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Ambient BTX measurements in Suzhou, China

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Abstract Within the Sino-Italian environmental protection cooperation framework established in 2002, a comprehensive air quality monitoring network has been developed in urban Suzhou, a medium-sized Chinese city, in compliance with European standards (Directive 96/62/EC). This paper is among the first attempts to present a systematic and scientific analysis of benzene, toluene, and xylenes (BTX) pollution in China. It presents our analysis of BTX space-related and time-related measurement results. Background BTX concentrations were investigated by passive sampler Analyst® in 2003. We depicted the spatial distribution of average BTX concentrations collected from three 15-day campaigns on isoconcentration maps. This is the first time such detailed BTX concentration maps have been developed in China in a city scale. Continuous measurement of BTX by automatic gas chromatography was carried out at two fixed monitoring stations, one in an urban residential zone and one in a heavy traffic zone, from April to December 2005. The results show similar seasonal trends at both sites, reaching their greatest level in December and their lowest level in August. The average daily profile of BTX shows greater fluctuation in spring and winter with clear morning and evening peaks. Daily average benzene, toluene, and *m,p*-xylenes concentrations for the study period were 2.64, 11.52 and 3.52 μg m^{-3}, respectively. The benzene/toluene ratio we found was lower in Suzhou than those published in studies of other worldwide cities, which indicates serious levels of toluene pollution from local stationary sources. The similarities in seasonal trend and spatial distribution in these manual and automatic measurement results were comparable with each other, though the concentration values differed.

Keywords BTX · Passive sampler · Automatic monitoring · China

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Introduction

The aromatic fraction of organic pollutants in the atmosphere has raised concerns due to their

significant adverse effects on human health. Polycyclic aromatic hydrocarbons with lower vapor pressure exist mostly in a solid phase and monoaromatics such as benzene, toluene, and xylene (BTX) exist in a gaseous phase. Toluene strongly affects the nervous system and benzene is a carcinogen (TOXNET 2000). Benzene has been added to the compulsory limit list of Directive 2000/69/EC because of its health danger (European Community 2000).

There are lots of efforts to study outdoor and indoor BTX pollution (Schneide et al. 2001). Field measurements have been undertaken in cities in Latin America, North America, Europe, Asia, Oceania, and China as well (Pilidis et al. 2005; Xu 2004). Most of these studies, however, investigated only one or several particular sites at a time. The number of samples was limited.

Our study in Suzhou, a medium-sized city in China, allows for an overall evaluation of spatial and temporal distribution of BTX concentrations with the magnitude dataset. The samples were collected at 100 points representative of the whole urban area using passive samplers. Automatic measurements were performed in addition to obtain a temporal resolution of BTX levels at two air quality monitoring stations (AQMS). The combination of manual and automatic measurements provided a basis for developing an understanding of BTX pollution in Suzhou. Our limited study of Suzhou contributes in a small way to the accumulation of a database as a foundation for a scientific study of the impact of these compounds on public health worldwide.

Experimental

Suzhou, with 1,650 km^2 total area and 2.07 million urban area population, lies near Shanghai in the center of the Yangtze River Delta, a strategically located city with many cultural and tourist attractions and an export-oriented economy. Suzhou's climate can be characterized as subtropical monsoon, a moist climate which is rainy-hot in summer and dry-cold in winter (Zhou et al. 2004).

We investigated average background BTX concentrations in 2003 on a city-wide basis in Suzhou during a preliminary assessment study using Analyst® diffusive samplers (Allegrini et al. 2003; Allegrini et al. 2004; De Santis et al. 2002). We commenced automatic monitoring of BTX at two fixed stations in 2005 after a comprehensive AQMS with nine fixed stations was established. For further information about the network, the readers are referred to Wang et al. (2008).

One hundred stations were sited and set up throughout Suzhou's 177.17-km^2 urban area to provide a spatial scheme for air pollutant measurement. Site selection was based on a grid we developed for the area under investigation. A location was chosen in each cell representative as much as possible of the pollution level not influenced by very local pollution sources. Two stations were equipped to continuously measure BTX by gas chromatography in highly representative high traffic and urban residential zones. The map in Fig. 1 depicts the locations of the 100 sites in eight administrative districts of Suzhou and two monitoring sites where station B1 is a residential type and station C1 is a traffic type.

In order to estimate annual average levels, August was chosen as representative for the rainy-hot period and October was chosen as representative for the dry-cold campaign, both considered typical months for those seasons in Suzhou. Three sampling campaigns were carried out from August 1 to 15, 2003, from August 15 to 30, 2003, and from October 15 to 30, 2003. Then, an AQMS was set up with nine fixed stations equipped with analyzers for SO_2, NO_x–NO_2, CO, O_3, PM_{10}, and meteorological sensors (Costabile et al. 2006).

The samples collected using both manual and automatic methods were analyzed using gas chromatography. The special analysis procedures were different, as described below. The analyses of all passive samplers were carried out between September and December 2003 in the Italian National Research Council's Institute for Atmospheric Pollution (CNR_IIA) laboratories. The aromatic hydrocarbons were eluted with 2 ml carbon disulfide from the passive samplers. Both passive samplers and the CS_2 solvent had negligible blanks for the determined analytes (lower than 0.003 mg ml^{-1} eluted solvent). Samples obtained by CS_2 elution were analyzed using a DANI GC 1000 gas chromatograph equipped with a 30-m, 0.32-mm

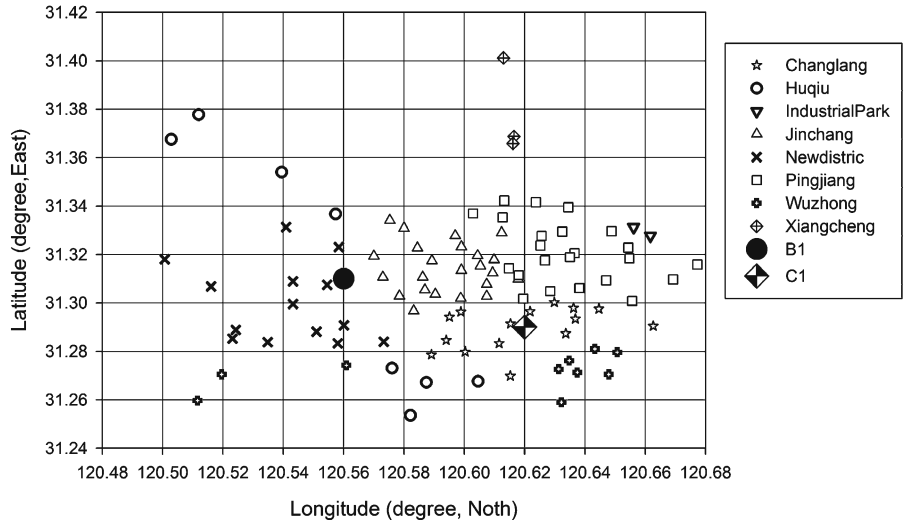


Fig. 1 Location of two fixed stations and 100 sampling points in eight districts in Suzhou

diameter, 3-mm film thickness "Vocol" capillary column (Supelco, Bellefonte, PA, USA), a FID, and a Hewlett-Packard HP 3395 integrator. The temperature program (2 min at 58°C, then 5°C min^{-1} up to 80°C, then 20°C min^{-1} up to 260°C in the final purging step) allowed the best resolution, avoiding overlap of any interfering peaks with the species to be determined. In order to confirm the analytical results, 10% of the samples were also analyzed by gas chromatography–mass spectrometry using a MSD 5971A-quadrupole model provided by Hewlett-Packard (Agilent Technologies, Cernusco S.N., Italy).

BTX in ambient air was analyzed simultaneously by gas chromatography analyzers (model GC955) equipped with a 15-m, 0.32-mm diameter, 0.45-μm capillary column, a PID, and a Hewlett-Packard HP-5 integrator, stationary phase 5% phenylmethyl silicone. The temperature program (5 min at 50°C, then 20°C min^{-1} up to 150°C for 10 min) was an increasing process. The preconcentration tube was eluted with Tenax sorbent at an adsorbing temperature of 10°C and a disadsorbing temperature of 180°C in 100 ml volume of sampling gas. The carrier gas contained a high percentage of nitrogen gas with flow at 1.5 ml min^{-1}. Concentration values were created each 30 min.

Gas chromatography analyzers (model GC955) with 30-min sampling frequencies were set up to run continuously at two fixed stations in an urban residential zone (station B1) and a heavy traffic zone (station C1). The instruments' response was corrected based on a regular calibration and adjusted to real temperature and pressure conditions. The data was collected using Argo software and compiled with Excel and OPSIS Report software, Arc View 8.2 software to create isoconcentration maps with Geostatistical Analyst and Spatial Analyst extensions.

Results and discussion

Spatial variation of BTX concentrations

The three manual measurement campaigns at 100 sites cover most of the urban area in Suzhou city. The spatial concentration distribution of BTX background concentrations was illustrated on isoconcentration maps (Fig. 2). It is noteworthy that benzene and xylenes concentrations reached maximum values within the downtown centre (most places in the Xiangcheng district in the north Suzhou city and hot points in Pingjiang district), which generally indicates that vehicle exhaust contributed significantly to higher benzene concentrations. Toluene pollution is greater in Pingjiang and Changlang districts in the east part of Suzhou where the city's chemical industries are located.

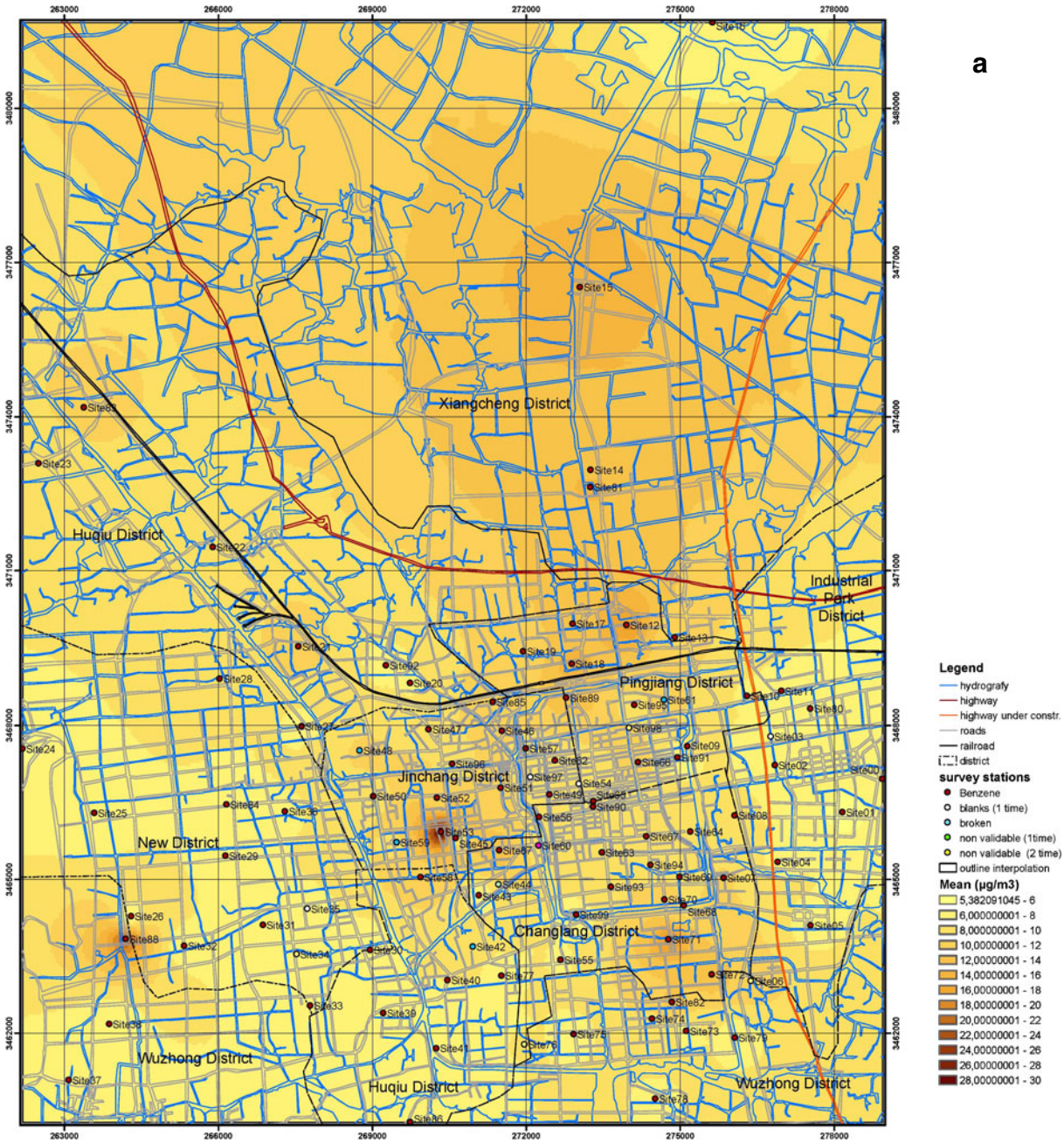


Fig. 2 Isoconcentration maps of benzene (**a**), toluene (**b**), and xylenes (**c**) mean values from three campaigns

BTX concentrations decreased progressively toward urban Suzhou's periphery.

This study presents the average BTX concentrations in the administrative areas. Total BTX mean values for the three campaigns differ in each district (Fig. 3), highest in Xiangcheng and Pingjiang districts (57.48 and 57.32 µg m^{-3}, respectively) and lowest in Wuzhong and new industry districts (39.92 and 41.87 µg m^{-3}, respectively). Given emission sources in small scale and basic

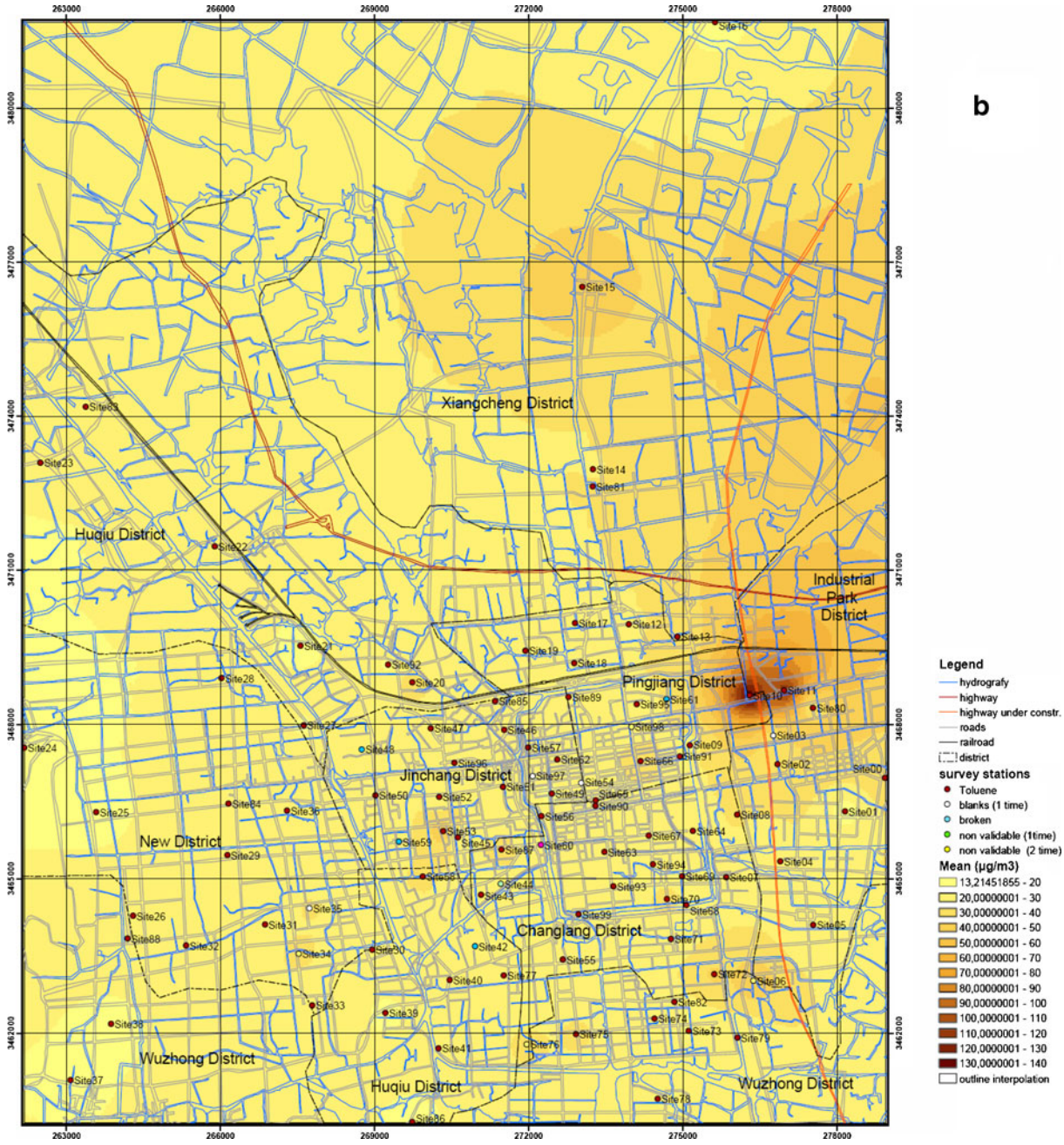
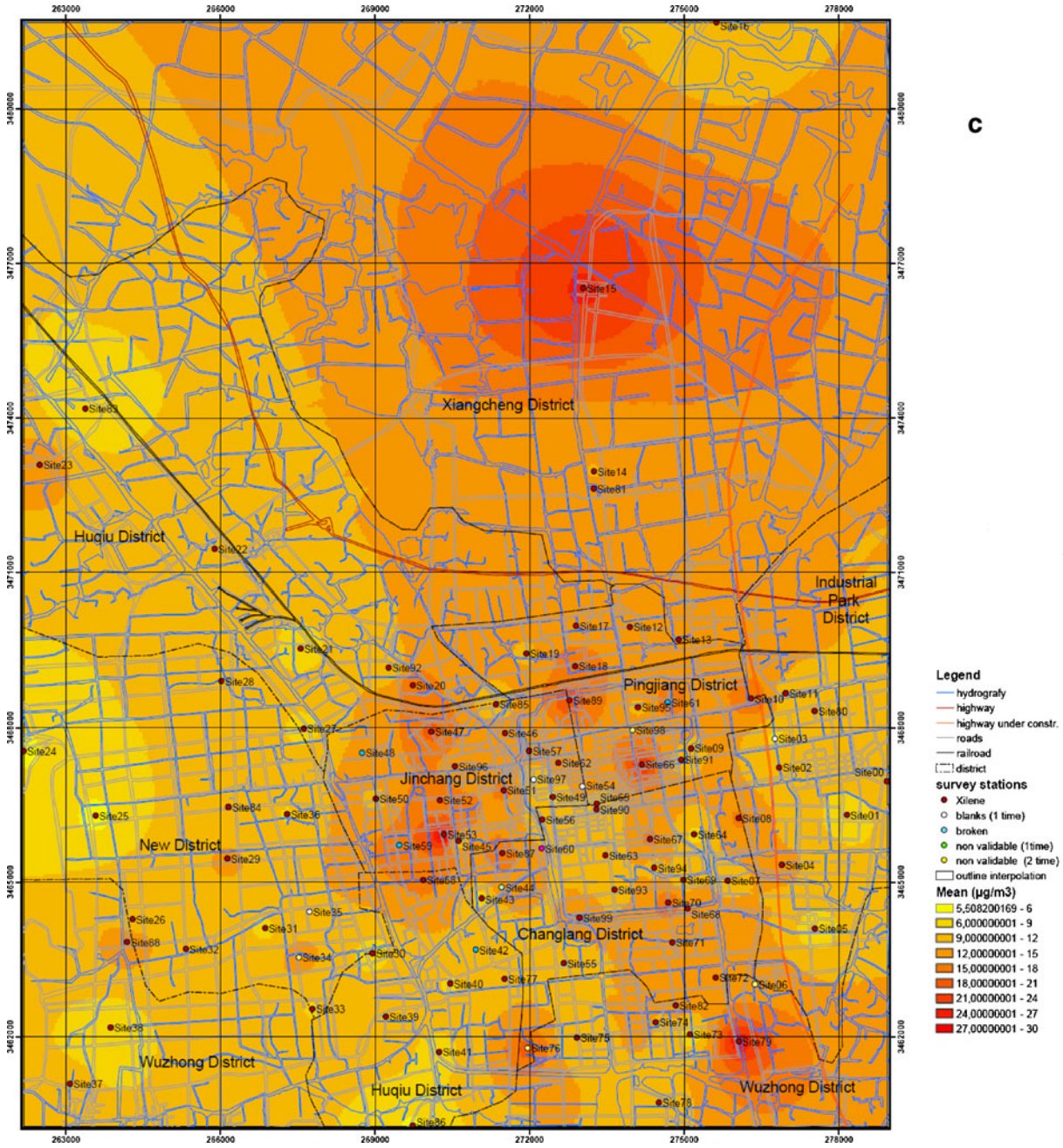


Fig. 2 (continued)

human exposure, sampling sites were also classified into several types, such as urban background exposure sites, residential population exposure sites, and traffic exposure sites. The measurement results from the three campaigns show variations in different types of sites with a high correlation to the emission sources.

Temporal variation of BTX concentrations

Continuous measurements by automatic gas chromatograph at two sites allow us to analyze the temporal variation of BTX concentrations. The monthly average at two monitoring sites shows similar seasonal trends, the average total BTX



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(Fig. 4) reaching its highest levels in December (28.77 µg m^{-3}) and its lowest level in August and September (9.40 µg m^{-3}), presenting a "U" shape for the yearly period. This observed seasonal trend was reverse to that reported in Beijing (Xu 2004) where the seasonal peak appeared in summer. This difference might be caused by different emission source characteristics in two cities, a big dissimilarity in climate conditions, or different study methods.

The daily average concentrations of BTX during the study period are also analyzed. Benzene

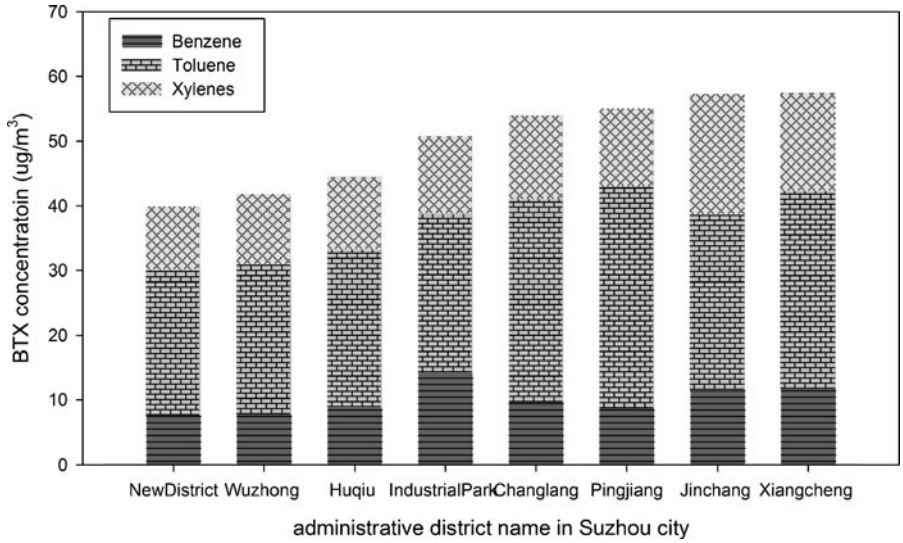

Fig. 3 BTX mean values of three campaigns in each district

presents its highest concentration of 8.15 μg m^{-3} and an average of 2.64 μg m^{-3}. The highest concentration recorded for toluene is 81.35 μg m^{-3} and an average of 11.52 μg m^{-3}. For xylenes, the concentration is 19.40 μg m^{-3} and an average of 3.52 μg m^{-3}. It also notes that benzene values are more regular than toluene and xylenes values. This can be explained by the fact that benzene is well known to be emitted from on-road and off-road mobile sources and, therefore, presents daily profiles corresponding to general traffic rush hours (Fig. 5a), while the emissions of toluene and xylenes into the atmosphere in the urban area are also mainly from vehicles but the contributions from stationary sources, especially from the fine chemical industry in Suzhou, are also significant.

BTX daily variations are presented (Fig. 5a–c) in spring, summer, autumn, and winter by averaging the corresponding time 30-min values in the whole months of April, August, October, and December, respectively. In general, BTX daily profiles all show a valley at noontime between peaks in the morning and in the afternoon. Peaks in benzene concentrations correspond with rush

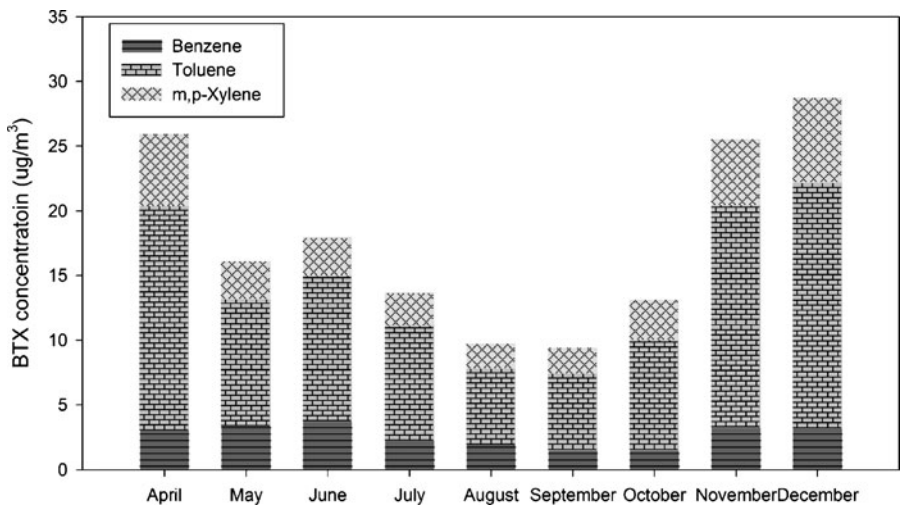

Fig. 4 Monthly average concentration of benzene, toluene, and xylenes from two automatic monitoring stations in 2005

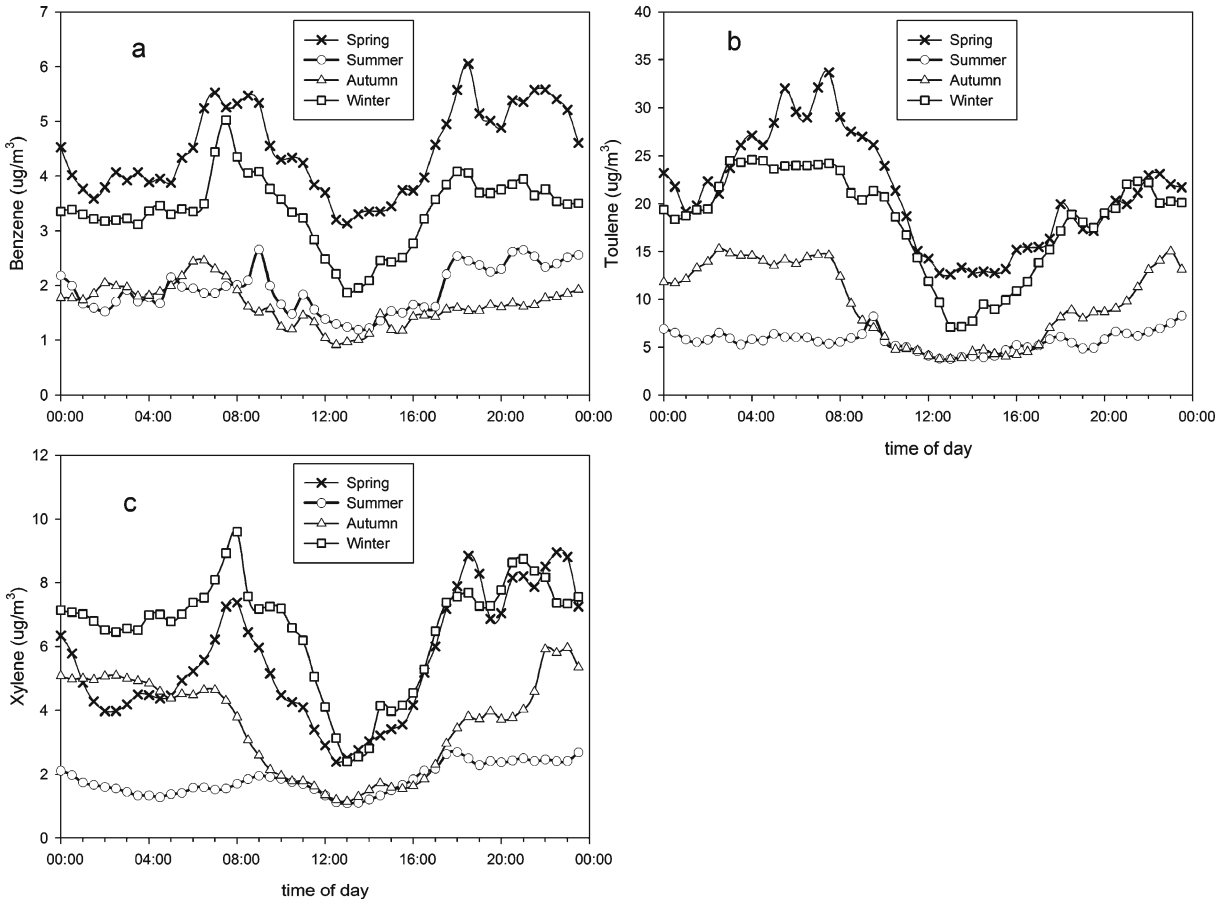

Fig. 5 Daily variation of benzene (**a**), toluene (**b**), and xylenes (**c**) during the four seasons

hour traffic and remain at high values during the night. Obviously, in spring and winter, the concentrations are higher with large fluctuations, while in other seasons, the values are lower and relatively equable, especially in summer. The local subtropical monsoon climate contributes significantly

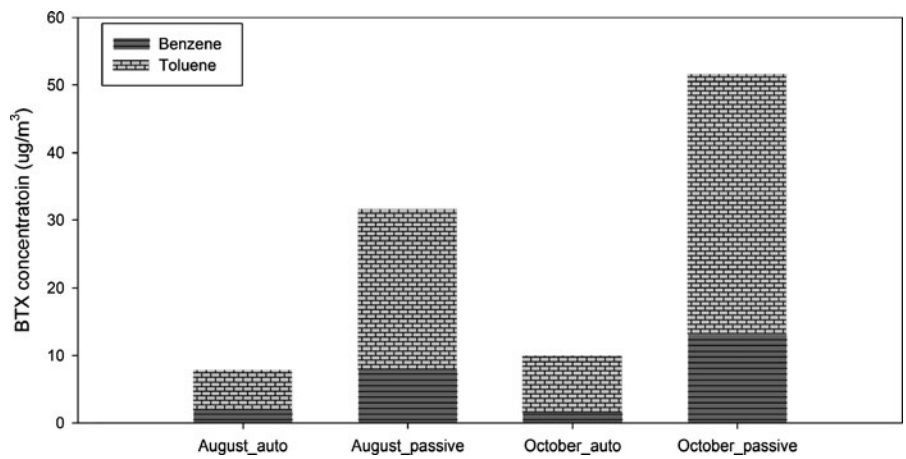

Fig. 6 Comparison of benzene and toluene concentration by automatic measurement and passive sampler

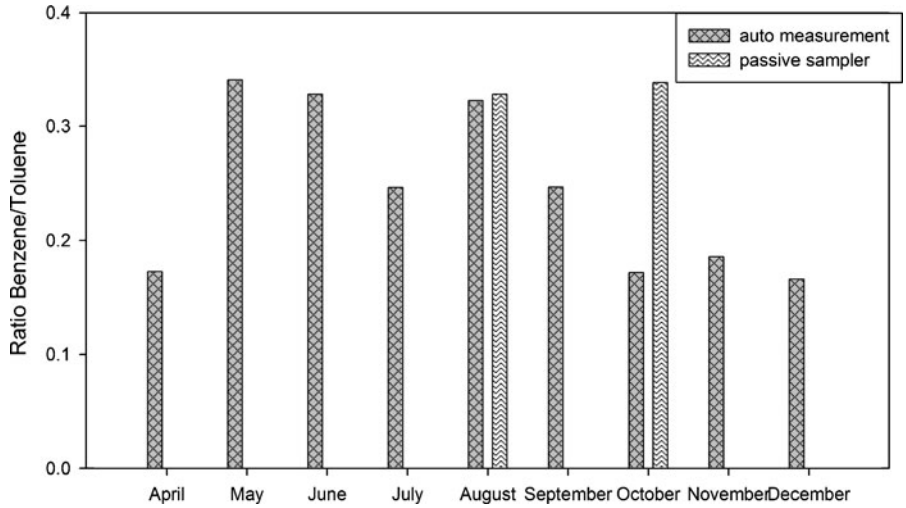

Fig. 7 Ratio of benzene to toluene calculated by the monthly average of automatic measurement and passive sampler data

to this seasonal variation. In summer, the monsoon dominates the weather, so when atmospheric conditions are highly unstable, the pollutants are easily diluted and BTX concentrations mostly remain at low values during the whole day. More photochemical reactions among air pollutants might also explain these results. Source emissions do not float by seasons in Suzohou; BTX concentrations consequently decrease in summer.

Integration of manual and automatic measurements

The measurement results derived manually using passive samplers and automatically using gas chromatography analyzer have been integratively analyzed in this section. Both of the measurement results show an increasing trend in BTX concentrations from August to October (Fig. 6), but the benzene and toluene manual measurement results are almost three times higher than the automatic measurements. Xylenes measured by passive samplers are total xylenes, including paraxylene, metaxylene, and xylene. The automatic measurements, on the other hand, using Gas955, analyze only paraxylene and metaxylene, so total BTX concentrations are numerically incomparable. A comparison between the Analyst passive sampling technique and the automatic reference methods has already been done by Bertoni

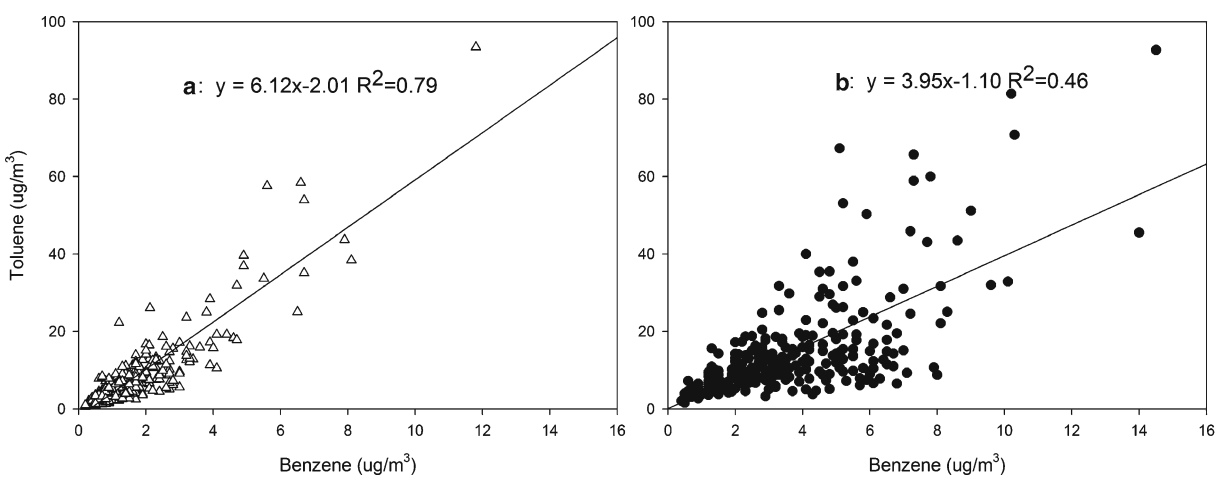

Fig. 8 Correlation of benzene and toluene at station B1 (**a**) and station C1 (**b**)

et al. (2000), which is not further studied in this work.

The higher average of benzene concentration (9.36 μg m^{-3}) obtained by manual measurement and 81% of the values exceed the European limitation (5 μg m^{-3}), but they are still low compared to most ambient concentrations reported worldwide (e.g., Fernandes 2002). In China, we have not had national regulation regarding ambient BTX limitation so far. The variation in different countries is due to the various possible sources of benzene and controlling strategies like gasoline regulation and measurement techniques used. Catalytic converters are widely used especially in North America to control vehicular emissions and result in low ambient benzene concentrations (e.g., Hao 2001).

We also found that the benzene/toluene (B/T) ratio increases in the warm period of the year but decreases in the cold period (Fig. 7). This differentiation could be explained by the difference in photochemical reactivity or photochemical ozone creating potential (POcP) of compounds. If the POcP of ethylene is identified as 100, then the POcP of benzene is 20 and of toluene is 55. During high insolation periods, toluene photodestructs and reacts with other atmospheric constituents. As a result, toluene is less abundant in relation to benzene. This ratio diminishes during cold months when both insolation and ambient temperature are greatly reduced. July is the rainiest month of the monsoon season in Suzhou and, as we expected, the evidence confirmed that the ratios were accordingly reduced. The B/T ratios are within the range from 0.16 to 0.38, significantly lower than in other cities worldwide where they vary in a range from 0.3 to 0.5 when associated with mobile sources (Fernandes et al. 2002).

Moreover, we calculated the correlation of benzene and toluene with daily average values by automatic measurements (Fig. 8). The correlation of benzene and toluene at station B1 ($R^2 = 0.79$) is higher than at station C1 ($R^2 = 0.458$). Theoretically, if the monoaromatics are emitted from mobile sources into ambient air, the average benzene and toluene concentrations correlate very well to each other at the traffic zone, and the coefficient indicates the compounds of used vehicle fuel (Palmgren 1999). In this case, our data might suggest that the fuel used in Suzhou could differ from that in Palmgren's study. More persuasively, there are other types of stationary sources which now exist near traffic station C1. These measurements also correspond with hot points in the manual measurement data shown on the isoconcentration maps.

Conclusions

A city-scale passive sampling investigation was performed in Suzhou both in summer and winter to determine and assess the BTX background levels. Isoconcentration maps provide visible spatial distributions of present benzene and xylenes concentrations, which are higher in the downtown center. Toluene concentrations are higher in the east part of Suzhou where the chemical industries are located. Concerning the administrative areas, total BTX mean values for the three campaigns differed in each district. They were highest in Xiangcheng and Pingjiang districts and lowest in Wuzhong and new industry districts.

Nearly one year of continuous measurement has built up a relatively large dataset. BTX monthly average records evidence a seasonal "U"-shaped trend, reaching its highest value in December and lowest value in August. The trend is affected by the local subtropical monsoon climate and inflected by obvious differences in daily variation. There are more fluctuations with higher peaks in spring and winter than in summer and autumn.

Though the average value of manual and automatic measurements differ a lot, the temporal and spatial distribution comply with each other that BTX concentrations in winter are significantly higher than in summer. Even source emissions are quite stable during the whole year in Suzhou.

The B/T ratio in Suzhou was observed to be larger during the warm period of the year and smaller during the colder period. The reason for the differentiation could be their different photochemical reactivity. The ratios fluctuated from 0.16 to 0.36, lower than other literature reported at 0.3–0.5, indicating higher toluene emissions from local sources, except for vehicles,

which should also be taken into account. The correlation of benzene and toluene is poorer at station C1 than at station B1, likely because the stationary sources other than vehicle emissions corresponded with manual measurement results showing a hot point near station C1. Given the fixed monitoring station sites, it suggests that the BTX measurements from this site do not give a representative monoaromatic pollution regarding the traffic zone. These data thus are inappropriate for roadside population exposure studies and strict traffic emission studies.

In order to observe and reduce BTX pollution in China in the future, it is necessary to establish relevant national regulations and carry out regional measurement studies.

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