Organic toxic air pollution in Macau and other coastal cities of South China Sea

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Abstract

Monitoring data of the organic toxic species for both particulate and vapor phases in the ambient air of Macau during 20-24 November 1995 are presented and compared with these of Hong Kong and Guangzhou. It is found that the distribution profiles of VOC and particulate PAH species in ambient air samples show a similarity, indicating common sources to each sampling site of Macau. The major source is identified to be vehicular exhaustion by examining characteristics of these profiles. The n-alkane scanning spectra of the samples identify a biogenous and natural source in the relatively clean areas. Only difference among the sites is on the pollution level which shows that heavily traffic > roof level > relatively clean areas. The organic toxic air pollution of HongKong and Guangzhou follows the similar distribution profiles of particulate PAHs and VOCs in the ambient air, which show common emission sources existing among these cities.

1 Introduction

Toxic organic species VOCs and particulate PAHs of ambient air in urban areas mainly come from vehicle emission. Kenski et al.[1] collected the VOC emission monitoring data of five American cities Detroit, Chicago, Beaumont, Atlanta and Washington from 1984 to 1988, showing that the number-one VOC emission source is from vehicular exhaustion (~40% of the total VOC emission) and then the gasoline evaporation (~10%). The other emission sources such as architectural coating, graphic arts, polyethylene and coke oven only account for small percents. The PAHs are formed by incomplete

combustion or pyrolysis of organic material containing carbon and hydrogen (Jones & Leber[2]). They are multi-ringed compounds and many are known to be carcinogenic (Lee et al.[3]). Motor vehicles are thought to be the major source of ambient air PAHs in the United States, accounting for 35% of the yearly total. Aluminum production and forest fires each contribute 17%, followed by residential wood combustion, coke oven, power generation and incineration which emit 12, 11, 6 and 3% of the total, respectively (Benner et al.[4]).

The present traffic condition in the urban areas of Macau is marked by vehicle overloading, 50,000 private cars and thousands of motorbikes as well as public buses running within the 6.7 km^2 urban area, and by crowed urban cores with narrow roads and lots of intersections and street canyons which are unfavorable for exhaustion emission dilution and dispersion. In urban areas of HongKong and Guangzhou, there exists the same situation, i.e., the worsening urban transportation conditions due to rapid economic development and population growth. The organic toxic air pollution in urban areas is a urgent environmental problem facing these cities.

The urban air quality monitoring system in Macau has run since 1990. The recent monitoring output showed that concentrations of the primary pollutants (TSP, CO, NO_x) and the secondary pollutants (O_3) related to vehicle emission were very high in the traffic-busy areas (Aveia Preta, Horta e Costa). Derwent et al.[5] collected air quality data from one year study at an urban roadside location in Central London including NO, NO_2, O_3, CO and 28 VOC species, showing a positive relation of VOCs with NO_x. Correlation between PAHs and NO_x concentrations were also reported by Colmsjo et al.[6], particularly, strong correlation between PAH and NO when sampled at street level with heavy traffic.

In this paper, field monitoring data of the toxic organic species for both particulate and vapor phases in the ambient air of Macau are presented and compared with these of HongKong and Guangzhou. It is attempted to identify control priority of the toxic air pollutants and their emission sources for these cities.

2 Experimental Sections

The sample sites were operated in both heavily traffic urban areas and relatively clean areas. VOC sampling occurs in ten urban sites which can be classified by three groups: heavily traffic intersections, bus stations, and relatively clean areas. The vapor phase of organic species VOCs were sampled using Carbotrap 300 Multi-bed Thermal Deposition Tube at both street ground

level (1.2 m) and roof-top level (12 m). The VOC species were adsorbed on the adsorption phase in the tube for laboratory analysis. The air samples were analyzed using TEKMAR3000/6032-HP5972GC-MSD systems in laboratory. Particulate PAHs sampling occurs in six urban sites including heavily traffic areas, roof-top level (20 m), and relative clean areas. Sampling of the ambient atmosphere was carried out using high-volume air samplers for 24 hours each time. The samples were analyzed with HP5890GC-HP5972GC-MSD systems.

3 Results and Discussion

3.1 VOCs

Emissions of VOCs are of concern because they promote ozone formation in the presence of oxides of nitrogen. Ozone is a key ingredient of photochemical smog. Figure 1 gives the typical TIC spectrum of VOC species in the Macau air samples, identifying fuel combustion residue e.g., toluene, tetrachloroethylene, xylene, and naphthalene, and plant and bacteria impacts e.g., camphene and D-limonene. Table 1 gives ambient air concentrations of VOCs in the ten sampling sites of Macau, which shows that major VOC species in the ambient air samples are benzene homologues (toluene, trimethyl benzene, etc.) and then chlorohydrocarbons. More than thirty VOC species were identified with nine being USEPA hazardous air pollutants which are toluene, ethyl benzene, chlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, benzene, and naphthalene. Quantities of the total VOCs for different sites follow that heavily traffic (622-1974 $\mu g/m^3$) > bus station (~530 $\mu g/m^3$) > relatively clean areas (108-262 $\mu g/m^3$).

It was found that the VOC concentration profile of each of the ten different sites followed the same pattern, which indicates a common emission source to each site. Table 2 gives VOC profile, i.e., the weight percentage of each of six major VOC species to the total $\sum$VOCs for each of the sampling sites. The pattern follows that toluene > trimethylbenzene > m+p xylene > 0-xylene > benzene > ethyl benzene. In their study for five American cities, Kenski[1] presented source fingerprints (weight percent of total VOC emission) for different source contributions to ambient air such as vehicular exhaustion, gas vapor, etc. The special profile of vehicular emission VOCs follows that toluene (7.65%) > trimethylbenzene (6.8%) > benzene (3.58%) > m+p xylene (3.51%) > 0-xylene (2.12%) > ethylbenzene (1.09%). Harley & Cass[7] collected the ambient VOC concentration data in Los Angeles for the period 27-28 August 1987 and found that toluene (60.7 ppb) > m+p xylene (29.3 ppb) > benzene (21.6 ppb) > 0- xylene (11.5 ppb) > ethylbenzene (9.2 ppb). Henry et al.[8] derived the composition of three VOC emission sources (vehicle, gas evaporation, gas headspace) from 550 ambient hourly concentration measurements of 37 C_2-C_9 VOC species, and for the vehicle emission source,

the ambient concentrations follow that toluene > m+p xylene > benzene > 0-xylene > ethylbenzene. These six VOC species are relatively unreactive in ambient air, i.e., an atmospheric half-life greater than about 19 hours and so they can be used to generalize the ambient VOC concentration profile due to vehicle emission. Comparison between this study and the above studies shows that the ambient VOCs in Macau are mainly emitted from vehicles.

Table 1. Concentrations of VOC species in the Macau urban air ($\mu g/m^3$)

	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
toluene	33.9	117.3	61.5	93.2	18.5	314.6	48.9	55.2	54.3	103.1
ethyl benzene	6.4	19.7	9.9	15.1	2.8	61.2	6.7	15.0	6.5	16.8
m+p xylene	20.9	68.8	27.2	41.9	4.8	140.4	16.2	49.0	15.0	33.6
0-xylene	9.4	29.8	15.8	16.1	1,9	53.4	5.9	27.2	4.6	10.1
styrene	3.2	10.6	6.6	7.1	1.8	45.7	3.6	11.4	5.5	16.8
trichloroethlene	2.5	3.6	14.3	20.9	13.3	96.3	27.9	35.3	12.6	92.6
tetrachloroethlene	4.0	12.7	27.6	27.7	5.2	190.0	12.2	11.5	15.2	122.6
chlorobenzene	0.3	0.2	0.3	0.3	0.1	4.4	0.1	0.1	0.1	2.0
1,3-dichlorobenzene	0.4	1.0	0.6	1.1	0.3	2.5	0.3	0.4	0.5	1.0
1,4-dichlorobenzene	0.4	0.5	1.2	1.6	0.3	4.6	0.3	0.2	0.8	0.5
acetic acid butylester	1.8	2.8	2.2	1.4	0.5	11.3	2.7	-	0.8	-
benzene	6.4	30.7	4.5	8.7	3.0	27.8	6.2	8.6	3.8	9.1
naphthalene	2.0	1.0	2.1	6.2	2.6	4.3	2.3	1.8	5.0	4.2
1-methylethyl benzene	1.1	8.4	1.6	2.2	0.1	6.9	0.9	5.6	0.9	2.1
propyl benzene	4.7	14.2	9.7	12.3	0.4	42.6	2.4	6.3	6.8	5.3
1ethyl 3methyl benzene	10.7	39.0	19.1	26.5	5.6	97.1	15.7	3.9	13.4	27.7
1ethyl 4methyl benzene	6.9	23.9	9.4	13.2	0.1	56.4	6.7	18.9	6.1	17.1
1,3,5-trimethyl benzene	4.5	24.8	8.4	10.7	1.7	53.8	3.8	6.9	5.4	11.7
1,2,4-trimethyl benzene	14.6	24.6	12.6	16.7	2.4	70.8	10.5	33.5	14.0	28.2
1,2,3-trimethyl benzene	7.6	12.5	6.1	8.1	1.6	59.9	4.9	21.6	4.6	30.3
1ethyl 2methyl benzene	11.9	48.7	17.0	25.3	3.9	126.2	12.6	25.6	7.0	26.7
C_4-benzene	80.0	96.0	61.4	68.7	28.1	301.0	92.2	88.1	60.9	153.6
pinene	3.4	4.3	4.0	4.7	0.7	14.5	4.4	8.6	1.5	6.3
camphene	1.4	2.3	0.7	-	0.4	11.4	5.8	5.7	-	3.0
limonene	3.8	3.8	3.4	2.1	0.7	18.1	3.4	18.3	1.7	10.5
indane	6.4	11.2	8.4	5.4	1.0	47.1	3.5	3.2	5.1	19.8
hexanal	4.4	6.6	1.5	10.9	2.4	62.1	11.5	51.4	9.8	30.3
heptanal	3.7	1.3	12.3	17.1	2.0	6.3	2.8	9.1	1.7	9.6
octanal	3.9	-	2.8	4.3	2.4	8.6	1.5	6.3	0.9	21.0
indene	1.7	2.5	1.5	0.7	0.2	7.6	0.7	2.2	0.7	3.0
ΣVOCs	262.3	622.8	353.7	470.2	108.8	1947.2	316.6	530.9	530.2	818.3

3.2 Particulate n-alkanes

The distribution profiles of n-alkanes of aerosols derived from contemporary biological sources (plant wax, soil, etc.) show a saw-tooth pattern with a strong odd carbon number predominance, namely, high carbon reference index (CPI), while those derived from fossil fuel components (petroleum, coal, etc.) show a pattern with no carbon number predominance (CPI ~ 1). Because of these

characteristics, the n- alkane profile has been used to explain the origin of atmospheric organic aerosols. Kadowaki[9] characterized carbonaceous aerosols in the Nagoya urban area and found that the lower n-alkanes (ca < C_{25}) were predominantly petrogenic and the higher ones (ca. > C_{25}) were biogenous.

Table 2. the VOC profiles for the ten sampling sites in Macau (species/Σ %)

	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
1. toluene/Σ	13	19	17	20	17	16	15	10	10	13
2. trimethylbenz.*/Σ	10	10	8	7.5	5	10	6	12	5	9
3. m+p xylene/Σ	8	11	8	9	5	7	5	9	3	4
4. 0-xylene/Σ	4	5	5	3	2	3	2	5	1	1
5. benzene/Σ	2	5	1	2	3	1	2	2	1	1
6. ethyl benzene/Σ	2	3	3	3	3	3	2	3	1	2

* trimetylbenz. = 1,3,5-trimetyl benzene + 1,2,4-trimethyl benzene + 1,2,3-trimethyl benzene.

The mass fragmentograms for particulate n-alkanes obtained in this studies can be classified into three cases. For the relatively clean areas (MP1 & 2), carbon number of the most abundant of n-alkane homologues (C_{max}) is relatively higher, i.e., C_{29}, C_{31} and the profile shows an odd carbon number predominance, which show that the natural source (plant wax) is important although the anthropogenic emission is still predominant (see Figure 2a). For heavily traffic areas (MP5 & 6), C_{max} is low, i.e., C_{24} and the odd carbon number predominance only exists for the n-alkanes larger than C_{27}, which show that the anthropogenic source (vehicle emission) is dominant (see Figure 2b). For M3 & 4, C_{max} = C_{25}, C_{29}, which is just the case in between.

Table 3 gives particulate organic yields of the ambient air samples in Macau, which shows a similar trend, i.e., impacts of vehicle emission on the organic yields of aerosols follow that heavily traffic areas > roof level > relatively clean areas. The sample site MP2 is located in the urban center so that the organic yield is close to the roof-level case rather than the clean area MP1.

The n-alkanes in the Macau samples are ranged in C_{14} - C_{40} and CPI = 1.28 while HongKong in the range of C_{14} - C_{39} and Guangzhou in C_{13} - C_{37}. In down town of Hong Kong, C_{max} = C_{24}, C_{23} and CPI = 1.07 while in the suburb, C_{max} = C_{27}, C_{29} and CPI = 1.22. For the heavily traffic area in Guangzhou, C_{max} = C_{21}, C_{22} and CPI = 1.10 and in the suburb, C_{max} = C_{29}, C_{31} and CPI = 1.86. A common trend exists among these cities in the particulate n-alkanes profiles of ambient air samples. The lipid yields of aerosols for Macau, Guangzhou and HongKong are 5.75 - 50.13 $\mu g/m^3$, 1.50 - 61.04 $\mu g/m^3$, and 2.42 - 9.21 $\mu g/m^3$, indicating that the HongKong air is cleaner than the other two cities.

Table 3. Particulate samples organic yields ($\mu g/m^3$)

	lipid yield	n-alkane yield	aromatic yield	non-HC* yield
MP1 univ. campus	5.75	0.86	0.26	4.50
MP2 garden	19.18	1.32	0.33	15.61
MP3 roof level	19.32	3.24	0.73	14.02
MP4 roof level	19.38	2.45	0.53	15.08
MP5 Costa	36.57	8.27	4.89	30.69
MP6 Preta	50.13	10.78	2.38	23.41

* non-HC - non-hydrocarbon species.

3.3. Particulate PAHs

Table 4. shows forty one particulate PAH species identified in ambient air of Macau and the PAH profiles are similar no matter where the sampling sites are, heavily traffic areas MP6, roof-top levels M4, or relatively clean areas MP1. This indicates sources common to each sites. Recent studies showed that PAHs have significant variation in their composition for different combustion sources and their composition profiles (fingerprints) in ambient air can be used for sources identification.

The two ring PAHs like naphthalene exist almost entirely in the gas phase and other five and higher-ring PAHs are predominantly adsorbed on particles. The intermediate three and four-ring PAHs are distributed between the two phases. In the papers of both Westerholm & Li[10] and Lowenthal et al.[11], they studied characteristics of PAH emissions of heavy-duty vehicles and found a correlation between the emission composition and the fuel composition. The emission includes both fuel combustion residue and PAH species produced during the combustion. Khalili et al.[12] studies source contributions (fingerprints) of PAHs by vehicle emission, coke oven, etc. and found that gasoline engines emitted high concentration of naphthalene while diesel engines emitted high alkyl-phenanthrene. Table 1. shows that naphthalene is in 1.0-6.2 $\mu g/m^3$ in the Macau VOC samples and Table 4 gives a high level of the phenanthrene group of particulate PAHs in Macau. Concentrations of six-ring PAHs such as indole[1,2,3-cd]pyrene and benzo[ghi]perylene were relatively high and 7-ring PAHs such as coronene were detected (see Table 4). All indicate the major PAH source in Macau is from vehicular exhaustion. Table 5 gives the particulate PAHs species identified in HongKong and the composition profile is similar to the Macau PAH profile, which indicates common sources to each city.

Table 4. Particulate Phase of PAHs in the Macau Air

Species	Molecular Mass	MP6	MP4	MP1
naphthalene		tr	nd	nd
1-methyl naphthalene		tr	tr	tr
2-methyl naphthalene		+	tr	tr
dimethyl naphthalene (5 isomers)	156	+	tr	tr
trimethyl naphthalene (6 isomers)	170	+	tr	tr
biphenyl		tr	tr	tr
methylbiphenyl	168	tr	tr	tr
dibenzofuran	168	+	+	tr
dimethylbiphenyl (4 isomers)		tr	tr	tr
fluorene	182	tr	+	+
C_1-fluorene (3 isomers)		tr	tr	tr
C_2-fluorene (3 isomers)		tr	tr	tr
phenanthrene	178	++	++	++
C_1-phenanthrene (4 isomers)	192	++	++	+
C_2-phenanthrene (7 isomers)	206	+	+	+
C_3-phenanthrene (4 isomers)	220	+	+	tr
tetramethyl phenanthrene		+	+	+
dibenzothiophene	184	tr	+	+
C_1-dibenzothiophene (2 isomers)	198	tr	tr	tr
C_2-dibenzothiophene (8 isomers)	212	tr	tr	tr
fluoranthene	202	++	++	++
pyrene	202	++	++	++
11H-benzo[b]fluorenon	216	+	tr	tr
11H-benzo[a]fluorenon	216	+	tr	tr
C_1-pyrene/fluoranthene (6 isomers)		+	tr	tr
C_2-pyrene/fluoranthene (2 isomers)		tr	tr	tr
benzo[a]anthracene	228	+	+	+
chrysene	228	++	++	++
C_1-chrysene/benzo[a]anthracene	242	+	+	+
benzo[b]fluoranthene	252	+++	+++	++
benzo[k]fluoranthene	252	+++	+++	++
benzo[e]pyrene	252	++	++	++
benzo[a]pyrene	252	++	++	+
perylene		tr	tr	tr
tetrabiphenyl	306	+	+	+
dibenzo(def,mno)chrysene	276	+	+	+
indole[1,2,3-cd]pyrene	276	+++	++	+
dibenzo[a,h]anthracene	276	tr	tr	+
benzo[ghi]perylene	276	+++	++	+
dibenzopyrene (3 isomers)	302	+	+	tr
coronene	300	+	+	tr

Table 5. Particulate Phase of PAHs in the Hong Kong Air

Species	Molecular mass	HK1	HK2	HK3	HK4
C_2-naphthalene	156	tr	tr	nd	nd
C_3-naphthalene	170	tr	tr	nd	nd
methylbiphenyl	168	tr	tr	nd	nd
dibenzofuran	168	tr	tr	nd	nd
9H fluorene	182	tr	tr	nd	nd
benzylnaphthalene	204	tr	tr	nd	nd
phenanthrene	178	+	+	tr	tr
C_1-phenanthrene (4 isomers)	192	+	+	tr	tr
C_2-phenanthrene	206	tr	tr	nd	nd
C_3-phenanthrene	220	tr	tr	nd	nd
dibenzothiophene	184	tr	tr	nd	nd
C_1-dibenzothiophene	198	tr	tr	nd	nd
C_2-dibenzothiophene	212	tr	tr	nd	nd
fluoranthene	202	++	+	tr	tr
pyrene	202	++	+	nd	nd
11H-benzo[b]fluorene	216	tr	tr	nd	nd
11H-benzo[a]fluorene	216	tr	tr	nd	nd
C_1-pyrene	216	+	+	nd	nd
C_1-fluoranthene	216	+	+	nd	nd
C_2-pyrene	230	tr	tr	nd	nd
benzo[a]anthracene	228	++	++	nd	nd
chrysene	228	++	++	nd	nd
C_1-chrysene	242	+	+	nd	nd
benzo[k]fluoranthene	252	+++	+++	tr	tr
benzo[e]pyrene	252	+++	+++	nd	nd
benzo[a]pyrene	252	++	+++	tr	nd
perylene	252	tr	tr	nd	nd
tetrabiphenyl	306	tr	tr		
m-tetrabiphenyl	306	++	++	++	+
dibenzo[def,mno]chrysene	276	+	+	nd	nd
indole[1,2,3-cd]pyrene	276	++	+	nd	nd
dibenzo[a,b]anthracene	276	tr	tr	nd	nd
benzo[ghi]perylene	276	++	++	nd	nd
coronene	300	+	tr	nd	nd
dibenzopyrene (3 isomers)	302	+	tr	nd	nd

notes: +++ - relatively very high level; ++ - relatively high level; + - relatively low level; tr - trace level; nd - not detected.

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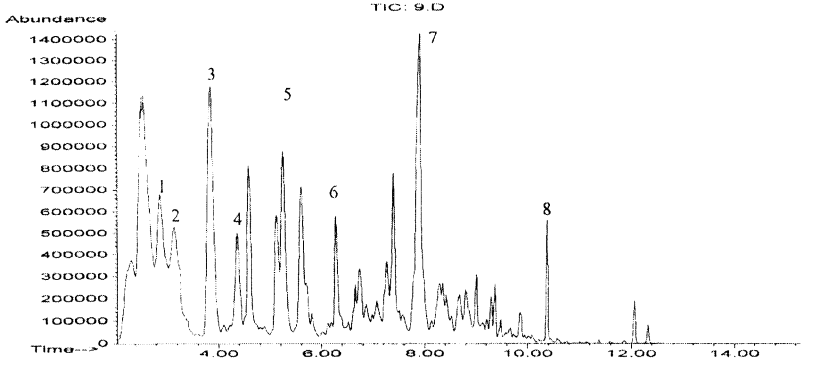

1-benzene; 2-trichloroethylene; 3-toluene; 4-tetrachloroethylene
5-C2-benzene; 6-camphene; 7-D-linonene; 8-naphthalene

Figure 1. TIC spectrum of VOCs in ambient air samples of M1

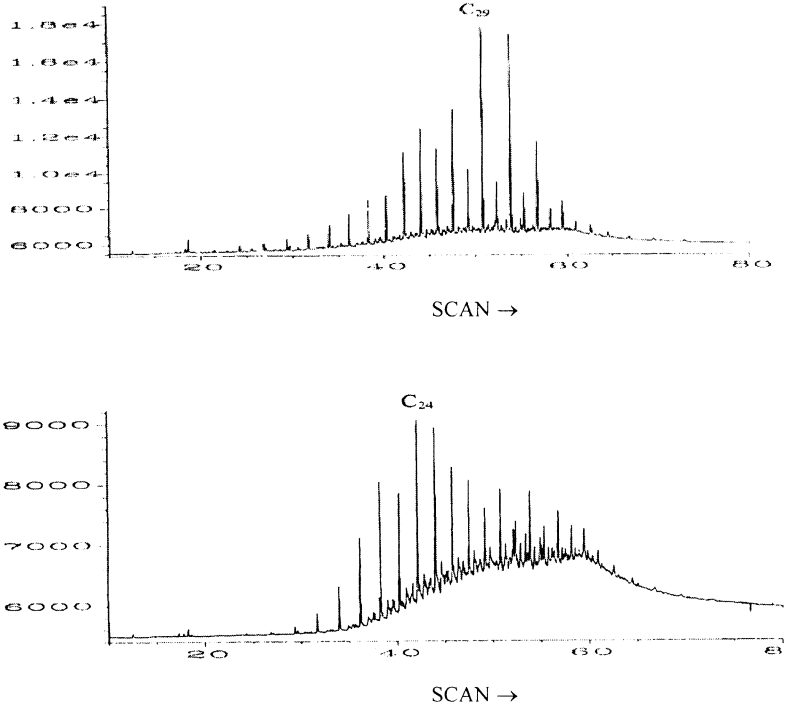

Figure 2. n-alkane carbon numbers profiles of ambient air samples in MP1 (above) and MP6 (below).