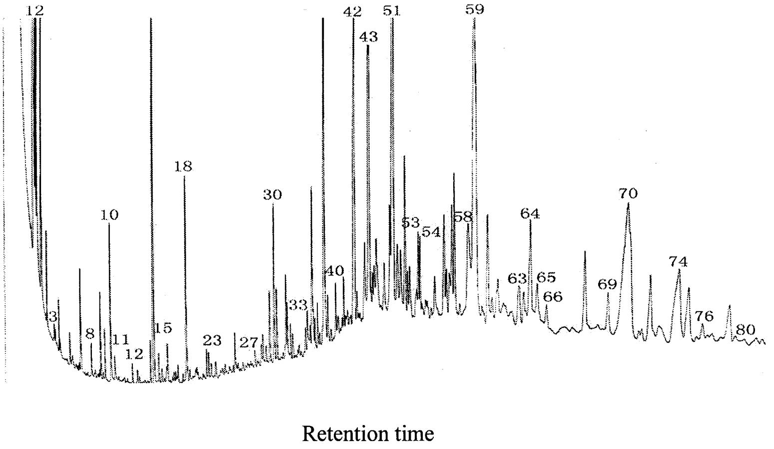

Figure 3. GC trace of the aromatic fraction

right column, see Table1). In benzene derivatives class, there were some substituted benzene compounds by alkyl, chloro, bromo, nitro and amino, few substituted phenols and containing nitrogen, sulfur and oxygen heterocyclic compounds. While in PAHs class, most components with three to five rings were parent PAHs and alkyl substituted PAHs. Some were PAHs derivatives with two rings, polycyclic aromatic ketones and heterocyclic compounds containing nitrogen, sulfur and oxygen. In addition, few chloro and hydroxy substituted PAHs also existed in the fraction. Table1 just gave major compounds and their concentrations due to the limit of pages, in which nine of 16 PAHs EPA priority pollutants were determined (by * marked). The benzo[a]pyrene (236ng/m^3) exceeded the Ambient Air Quality Standard of China (10ng/m^3) about 20 times. In order to estimate the different sources of PAHs present in the TSP, some ratios were calculated according to literatures (Sicre MA et al., 1987; Juan CC et al., 1989). The value of Fluoranthene/pyrene (Fl/Py) was 0.97 that agree with the range from 0.6 to 1.4 in crude and fuel oil. The benz[a]anthracene/chrysene (Bz[a]an/Chr) ratio as 0.22 was also in the range of crude and fuel oil (0.24 to 0.40). For the index benzo[a]anthracene/benz[a]anthracene + chrysene + triphenylene (Bz[a]an/Bz[a]an+Chr+Try), value around 0.18 also showed a petrogenic contribution (0.16±0.12 in crude oil). Above three indexes all confirmed the petrogenic inputs in the investigated region. Following two ratios proved the presence of other sources, one is the Ph/Ph+An (phenanthrene/phenanthrene + anthracene) ratio was about 0.98 in crude oil and 0.77 in car emissions, while the value in this paper was 0.94 indicated a small contribution of car tail gas pollution. Another index: the Bz[e]py/Bz[e]py+Bz[a]py (benzo[e]pyrene/ benzo[e]pyrene + benzo[a]pyrene) was 0.41 revealed the fact of hard coal combustion according to Sicre MA et al. (1987) (0.87±0.11 in crude oil and 0.43±0.04 in hard coal combustion). From the above PAHs ratios it can be concluded that more than one source are contributing to PAH mixture of the TSP, a high level of petrogenic contamination

Table 1. Name and content (C, ng/m^3) of major aromatic pollutants in the TSP.

Name	C	Name	C
Chlorobenzene	988	2,7-Dimethylphenanthrene	21.3
Ethylbenzene	202	Fluoranthene*	245
Bromobenzene	5.74	Pyrene*	252
1,3,5-Trimethylbenzene	0.35	Benzo[b]naphtho[23d]furan	12.9
1,4-Dichlorobenzene	1.63	1-Hydroxypyrene	2.11
trans-Decahydronaphthalene	0.11	Benzo[k]xanthene	9.37
Nitrobenzene	0.19	7H-Benzo[c]fluorene	12.7
2-Nitrophenol	15.5	2,4,5,7-Tetramethylphenanthrene	0.25
1,2,3,4-Tetrahydronaphthalene	1.10	2-Methylfluoranthene	42.5
4-Bromobenzenamine	109	n-Phenyl-2-naphthalenamine	21.3
Benzothiazole	14.9	iso-Methypyrene	370
2-Dimethylnaphthalene	5.77	o-Terphenyl	12.4
1-Ethylidene -1H-indene	4.58	1,3-Dimethylpyrene	30.1
4-Nitro-2,6-dimethylphenol	1.12	7H-Benz[de]anthracen-7-one	29.9
Diphenylether	9.24	Triphenylene	16.9
p-Nitroaniline	1.92	Benz[c]acridine	52.3
Diphenylmethane	0.59	Benzo[b]naphtha[23d]thiophene	6.93
Butylated hydroxytoluene	127	Benzo[a]anthracene*	121
Dibenzofuran	1.95	Chrysene*	538
1-Methyl-2,4-dinitrobenzene	3.34	Benzo[b]carbazole	180
iso-Trimethylnaphthalene	0.79	Di-n-octyl phthalate	16.9
3-Chlorobiphenyl	1.53	11H-Benzo[a]carbazole	0.58
1H-Phenalene	8.07	1-Nitrofluoranthene	72.5
9,9-Dimethyl-9-silafluorene	1.01	iso-Methtylchrysene	108
9-Methyl-9H-fluorene	0.95	iso-Dimethylbenz[a]anthracene	35.5
9H-Fluoren-9-one	0.64	2,2'-Binaphthalene	19.5
Dibenzothiophene	9.08	9-Phenylanthracene	0.41
Phenanthrene*	8.47	1,2-Dihydroindeno[123cd]pyrene	0.27
Anthracene*	0.58	Dibenzo[ah]anthracen*	44.8
Bis(2-methylpropyl) phthalate	95.6	Perylene	203
Thioxanthene	0.48	Benzo[e]pyrene	162
iso-Methylphenanthrene	0.15	4,5-Oxide-benzo[a]pyrene	121
iso- Methylphenanthrene	11.9	Benzo[k/j]fluoranthene*	31
6H-Cyclobuta[jk]phenanthrene	0.91	Benzo[a]pyrene*	236
iso-Methylphenanthrene	1.96	11H-Indeno[21a]phenanthrene	0.15
iso-Methylphenanthrene	3.29	iso-Methylperylene	18.8
Dibutyl phthalate	2.36	3-Methylbenz[j]aceanthrylene	0.39
9,10-Anthracenedione	6.61	3-Methyl-1-cholanthrenol	0.78
Oxybenzone	8.15	iso-Methylperylene	0.19
2-Ethylanthracene	19.7	Benzo[a]naphthacene	0.26

together with a light pollution from car emission and coal combustion were present.

The polar fraction in which over one hundred compounds were tentatively identified mainly contained aliphatic alcohols, carboxylic acids, carboxylic acid esters, ketones, aldehydes and containing sulfur, nitrogen and oxygen heterocyclic compounds and their derivatives. It was noteworthy that some azaarenes with two to four rings such as quinoline, acridine benzo[f]quinoline and their derivatives also presented in this fraction. These compounds like their parent compounds (PAHs) also were the products of incomplete combustion processes, which further evidence the pollution of fossil fuels. This study showed that it is available to use the combination of the GC-MS and GC methods without each standard for the rapid identification and quantitative unknown organic pollutants in atmospheric particulates. Furthermore, by means of fractionation of quantities of n-alkanes and PAHs respectively, the part pollution sources can appoint by varies alkanes and PAHs ratios.

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