Bull. Environ. Contam. Toxicol. (2004) 72:233–239

DOI: 10.1007/s00128-003-9022-7

Bulletin of Environmental Contamination and Toxicology

Concentration Level of Fine Airborne Lead in Beijing, People's Republic of China

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Received: 16 May 2003/Accepted: 15 October 2003

Motor vehicle emission is a major source of airborne lead since organic tetraalkyl lead (TAL) was added to petrol as the anti-knock agent, which reacted with ethylene dihalide (EDH) and then emitted lead in the form of PbBrCl predominantly (Hirschler et al., 1957; Habibi 1973). Airborne bromine and lead were often used as tracer of leaded gasoline vehicle exhaust because bromine has few additional sources, however chloride has many other sources such as coal burning and marine aerosol (Patty, 1963). In China, with the steady development of the economy the vehicle stock increased rapidly with the average annual rate increasing at 14% and is anticipated reaching 45-50 million vehicles in 2010. Motor vehicles become gradually the important source of air pollutants in the urban area. At the same time, coal burning remains the major energy source in many fields such as power plants, industry and especially in wintertime for the heating supply. It was estimated that the coal burned directly was about 10^9 t y^{-1} accounting for 84% of the total consumed coal (Luo et al., 2002). Therefore, the air pollution in China has been characterized with the mixture of coal burning and motor vehicle, thus changed from the simple coal burning pollution in the past. As the capital city and with a population of approximately 12,000,000 people, Beijing faces a heavy air pollution problem with the rapid increase of motor vehicle stock that has reached 1,700,000. The situation was expected to be better by banning leaded gasoline from July 1997. However, because there is lacking a continuous study of fine particulate matter (with the dynamic diameter less than 2.5 μm, $PM_{2.5}$) in the past years, the airborne lead concentration level as well as the source contribution is not so clear.

In this study, we continuously collected $PM_{2.5}$ samples during 1999 - 2000, and performed multiple regression analysis of lead with other chemical species, including bromine, elemental carbon and organic carbon, in order to find the relationship between these species.

MATERIALS AND METHODS

Low-flow rate samplers (LFS, Aerosol Dynamic In., Berkeley, CA) were applied to collect fine particle samples from July 1,1999 to June 1, 2000 at two sampling sites in Beijing. One site located on the campus of Tsinghua University (THU) near a residential area; another was at an air monitoring station at Chegongzhuang

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(CGZ) between the second and third ring road, neighboring traffic artery. The distance between two sites is about 10 km. The sampler was installed on the roof of 3m-height bungalow at each site, thus the inlet height above the ground was about 4.5m. Each LFS has three parallel sampling inlets to collect $PM_{2.5}$ samples for analysis of water-soluble ions, inorganic elements and carbonaceous particles, respectively. The sampling flow rate is 0.4 l min^{-1} with duration 7 days. Moreover, the gas pollutants such as nitrogen oxides and sulfur dioxide were monitored for the same sampling period at the CGZ site. Three analytical technologies were used including X-ray fluorescence (XRF) method for inorganic elements, ion chromatography (IC) method for water-soluble ions and thermal/optical reflectance (TOR) method for organic carbon (OC) and elemental carbon (EC), respectively. The process of sample collection and chemical analysis has been introduced in detail in previous work (He et al, 2001).

RESULTS AND DISCUSSION

The uncertainty of Pb measured by XRF method at CGZ site was 0.007 μg m^{-3} (He et al, 2001). Samples with Pb level below the detection limits were excluded. The annual lead concentrations during the entire sampling period ranged from 0.12 μg m^{-3} to 1.02 μg m^{-3} at THU site, with the average value 0.334 ± 0.172 μg m^{-3}, and from 0.01 μg m^{-3} to 1.20 μg m^{-3} with 0.302 ± 0.195 μg m^{-3} at CGZ site. It was obvious that the average concentrations at both sites were lower than the stated Pb annual concentration of the Ambient Air Quality Standard (GB3095-1996), 1.0 μg m^{-3}, as well as the long-term average concentration 0.5-1.0 μg m^{-3} brought forward by the World Health Organization (WHO).

In this study the $PM_{2.5}$ samples were divided into four groups according to the seasons as follows: summer samples (from July 1 to August 30,1999), autumn samples (from September 1 to November 3), winter samples (from November 4,1999 to March 2, 2000) and spring samples (from March 3 to June 1). For both sites, there are strong seasonal variations of Pb with the highest value in winter (the heating period), 0.40 μg m^{-3} on average, as illustrated in Figure 1. This seasonal variation characteristic is comparable to those results reported in other studies and will be discussed in detail later. From the monthly variation plotted in Figure 2, the highest Pb concentration level appeared during November, 0.68 μg m^{-3} for THU site, twice of the average concentration 0.334 μg m^{-3}; 0.74 μg m^{-3} for CGZ site, about 2.5 times of the average concentration 0.302 μg m^{-3}. Both concentrations have exceeded the Pb daily average value 0.5 μg m^{-3} prescribed in the *National Ambient Air Quality Standard* (GB3095-1996). The lowest value at both site appeared in July, approximating to 0.18 μg m^{-3}.

It was reported that Pb concentration was 7.3 ng m^{-3} in clear continent aerosol of Beijing rural area (Wang, 1999), and was 0.22 μg m^{-3} in Total Suspended Particle (TSP) in 1980s (Chen et al., 1988). Zhang et al. (1998) reported that Pb concentration in fine aerosol reached 0.38 μg m^{-3} in 1992 and 0.35 μg m^{-3} of TSP in 1998. It is evident that the lead concentration in this study (from 1999 to 2000)

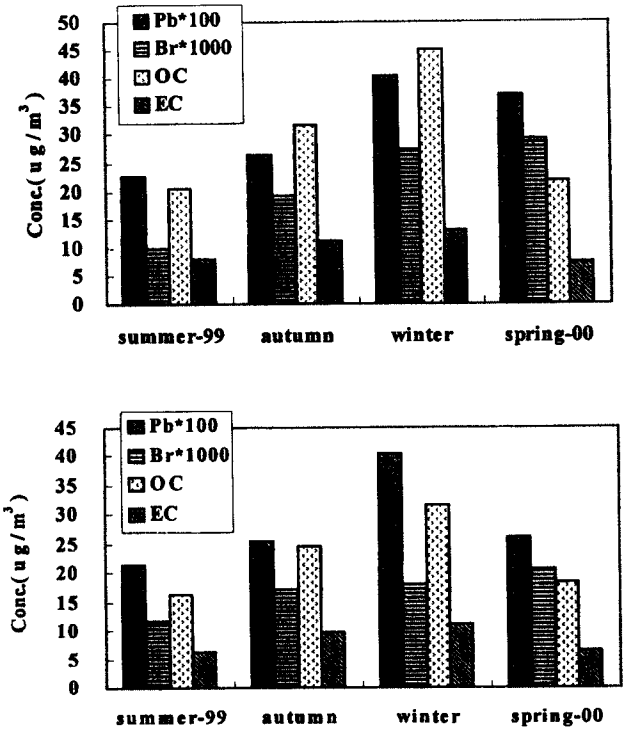

Figure 1. Seasonal variation of Pb, Br, OC and EC for THU and CGZ site, July 1, 1999 to June 1, 2000.

is lower than those of 1992 and 1998 just discussed above. Probably it can be attribute to the use of nonleaded gasoline from July 1, 1997 in Beijing. Other cities in China, for instance, Tianjin, showed the similar tendency. During 1980s the Pb concentration was 0.24 μg m^{-3} (Chen et al, 1988). In 1997 the annual average concentration of ambient Pb was 0.54 μg m^{-3}. After January 1998, when the leaded gasoline had been banned, the annual value was 0.32 μg m^{-3} that decreased of 40.7% compared with 1997 (Li et al, 2000). It was obviously the effect in those cities by using nonleaded gasoline to decrease the ambient Pb concentration. However, it remains high compared with other countries such as America, Japan and most European countries, where the Pb level has dropped down to 0.1 μg m^{-3}.

Pb, Br, OC and EC are usually regarded as the species relating to anthropogenic activities, especially the combustion process. Br is mainly emitted from the motor vehicle since it has few other industrial sources and low natural background from marine aerosols, and is good tracer elements of motor vehicle exhaust together with Pb (Harrison et al, 1983). As the major atmospheric components carbonaceous particles (OC and EC) account for about 15-20% of TSP and

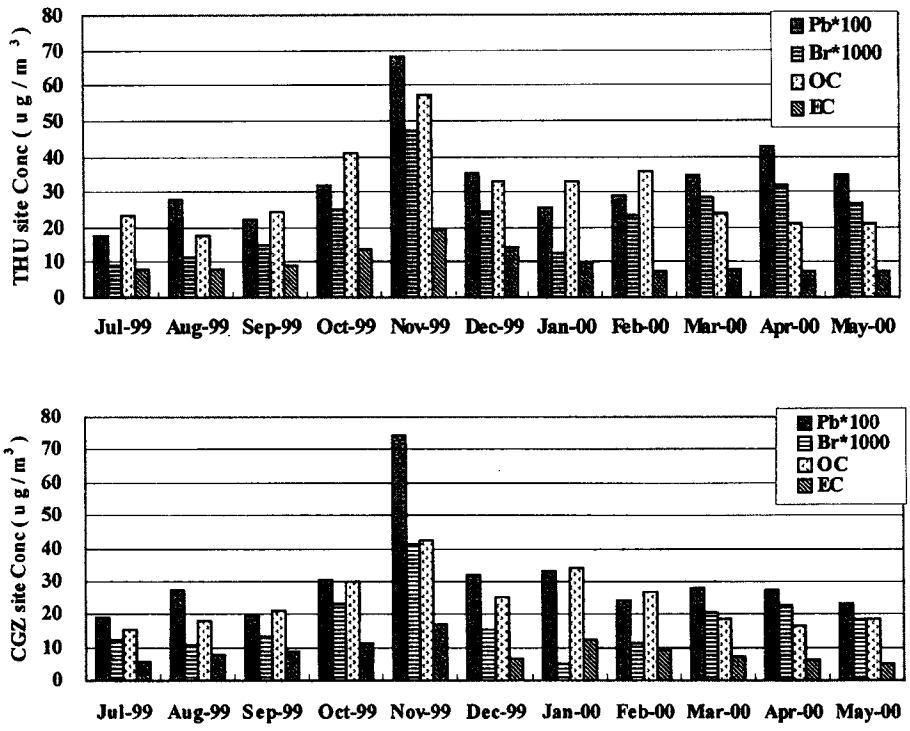

Figure 2. Monthly variation of Pb, Br, OC and EC for THU and CGZ site, July 1, 1999 to June 1, 2000.

40-60% of fine particles (Chi et al., 1999). EC is emitted directly from incomplete combustions of fuel (coal, oil) and biomass burning. OC can be divided into two types, primary OC (POC) and secondary OC (SOC). The former comes mainly from the combustion process of coal, oil and biomass burning, as well as the process of geology, chemical industry (Chow et al, 1995). In the Los Angeles about 7.5-18.3% of fine organic particles are emitted directly from motor vehicle exhaust (Fraser et al, 1999). The average concentrations of Br, OC, and EC were 0.023 μg m^{-3}, 29.61 μg m^{-3} and 10.19 μg m^{-3}, respectively; the seasonal and monthly variations are illustrated at the same time with those of Pb in Figure 1 and 2.

By analyzing the regression results between Pb and Br, the vehicle contribution could be estimated, as well as the additional sources of Pb (Liu et al., 1995). In this paper, regression analysis was first applied to all the sample concentrations during the entire sampling period. As shown in Table 1, at THU site, the correlation coefficient (R^2) is 0.79, with an intercept of 82.77 ± 23.01 ng m^{-3}. For CGZ site, after deleting those data below the analysis uncertainty (0.007 μg m^{-3} for Pb and 0.003 μg m^{-3} for Br), the R^2 and intercept are 0.70 and 65.27 ± 29.81

Table 1. Comparison of the correlation coefficient (R^2) between heating period and all the sampling period at two sites.

	All the sampling period (Jul. 1,1999~Jun.1, 2000)		Samples of heating period (Nov. 4, 1999~Mar.2, 2000)	
	THU site	CGZ site	THU site	CGZ site
Pb vs. Br	0.79	0.70	0.81	0.86
Pb vs. OC	0.55	0.64	0.81	0.82
Pb vs. EC	0.42	0.64	0.64	0.82

ng m^{-3}, respectively. Obviously, the correlation between Pb and Br is good at both sites, indicating that Pb and Br were probably emitted from the same pollution source, motor vehicle. There is positive intercept on Pb, that is, regression line hasn't passed the zero, implied the possible existence of additional sources for Pb except motor vehicle. Liu et al (1995) considered that the positive intercept on Br for the clean sites meaning the marine source for Br. In this study, we found no excess Br from other source since the positive intercept lay on the Pb axis. The average Br/Pb ratio 0.068 was higher than that of in rural area of North China reported by Winchester et al. (1981), however much smaller than the ethyl ratio (0.386), as well as those of other cities such as 0.36 in Brisbane fine particle (Chan et al., 1997), 0.48 in Sydney petrol (Cohen et al., 1994). It presented seasonal variation with the lowest value 0.046 in summer, which possibly due to the loss of Br under the high temperature (Chan, et al., 1997). The facts of the strong correlation between Pb and Br together with the positive intercept on Pb axis, as well as the low Br/Pb ratio implied that motor vehicle exhaust remained the major source of Pb in Beijing, and there were probably additional source contributions. Weak correlation between Pb and EC can be observed during the whole sampling period for both sites as shown in Table 1, with R^2 of 0.42 and 0.64, respectively. Similar to Pb vs. EC, correlation for Pb and OC is weak too, with R^2 of 0.55 and 0.64, respectively.

As described above, the highest concentration of Pb appeared in winter season, which was similar with those reported in other studies (for example, Kim et al., 1997; Simpson et al., 1994; Tripathi et al., 1994). However, in those studies the highest Pb level in winter was mainly attributed to the meteorological conditions such as wind speed and direction, temperature and so on. In this work there's weak negative relationship between lead concentration and wind speed in wintertime, with R^2 of 0.4. Therefore, we considered that meteorological conditions were not the major factors that aggravated the Pb pollution. Whereafter we reapplied the regression analysis for the concentrations of Pb vs. Br, OC and EC during heating period (from Nov. 4, 1999 to Mar. 2, 2000). As shown in Table 1, the correlation coefficient (R^2) of Pb and Br at THU and CGZ site are 0.81 and 0.86, respectively, which have changed little compared with those of the entire sampling period. However, the R^2 of Pb vs. EC and OC increase obviously, 0.81 and 0.65 for THU site, 0.82 and 0.82 for CGZ site, respectively. These changes might be attributed to the coal burning process because in north China, coal

remains the major emery source consumed by domestic boiler and central heating during winter. It was reported that in China the Pb content in coal was 20 mg kg^{-1} on average, four times as high as that of in America (Ren, et al., 1999). About 12,000 ton of Pb was emitted to the air by coal burning every year (Luo, et al., 2002). From the strong correlation of Pb vs. EC and OC, we considered that coal burning was another major source of Pb pollution in Beijing besides motor vehicle exhaust. By comparing the Pb concentration in wintertime (0.40 $\mu g\ m^{-3}$) with those in other three seasons (0.29 $\mu g\ m^{-3}$ for THU and 0.24 $\mu g\ m^{-3}$ for CGZ on average), the coal burning contribution to Pb was estimated about 40% for THU and 29% for CGZ site, respectively.

Acknowledgments. This work was supported by GM Research and Development Centers. We thank the Desert Research Institute (DRI) for the analyses of the inorganic elements and the carbonaceous compounds.

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