Exposure to hazardous volatile organic compounds, PM$_{10}$ and CO while walking along streets in urban Guangzhou, China

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Received 8 January 2004; accepted 14 July 2004

Abstract

Toxic air pollutants in street canyons are important issues concerning public health especially in some large Asian cities like Guangzhou. In 1998 <18% of Guangzhou citizens used public transportation modes, with a majority commuting on foot (42%) or by bicycle (22%). Of the pedestrians, 57% were either senior citizens or students. In the present study, we measured toxic air pollutants while walking along urban streets in Guangzhou to evaluate pedestrian exposure. Volatile organic compounds (VOCs) were collected with sorbent tubes, and PM$_{10}$ and CO were measured simultaneously with portable analyzers. Our results showed that pedestrian exposure to PM$_{10}$ (with an average of 303 µg/m$^3$ for all samples) and some toxic VOCs (for example, benzene) was relatively high. Monocyclic aromatic hydrocarbons were found to be the most abundant VOCs, and 71% of the samples had benzene levels higher than 30 µg/m$^3$. Benzene, PM$_{10}$ and CO in walk-only streets were significantly lower ($p<0.05$) than in traffic streets, and the differences in exposure levels between new urban streets and old urban streets were highly significant ($p<0.01$). Pedestrian exposure to toxic VOCs and PM$_{10}$ was higher than those reported in other public transportation modes (bus and subway). The good correlations between BTEX, PM$_{10}$ and CO in the streets indicated that automotive emission might be their major source. Our study also showed that the risk to pedestrians due to air pollution was misinterpreted by the reported air quality index based on measurement of SO$_2$, NO$_x$ and PM$_{10}$ in the government monitoring stations. An urban roadside monitoring station might be needed by air quality monitoring networks in large Asian cities like Guangzhou, in order to survey exposure to air toxics in urban roadside microenvironments.

Keywords: Volatile organic compounds; Respirable particulate matter; Carbon monoxide; Urban air pollution; Pedestrian exposure

1. Introduction

Urban air quality in many large cities is adversely affected by air pollutants such as particulate matter (PM) and hazardous air pollutants (HAPs). Various studies have provided evidence that PM $<$10µm, especially PM $<$2.5µm, is associated with morbidity
and mortality rates particularly due to cardiovascular and respiratory illness (Samet et al., 2000a, b; Peters et al., 2001; Pope et al., 2002). Volatile organic compounds (VOCs) in the urban atmosphere are also of great concern due to their effects on human health and atmospheric environment. They may pose significant health risks (Calabrese and Kenyon, 1991; Victorin, 1993) and play an important role in atmospheric chemistry as precursors of secondary pollutants (Carter, 1990; Bowman et al., 1995; Odum et al., 1997; Wakamatsu et al., 1999). Vehicular emission has long been recognized as one of the major anthropogenic sources of these air pollutants in urban areas (Pfeffer, 1994; Clark and Ko, 1996). Because of the relatively heavy traffic and/or adverse dispersion conditions in urban areas, these pollutants may accumulate to levels that cause damage to air quality and human health in street canyons (Spadaro and Rabl, 2001). Human exposure to these pollutants while commuting in urban streets has been widely investigated (Jo and Choi, 1996; Jo and Park, 1998, 1999; Cocheo et al., 2000; Chan et al., 2001, 2002a, b, 2003).

As the central city in the Pearl River Delta and in south China, Guangzhou has a population of 8.5 million with a population density of 2293 km$^{-2}$ in its urban areas in 2000. The number of motor vehicles had increased from 331,200 in 1990 to 1,350,400 in 2000, with an average annual increase of 15.1%; 70.1% of these in 2000 were motorcycles. Previous studies showed that emission factors of Chinese motor vehicles were much higher than those reported in developed countries (Fu et al., 2001). Traffic-related air pollution is a major environmental problem in many large Chinese cities, including Guangzhou (Zhang et al., 1999). Relatively high levels of monocyclic aromatic hydrocarbons have been reported in roadside microenvironments in rush hours and in public transportation modes in Guangzhou (Wang et al., 2002; Chan et al., 2003). Also, traffic-related air pollutants such as PM$_{10}$ and CO frequently exceeded the guideline levels in the National Ambient Air Quality Standard of China (NAAQSC) (Qian et al., 2001).

According to the survey of 10,000 families in Guangzhou by Deng et al. (2000), people in Guangzhou on average went out 2.11 times a day for an average of 37 min each time. Like many other Asian cities, there are typically more pedestrians in urban Guangzhou than in urban cities of most developed countries. In 1998, 41.9% of Guangzhou citizens commuted on foot, with 24.5% by bicycle and only 17.5% by public transportation modes; among the walkers 32.1% and 24.45% were senior citizens and students, respectively (Deng et al., 2000). Since a large proportion of Guangzhou citizens went out on foot or by bicycle with direct exposure to air pollutants in street canyons, the present study was designed to investigate exposure of pedestrians to toxic VOCs, PM$_{10}$ and CO when walking in typical urban streets in Guangzhou.

2. Experiment

2.1. Sampling

Typical urban streets were selected in four districts of Guangzhou, namely Liwan, Yuexiou, Dongshan and Tianhe, with population densities of 40,240, 38,362, 32,341 and 10,243 people per square kilometer in 2000, respectively. Fig. 1 shows streets where samples were collected. Tianhe is the new urban district planned in 1985. It has rapidly developed in recent years and now has the highest GDP among Guangzhou’s ten districts and two counties. The other three districts are old urban districts. Streets 1–6 are old urban streets (OUS) and streets 7–12 are new urban streets (NUS). Streets 1–3 and 12 are located in the most popular shopping centers in Guangzhou, with a daily flow of over 100,000 people. Street 1 is a walk-only street (WS) with no admission to motor vehicles; street 2 is a part-time walk-only street (PWS) and vehicles are not admitted between 19:00 and 22:00 on weekdays and between 13:00 and 22:00 at

![Sampling street](image-url)
weekends; other streets are all ordinary traffic streets (TS) with sidewalks.

Samples were collected between 07:00 and 19:00 on 1 and 2 February 2002 while trained graduate students walked along six routes, namely route 1 (street 1), route 2 (street 2), route 3 (streets 3–5), route 4 (street 6), route 5 (streets 7 and 8) and route 6 (streets 9–12). Sampling was conducted once every 2 h. Each time, the sampling duration was about 30 min, depending on the length of the streets. (In routes 1 and 2 we traversed both sides of the streets.) Also, for each route, one student counted the flow of motor vehicles using a Model 3130 TouchCounter™ (CONTROL Company, Texas, USA). VOCs were collected by the commercial 7” × 1/4” Tekmar stainless-steel multi-sorbent tubes (Part No. 14-1677-203, Tekmar Company, USA) packed with Tenax TA and Carbosieve S-III. Sampling inlets were at about 1.2 m above the ground. Air was drawn through the sorbent tubes with a portable sampling pump (Air-Check-52, SKC Inc., USA). The sampling flow rate was set to 100 ml min⁻¹ and monitored by a portable digital flow meter (DC-LITE, BIOS, USA) during the sampling. Throughout the study, the variations of flow rate were <2% in the sampling periods. While sampling VOCs, PM₁₀ was simultaneously measured directly by portable DustTrak analyzers (Model 8520, TSI Inc., USA), and CO, CO₂, temperature and relative humidity by portable Q-Trak analyzers (Model 8551, TSI Inc., USA). The portable analyzers were sent back to TSI Inc. for calibration once every 6 months. Pre- and post-zero checking of the DustTrak analyzers was also carried out during our field monitoring. These portable analyzers took a reading every 15 s, and data were recorded and retrieved on a personal computer using TSI Trakpro software. Measurements of PM₁₀ and CO during each sampling of VOCs were averaged as the corresponding exposure levels. The means of PM₁₀, CO and hazardous VOCs in different types of streets were compared using Student’s t-test by SPSS software.

2.2. VOC analytical methods

VOCs were analyzed with a thermal desorption system (Tekmar 6000 AeroTrap, Tekmar Company, USA) coupled to a Hewlett-Packard Model 5972 gas chromatograph/mass selective detector (HP 5972 GC/MSD). The sampling tubes were thermally desorbed for 20 min at 225 °C with a flow (40 ml min⁻¹) of ultra-pure helium (>99.999%) passing through and carrying the desorbed VOCs to a pre-concentration trap at −40 °C. Following the tube desorption, the trap was thermally desorbed at 225 °C for 4 min, and VOCs were transferred to HP 5972 GC/MSD for determination. An HP-VOC capillary column (60 m × 0.32 mm id × 1.8 μm film thickness) was used and carrier gas was ultra-pure helium. The GC oven temperature was set initially to 35 °C for 2 min, increasing at a rate of 5 °C min⁻¹ to 220 °C and then holding for 10 min. Major MSD conditions included ionization by EI, data acquisition mode of SCAN and mass range of 35–300 amu.

Compounds were identified by their retention times and their mass spectra. Standard gas mixtures (1.0 ppm) (Supelco TO-14 Calibration Mix) were first dynamically diluted with zero air, then sampled and analyzed using identical conditions to those for the field samples, and 7-point calibration (0.0, 1.0, 5.0, 10.0, 20.0, 40.0, 50.0 ppbv) was performed for quantifying the VOCs in the air samples. The detection limits of our method for all compounds listed in USEPA standard method TO-14 were <0.2 μg m⁻³.

3. Results and discussion

3.1. Exposure levels of aromatic VOCs

VOCs detected in the air samples were dominated by aliphatic and aromatic hydrocarbons, but this study was mainly focused on aromatic and chlorinated VOC species due to their roles as toxic organic pollutants. The means and standard deviations of major VOCs are listed in Table 1. For aromatic VOCs, toluene is the most abundant compound followed by benzene; their concentrations ranged between 13.6–158.1 and 7.9–120.9 μg m⁻³, with average values of 79.7 and 44.7 μg m⁻³, respectively. A short-term (30 min) ambient air quality standard of 30 μg m⁻³ for benzene has been established in Texas, USA (USEPA, 1992). Our sampling periods were approximately 30 min, and we found that 71% of the air samples exceeded this benzene limit of 30 μg m⁻³. Benzene is a carcinogenic compound causing leukemia. In the UK, the ambient air standard for benzene is 5 ppb (16 μg m⁻³) (running annual mean). High benzene exposure levels of pedestrians from this study indicated the importance of reducing the health risks of these hazardous VOCs and the necessity of VOC emission control. In recent years, the incidence of childhood leukemia in China’s urban areas has increased sharply, and about 350 children each year in Guangzhou develop leukemia (personal communication). The World Health Organization (World Health Organization (WHO), 1999) has estimated that a lifetime exposure of 1 μg m⁻³ of benzene leads to about six cases of leukemia per 1,000,000 inhabitants. To what extent is childhood leukemia in Guangzhou related to exposure of HAPs? This might be an important issue that needs further investigation.

Compared with rush-hour levels of benzene, toluene, ethylbenzene and xylenes (BTEX) at roadsides in Guangzhou in November 1996 (Wang et al., 2002), BTEX in roadside microenvironments in Guangzhou in 2002 also maintained relatively high levels, and the
average level of toluene was quite near its rush-hour average in 1996. In around 2000, the gasoline used in Guangzhou was changed from leaded to unleaded. This change might reduce the lead exposure but possibly gives rise to the VOC emission, especially emission of toluene and other monocyclic aromatic hydrocarbons. The rapid increase in the number of motor vehicles, in addition to the change of oil types, might offset much of the efforts by the local government to lower the levels of toxic air pollutants like BTEX in roadside microenvironments. Pedestrian exposure to BTEX, especially benzene, was much higher compared with the exposure of BTEX in other transportation modes such as subway and bus (Chan et al., 2003; Table 1). This comparison, however, might need more supporting data from further monitoring since a bus will travel along many different streets during its journey.

3.2. Exposure levels of chlorinated VOCs

For chlorinated VOCs, carbon tetrachloride (CT), trichloroethylene (TriCE) and tetrachloroethylene (TetCE) were widely detected, with average concentrations of 4.8, 4.5 and 5.1 µg m\(^{-3}\), respectively. These halocarbons have a purely anthropogenic origin and are considered probable human carcinogens (International Agency for Research on Cancer IARC, 1999). They may also catalyze the destruction of ozone both in the stratosphere and troposphere (Elliott and Rowland, 1987). In the Pearl River Delta, the detected background level of CT was 110 pptv (~0.76 µg m\(^{-3}\)) (Wang et al., 2004), quite near those reported in Atlantic and European air masses from 1987 to 1994 (Simmonds et al., 1996), but higher than reported recently in Athens, Greece (Glavas and Moschonas, 2002). In the clean atmosphere in the Pearl River Delta, TetCE ranged from below 1 to 50 pptv (Wang et al., 2004). In the present study, much higher concentrations of these chlorocarbons in contrast with their background levels indicated that they had emission sources in the urban area of Guangzhou. The concentration of CT, whose industrial use was banned in China in 2003, was up to 32.1 µg m\(^{-3}\) in one sample from traffic streets in the old urban area. The lowest level of CT detected in the streets, however, was only 0.8 µg m\(^{-3}\), which was the same as the background level in the Pearl River Delta.

3.3. Exposure levels of PM\(_{10}\) and CO

Compared to the exposure levels of PM\(_{10}\) and CO in public transportation modes in urban Guangzhou (Fig. 2), pedestrian exposure to PM\(_{10}\) on average was higher, and exposure to CO on average was lower. Air-conditioned transportation modes circulate and cool only the air inside the vehicle compartment, with limited air exchange with the outdoor air. Non-air-conditioned
transportation modes, often with their windows open, had higher levels of PM$_{10}$ due to the penetration of outdoor polluted air into the vehicle compartment (Chan et al., 2002b). Among the different commuting modes including walking, only CO in taxis exceeded the NAAQSC (hourly mean). Higher CO in taxis and private cars was also observed in Hong Kong (Chan and Liu, 2001; Chan et al., 2002c).

3.4. Roadside exposure levels and reported air quality index

According to the air quality index (API, based on the levels of NO$_x$, SO$_2$ and PM$_{10}$) reported by government monitoring systems in Guangzhou, air quality during the sampling days was fair (air quality/API: good/0–50, fair/51–100, unhealthy/101–200, very unhealthy/201–300 and hazardous/> 300). If taking into consideration the PM$_{10}$ we measured in the streets, we would get an API indicating unhealthy or even very unhealthy air quality in the streets. This suggests that the reported API may not reflect human risk due to air pollution in urban microenvironments like street canyons. The government monitoring stations in Guangzhou are all located more than 15 m above the ground. As there is typically an exponential decrease in air pollutant concentration with height in urban streets (e.g. Chan and Kwok, 2000), the concentrations measured by the government monitoring stations would be much lower than the levels at human breathing height in the streets. Ortiz et al. (2002) also pointed out that some VOC levels in microenvironments were higher than those from the metropolitan automated monitoring system located at least 3 m above the ground. The study by Cocheo et al. (2000) indicated that the actual outdoor benzene exposure of people was higher than the value calculated from the daily urban average benzene concentration and the time spent outdoors, since people are often exposed in streets where the highest benzene levels are found. Considering the high exposure levels of some pollutants in streets and the much greater pedestrian density in Asian cities like Guangzhou, it would be helpful if a roadside monitoring station was included in the government monitoring system to survey human exposure to air pollutants in urban areas.

3.5. Variations of exposure levels in different types of streets

Levels of benzene, PM$_{10}$ and CO between PWS and TS were not significantly different ($p > 0.05$), but they were significantly different between WS and PWS ($p < 0.05$) and between WS and TS ($p < 0.05$). The differences in benzene, PM$_{10}$ and CO levels between OUS and NUS were highly significant ($p < 0.01$). Benzene in NUS averaged less than a quarter of that in OUS, and was below the 5 ppb ambient air standard in the UK (annual mean). CO, solely from combustion processes in the urban streets, was 78% and 79% lower in the WS than in the PWS and TS, respectively. PM$_{10}$ in the WS, however, was only 26% and 16% lower than in PWS and TS, respectively. Benzene in the WS was nearly 30% lower than in PWS or TS. The results indicated that vehicle traffic control in the popular WS do have effects in lowering pedestrian exposure levels of some pollutants, especially traffic-related ones like CO. In contrast, CO$_2$ levels in WS, PWS and TS averaged 896, 880 and 786 ppm, respectively. WS and PWS had much higher flows of people and thus possibly a greater contribution of CO$_2$ from human breath. This may also explain the lower CO$_2$ in TS.

Street levels of air pollutants varied with traffic and environmental conditions, such as driving speeds, traffic density, wind, humidity, temperature and street canyon configurations (Chan et al., 2001; Broderick and Mamane, 2002; Vardoulakis et al., 2003). According to our counting of traffic flow (on average, 2424 and 3211 motor vehicles per hour in old and new urban streets, respectively), the new urban streets had even heavier traffic than the old urban streets in the study period. The highly significant difference between OUS and NUS probably resulted from the different geometry of the streets. Air pollutants such as suspended particulates disperse more easily out of a street canyon that has a lower height-to-width ratio (H/W) (Lee and Park, 1994; Chan and Kwok, 2000). On average the H/Ws are lower than 1.0 in the new urban streets but more than 2.0 in...
the old urban streets. Moreover, building heights on both sides of old urban streets are typically close to each other; in the new urban streets studied, however, building heights on one side are much lower than on the other side. These street configurations in the new urban areas might make it easier for the air pollutants to disperse from the streets.

3.6. Correlations of pollutants and source implications

Compared to those reported in other traffic-related sites, the BTEX pattern in this study was identical to that in London, but different from those in other Chinese cities such as Changchun, although their B/BTEX ratios were relatively close (Fig. 3) (Liu et al., 2000; Chan et al., 2002; Derwent et al., 1995; Grosjean et al., 1998). The different pattern of BTEX ratios might suggest considerable differences in the nature of air pollution in these cities (Gee and Sollars, 1998). The linear correlations between BTEX, PM$_{10}$ and CO for all samples are listed in Table 2. BTEX and PM$_{10}$ in the streets were all significantly correlated ($p < 0.01$) with CO, which was a tracer of vehicle emission in urban street canyons. The potential of monoaromatic hydrocarbon ratios as indicators of emission sources or atmospheric age was discussed both from emission profiles (e.g. Nelson and Quigley, 1984) and from ambient air monitoring in various cities (e.g. Monod et al., 2001). In this study, the very good correlation between CO, xylenes and ethylbenzene also confirmed that ethylbenzene and xylenes in streets were largely from automotive emissions. Ethylbenzene, the least reacting C$_2$-alkylbenzenes, was a good proxy of automotive emission in urban street canyons. The higher X/E ratio (4.3) observed in the study also implied that these monoaromatic hydrocarbons were very fresh from on-road automotives. PM$_{10}$ might have contributions from construction activity, geological dust, road dust re-suspension and secondary formation other than from vehicle emission. Probably for this reason, the observed correlations between PM$_{10}$ and CO and between PM$_{10}$ and ethylbenzene were not as good as those between BTEX and CO. Also, the difference in PM$_{10}$ levels between OUS and NUS was not as significant as those of BTEX and CO levels. Why was PM$_{10}$ very high but CO relatively low in these streets if PM$_{10}$ was also largely traffic-related? A possible explanation is that, unlike CO, PM$_{10}$ might come not only from traffic emissions, but also from road dust re-suspension caused by passing motor traffic. Nonetheless, a further investigation on PM$_{2.5}$ levels and chemical speciation of aerosol would help to diagnose the sources of PM in the street canyons.

4. Conclusions

In this study from sampling-while-walking instead of sampling in fixed sites, we investigated pedestrian exposure to hazardous volatile organic compounds, PM$_{10}$ and CO in urban Guangzhou, and found relatively high exposure levels of benzene and PM$_{10}$. BTEX and PM$_{10}$ in the streets were highly traffic-related, but varied significantly with traffic conditions.

![Fig. 3. Percentages of BTEX species at traffic-related sites in different cities. 1, this study; 2, Liu et al. (2000); 3, Chan et al. (2002); 4, Derwent et al. (1995); 5, Grosjean et al. (1998).](image-url)
and street configurations. The roadside exposure levels were not well indicated by the reported API from the local government monitoring networks, and it might be necessary to enforce air pollution monitoring in roadside microenvironments in the government monitoring systems. Also, from the comparison of exposure to air pollutants by walking and in public transportation modes (buses and subway), commuting on foot instead of by subway or bus (especially air-conditioned bus) may increase exposures to HAPs due to longer journey times and higher concentration levels in street canyons.

Acknowledgments

Supports from the Guangdong Environmental Protection Bureau and the Department of Science and Technology of Guangdong Province are gratefully acknowledged. This study was funded partially by the Natural Science Foundation of China (No. 40203011), Ministry of Science and Technology of China (No. 2002CB410803) and Chinese Academy of Science (KZCX3-SW-121). The authors appreciate the technical support from the Rowland/Blake Group at the University of California at Irvine by providing a VOC standard gas mixture as an independent check of VOC analysis. The efforts of two reviewers have greatly improved the quality of this manuscript and are sincerely appreciated.

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