

Distributions of phthalic esters carried by total suspended particulates in Nanjing, China

Wenxin Wang · Yinlong Zhang · Shuiliang Wang ·
Chinbay Q. Fan · Hui Xu

Received: 8 May 2011 / Accepted: 15 November 2011 / Published online: 8 December 2011
© Springer Science+Business Media B.V. 2011

Abstract Atmospheric trace phthalic esters (PAEs) carried by total suspended particulates were systematically investigated. A total of 450 air samples were collected at six typical locations and three specific micro-environmental sites (a stadium with a new plastic track, new cars, and a farming greenhouse with plastic film) in Nanjing metropolitan area of China from April 2009 to January 2010. The samples were analyzed by high-performance liquid chromatography and ultraviolet detection. The results are summarized as follows: (1) The dominant PAEs are dimethyl phthalate (DMP), dibutyl phthalate (DBP), and diethylhexyl phthalate (DEHP), which were found in the atmosphere of Nanjing. The average concentrations of DMP, DBP, and DEHP were 10.5 ± 1.2 , 62.3 ± 4.5 , and 33.3 ± 2.5 ng m⁻³, respectively, constituting 9.9%, 58.7%, and 31.4% of total PAEs (106 ± 8.2 ng m⁻³). (2) The dynamic variations of

atmospheric PAEs in the three specific micro-environmental sites showed that the PAE concentrations in the stadium with a new plastic track reduced to normal after 1 month remediation, while new cars need 6 months to remove their effect. The levels of PAEs in a farming greenhouse with plastic film were relatively high, but little PAEs accumulated in vegetables. (3) The vertical profiles from 1.5 to 40 m above ground display some fluctuations in PAE concentration, but no significant height dependence. This information will make a valuable contribution to the examination of the influence of atmospheric PAEs on the environment and human health.

Keywords Phthalic esters (PAEs) · Vertical distributions · Urban air pollution · Total suspended particulate (TSP) · Specific micro-environmental sites

W. Wang (✉) · Y. Zhang · S. Wang
College of Forest Resources and Environment,
Nanjing Forestry University,
Nanjing 210037, China
e-mail: wwx973555@yahoo.cn

C. Q. Fan
Gas Technology Institute,
1700 S. Mt. Prospect Rd.,
Des Plaines, IL 60018, USA

H. Xu
School of Environment Studies, Nanjing University,
Nanjing 210008, China

Introduction

Phthalic esters (PAEs) are one of the major chemical pollutants that exist widely in the global environment (Prokúpková et al. 2002; Clausen et al. 2004; Wensing et al. 2005). They are used in the manufacture of plastics, adhesives, cellulose film coating, and rubber (about 85% of the whole production) as indispensable plasticizers for increasing the flexibility of high molecular weight polymers (Casajuana and Lacorte 2003; Jonsson and Baun 2003). In

plasticizers, PAEs are not chemically bound to polymer chains and easily release to the environment, causing environmental hazards, such as the pollution of air, the contamination of water and soil, and serious effects on the food chain and human health (Staples et al. 1997). The environmental tracking of PAEs, including their estrogenic properties, is very important (Rhodes et al. 1995; Sung et al. 2003). The USA and several other countries classified the most commonly occurring PAEs as primary pollutants (Staples et al. 1997). The presence and persistence of PAEs in air depend on their chemical–physical properties and degradation processes (Vitali et al. 1997). The half-life values ($t_{1/2}$) of PAEs are in the range of years (Gavala et al. 2003) and the $t_{1/2}$ of PAEs adsorbed on total suspended particulates (TSPs) in the air (Wensing et al. 2005) could be even longer. Therefore, TSP–PAEs are one of the main pathogenic factors that are harmful to human health (Arcadi et al. 1998).

A large amount of PAEs are produced and consumed each year (Chen et al. 2006; Gao et al. 2005). Literature searches indicate that the atmospheric concentrations of PAEs have been monitored in some countries (Colón et al. 2000; Wang et al. 2000), but few publications on this topic exist about China. Governmental regulations of PAEs' limits vary in different countries (Bornehag et al. 2004; Fujii et al. 2003; Hartmann et al. 2004). No limits of PAE pollution in air have been established due to a lack of PAEs tracking records. Nanjing, as both a modern and ancient city in China, has continuous metropolitan modifications and constructions leading to serious urban air pollution. Coal combustion, soil/building trade, and metallurgy, the traditional pollution sources, contribute 80–90% of TSP to airborne particulate pollution in Nanjing. Of this 80–90% of TSP, building construction contributes 42.5%, coal combustion contributes 22.1%, soil dusts contribute 19.5%, and metallurgy dusts contribute 1.6% (Nanjing Environmental Monitoring Station 2011).

In this paper, we report our systematic investigation of major PAEs carried by TSP in the Nanjing metropolitan area. In this analysis, the concentration of each major PAE component—dimethyl phthalate (DMP), dibutyl phthalate (DBP), and diethylhexyl phthalate (DEHP)—of the total measured PAE concentration was determined. The PAE mapping explores information on PAEs' dynamic variations in three specific micro-environmental sites (a stadium

with a new plastic track, a new car parking lot, and a farming greenhouse with plastic film) and their effect on local air quality. The vertical profile of particulate PAEs was also generated from 1.5 to 40 m above the ground. Our results provide an insight into possible control strategies that might be used to improve the air quality in those areas.

Experiment

Reagents

Fourteen standard PAE compounds were purchased from Acros Organics (NJ, USA). LC-grade methanol, acetone, and n-hexane were supplied by Scharlance Chemie SA, Barcelona, Spain. Standard stock solutions ($100 \mu\text{g mL}^{-1}$) containing these PAEs were prepared in methanol and stored at 4°C . Work solutions were prepared daily by appropriate dilution of the stock solutions with methanol. Ultrapure reagents free of PAEs (Shanghai Chemical Reagent Co., China) and Milli-Q purified water (Millipore, Eschborn, Germany) were used.

Description of sampling sites

Six typical sites and three specific micro-environmental sites in Nanjing were selected for this study. Site S10 was designed specifically to determine the vertical profile of particulate PAEs. Table 1 summarizes the general characteristics of the sampling locations.

Collection materials and sampling protocols

A model KB-6120 sampler (Qingdao Jinshida Instrument Plant, Qingdao, China) was used at each site for collecting TSP samples. Air inlets were 1.5 m above the ground, and the air volume of every continuous collection on-site was 72 m^3 . Prior to sampling, the glass fiber filters (Whatman GF/F) were baked at 500°C for 4 h to remove trace organic compounds. After samples were collected, the filters were sealed in an aluminum foil bag and stored in a freezer at -4°C . Special distributions were taken into account in April, July, and October 2009 and January 2010. Each collection period was 10 days. TSP collection started at 8:00 a.m. and ended at 8:00 p.m. The total number of samples collected in this

Table 1 General characteristic of the ten monitoring sites

Site	Sampling zone	<i>N</i>	Site characteristic and measurement period
S1—Mai-Gao Bridge	Industrial zone	36	Approximately 10 km north of the center of Nanjing; has thermoelectric power plant, steel and petrochemical manufacturing, chemical plant, plastic plant, and an oil refinery (April 2009–January 2010)
S2—Zhong-Hua Gate	Traffic zone	36	10 km south of the center of Nanjing; adjacent to major highways with heavy traffic, where air quality is strongly impacted by roadway dust (April 2009–January 2010)
S3—Cao-Chang Gate	Cultural zone	36	5 km west of the center of Nanjing. (April 2009–January 2010)
S4—Shan-Xi Road	Commercial zone	36	2 km northwest of the center of Nanjing with a small residential area nearby (April 2009–January 2010)
S5—Xuan-Wu Lake	Scenic zone	36	A relatively non-polluted area located about 2 km east of the center of Nanjing at the hillside of Zijin Mountain (April 2009–January 2010)
S6—Rui-Jin Road	Residential zone	36	2 km southeast of the center of Nanjing (April 2009–January 2010)
S7—on a new plastic track	Micro-environmental site	45	3.5 km northeast from city center. Nanjing Forestry University Stadium, where the new plastic track was built (July 2009)
S8—in new cars	Micro-environmental site	72	The new 3000 Santana cars parked in Nanjing Forestry University campus (July–December 2009)
S9—in a plastic vegetable shed	Micro-environmental site	45	The farming greenhouse in Jiangning District, the south suburb of Nanjing, with dimensions 30 m (length)×15 m (width)×2.1 m (height) (December 2009–January 2010)
S10—in the front of the administrative building of Nanjing Forestry University	For vertical distribution	72	50 m in the front of the main gate of the administrative building of Nanjing Forestry University, a large residential area and a scenery district, is free of any local industries that contribute to air pollution (July 2009–April 2010)

N number of samples

campaign is 450, and the number of samples collected at each location is listed in Table 1.

To ensure the reliability of our determinations, before sampling, the samplers were carefully cleaned and calibrated. Equipment was preconditioned and checked for blank levels of PAEs. All pumps were calibrated using an electronic flowmeter in the field. The electronic flow meters were calibrated using a mini buck soap bubble meter in laboratory before and after sampling. Throughout the study, the variations of flow rate were <2% in the sampling periods. All filters were conditioned for 24 h by desiccating under refrigeration (Lamb and Adin 1983).

Sample extraction and concentration

The low levels of PAEs were extracted and the complex matrix of samples was designed to ensure a reliable determination. In the laboratory, the weight of

suspended particulate was obtained by subtracting filter tare value. The filters were then cut into strips and soaked with appropriate amount of n-hexane and acetone mixture (1:1, v/v) for 30 min under ultrasonic agitation in a 500-mL clean glass jar sealed with a Teflon-lined cap. Ice was used to keep the temperature of the ultrasonic bath below 10°C to prevent the target compounds from any evaporation.

After agitation, the solution was filtered through a baked glass fiber paper in Pasteur pipettes to remove any particles and further concentrated to about 1 mL by rotary evaporation at 4°C under vacuum (Heidolph, Germany). Then, 1 mL of solution was added into a 300×10 mm (I.D.) glass column filled with 13 g treated silica gel and 4 g of neutral alumina (grade II); eluted with 100 mL of acetone and n-hexane mixture (1:9, v/v). The eluate was concentrated to near dry in rotary evaporation at 4°C under vacuum and then diluted with 1 mL of methanol for high-performance liquid

chromatography (HPLC) analysis. Meanwhile, a blank assay was carried out with a blank filter as described above (Psillakis et al. 2004; Peñalver et al. 2001).

The vegetable sampling was carried out in the farming plastic greenhouse located in Jiangning District, the south suburban of Nanjing. Nine tomatoes were collected in different spots and then washed with tap water. From each tomato, a 10-g portion was cut, to which an appropriate amount of acetone and n-hexane mixture (1:1, *v/v*) was added, and then, it was stirred at high speed for 5 min. The residue was discarded after ultrasonic extraction for 30 min below 10°C to prevent any volatilization of the target compounds. The filtrate was extracted twice with n-hexane and acetone mixture (1:1, *v/v*); the organic phase was concentrated to near dry by rotary evaporation at 4°C under vacuum. Later procedures were similar to the above preparation of TSP samples (Psillakis et al. 2004).

Sample analysis

Analytical methods and the procedures were outlined by Peñalver et al. (2001) and Guo and Wang (1997). An HPLC (model 600, Waters Inc., USA) with a UV detector (model 2996, Waters Inc., USA), equipped with a 250×4.6 mm (I.D.) ODS column (Waters Inc., USA), was used for the separation and quantification of PAEs. Ten microliters of the filtered sample solution was injected into the ODS column placed in an oven at room temperature. The chromatograms were recorded by a Waters Empower Chromatography Manager System (Waters Inc., USA). The eluant used was the mixture of 90% methanol and 10% water at a flow rate of 1.0 mL min⁻¹. Detection was set at a wavelength of 228 nm. An ultrasonic cleaner (The Second Medical Instrument Plant, Beijing, China) was used for sonication of sample solution and mobile phase. All organic solvents used were tested for possible contaminants. Blanks were extracted and examined to provide an assessment of the blank contamination introduced by laboratory procedures, and field blanks were prepared and handled by exactly the same procedures as those used for the source samples for contaminants. The individual components in the TSP samples were identified by comparison with the above standard reagents. The analytical method validation was

confirmed with fortification and recovery studies (Batlle and Nerín 2004). The overall precision of the HPLC was < ±10% for all of the individual PAEs.

Quality assurance

Since phthalates are ubiquitous environmental contaminants, considerable care must be taken to avoid sample contamination, which is one of the main problems throughout the analytical process. All plastic instruments were strictly prohibited in the experiments (Tan 1995). The detected PAEs species were DMP, DBP, and DEHP. For the recovery evaluation of the PAEs by this method, a certain amount of the standard mixture, whose concentrations were similar to those in real samples, was spiked onto one half of a clean filter. After drying, it was treated as a real sample. The mean recovery (*n*=6) was calculated from the difference in the obtained concentration between the spiked sample and the unspiked one. The mean recovery fell 88–105% for DMP, DBP, and DEHP and the relative standard deviation was 3.8–9.2%. All data present here were corrected by the recoveries. The recoveries from standard spikes were treated and processed like samples. The detection limit of the PAEs by this method was defined as the signal/noise ratio of 3. The detection limits were 0.05 ng for DMP, 0.01 ng for DBP, and 0.06 ng for DEHP, respectively. To check any contamination during sampling, transporting, and storing of air samples, a field blank sample (a clean glass fiber filter) was collected at each sampling site in each collection. The field blank filter was placed unopened next to the samplers for the duration of sampling, after which they were returned to the laboratory and treated as regular samples. Laboratory blanks (clean filters) were run and analyzed simultaneously with every nine samples. The blank tests for PAEs were accomplished using the same procedure as the recovery tests without adding the known standard solution before extraction. In this study, the total concentrations of PAEs in each field blank, including laboratory blanks, were found to be less than the detection limits (Jakobsen et al. 2003).

Statistical methods

To characterize the distribution of the data, all data present here were distributed as arithmetic means of

nine observations ± SD. Analytical precision of PAEs measurement was determined by replicated measurements of separate aliquots of a representative number of samples. The relative standard deviations were calculated to determine the precision of the analysis.

Results and discussions

Distribution of PAEs at six typical locations

There are 14 important commercial PAEs for consideration: DMP, diethyl phthalate, diallyl phthalate, di-n-propyl phthalate, DBP, diisobutyl phthalate, butylbenzyl phthalate, butyloctyl phthalate, diheptyl phthalate, di-n-octyl phthalate (DOP), diisooctyl phthalate, DEHP, diisononyl phthalate, and diisodecyl phthalate. Among them, DMP, DBP, and DOP have been listed as priority pollutants by China National Environmental Monitoring Center and the US Environmental Protection Agency (National Bureau of Environmental Protection 1992; Adams et al. 1995; Rhodes et al. 1995). The results of this survey highlight that in the Nanjing atmosphere, only DMP, DBP, and DEHP could be identified and quantified in TSP during the measurement period; other PAEs were found to be less than their detection limits. They could be detected at almost every site. Figure 1 shows the annual averaged PAE concentrations associated with TSP for six typical locations.

As shown in Fig. 1, the atmospheric averaged levels (in nanograms per cubic meter) were: DMP,

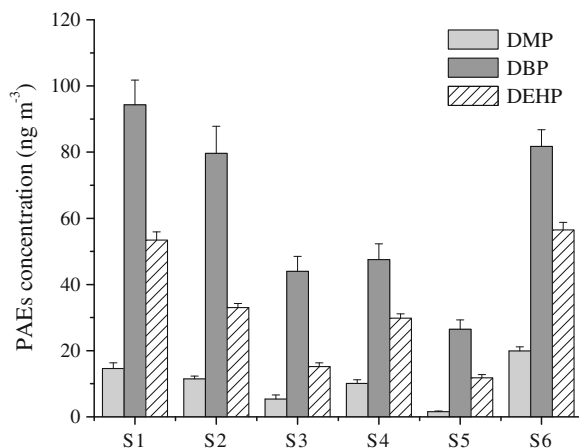


Fig. 1 Particulate PAE concentrations at each site from April 2009 to January 2010

10.5±1.2 ng m⁻³; DBP, 62.3±4.5 ng m⁻³; DEHP, 33.3±2.5 ng m⁻³. The concentrations in total and of the three target compounds were observed at each site. The highest level of ΣPAEs (here, ΣPAEs is the sum of DMP, DBP, and DEHP) occurred in site S1, followed by S6, S2, S4, S3, and S5 sites, with total concentrations of 160.1, 153.2, 128.3, 85.6, 68.3, and 40.7 ng m⁻³, respectively. Based on the above results, our analysis is as follows:

1. The distribution of PAEs at six typical sites differed greatly. The reasons could be (a) the distribution of emission sources, (b) meteorological conditions, and (c) characteristics of sampling sites (Tong et al. 1999). Their mean concentrations at S1 and S6 sites were about two to three times of that at S3 and S5 sites. The highest level of PAEs was obtained at sampling site S1, which is an industrial area. There are various chemical pollution sources, also including PAE emission. The high level of ΣPAEs denotes a high industrial contribution with respect to the typical industrial emissions. The second highest level of PAEs was observed at sampling site S6, which is in a residential area with dense population. At S6, PAEs come from indispensable polymer-related products in our daily life, mainly including plastic articles, house finishing material, and synthetic leather and lacquers (Casajuana and Lacorte 2003; Jonsson and Baun 2003).
2. In the high-density commercial zone (sampling site S4), increased plastic consumption would produce more pollution sources. The commercial emission could be an important source of PAEs in Nanjing. Many multi-story shopping buildings are the sources of volatile plasticizer PAEs that lead to remarkable levels of atmospheric pollution. However, the traffic site S2 showed high level of PAEs, which could be due to the resuspended road dusts by dense traffic flow. S2 definitely is strongly affected by heavy particulate pollution (Nanjing Environmental Monitoring Station 2011) because PAEs are adsorbed on/in particulates.
3. In addition, the site S3 lies in a cultural/educational area with schools, hospitals, theaters, cinemas, and a bookshop. The levels of PAEs observed at this site are mainly from personal emissions. S5 represents the scenic area, which is

located at the hillside of Zijin Mountain and is a relatively non-polluted area. The PAE levels are much lower than that of other sites. However, S5 is adjacent to city center, surrounded by a popular resort area, where total and individual PAE levels appeared to be significant (in 40.7 ng m^{-3}) and cannot be considered as a background in Nanjing urban area.

- Overall, the three PAEs were distributed widely due to high consumption of PAEs, especially DBP and DEHP. Both DBP and DEHP are main additives used in our manufacturing industries (up to 90% of total output) (Chen et al. 2006). Since the vapor pressure of DBP is about 100 times greater than that of DEHP, DBP evaporates more easily, leading to the highest observed atmospheric level (Thurén and Larsson 1990). PAEs are stable and are difficult to be chemically degraded (Tanaka et al. 2000) in the atmosphere. Sources of PAEs (Becker et al. 2004; Cadogan et al. 1993) could be emissions of various plastic articles, building materials, home furnishings, car interiors, and food packaging (Afshari et al. 2004; Teil et al. 2006). Thus, the particulate PAE distribution in Nanjing might reflect the global print of diverse sources for anthropogenic activities.
- The PAE concentrations measured in this study are compared with literatures (Table 2). Although the conditions of the studies from literature are different from our study, they provide a verification of PAEs associated with TSP in different regions. Table 2 showed that total and single PAEs levels in the urban atmosphere of Nanjing are generally higher than that in other areas of world, indicating the urgency of reducing PAE pollution to protect public health in Nanjing.

Dynamic variations of PAE concentrations in the three specific micro-environmental sites

PAEs are widely used as plasticizers and additives in many daily used products such as plastics, pesticides, paints, and cosmetics (Cai et al. 2003). As PAEs are not chemically bound in these products, they can be released from these products over time and emitted to the environment during their production, manufacture, and utilization (Fujii et al. 2003). To further assess the effects of PAEs emitted from various daily materials on regional air quality in more detail, three specific micro-environmental sites were investigated, i.e., a stadium laid with new plastic track, a parking lot with new cars, and a farming greenhouse with plastic film. A no adverse effect level of 4.8 mg/kg bw/day for testicular toxicity had generated from a three-generation reproductive study in rats (CSTEE 2004). In a worst scenario, children 0.5–3 years have been estimated to have an indoor air exposure of $22 \text{ } \mu\text{g/kg bw/day}$ (CSTEE 2004). Sheldon et al. (1993) reported that the worst case air contained concentrations of PAEs that were approximately 100-fold higher than those reported in the 90th percentile (240 ng m^{-3}) by 125 California homes during the daytime.

On a stadium laid with a new plastic track

In order to clearly illustrate the dynamic variations of airborne PAE concentrations on a stadium with a new plastic track (Fig. 2a), air samples were collected at the first day of every 10-day period. On the first day, high levels of DBP up to $1,990 \text{ ng m}^{-3}$, DEHP up to 729 ng m^{-3} , and DMP up to 306 ng m^{-3} were recorded from emission of the new plastic track. On

Table 2 Comparison of averaged PAE concentrations in air with other studies

PAEs	Nanjing China (this study)		Guangzhou China (Gao et al. 2005)		Paris, France (Teil et al. 2006)		Sweden (Thurén and Larsson 1990)		Netherlands (Peijnenburg and Struijs 2006)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
DMP	10.5	ND–75.0	–	–	–	–	0.1	ND–0.3	–	–
DBP	62.3	22.0–150.0	223	45–421	1.7	3.0–49.9	–	–	10.3	9–70
DEHP	33.3	4.9–52.0	213	34–572	2.0	0.28–77.0	5.4	2.4–10.4	11.9	8–333

Units are expressed in nanograms per cubic meter

ND non-detectable, DMP dimethyl phthalate, DBP dibutyl phthalate, DEHP diethylhexyl phthalate

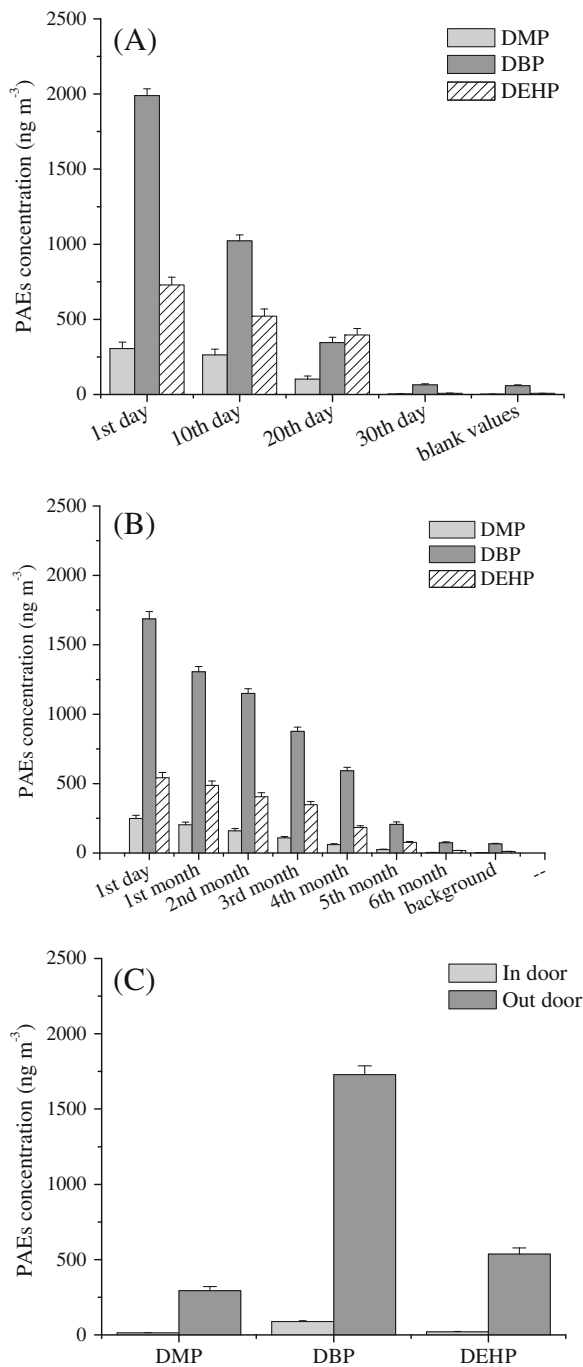


Fig. 2 Dynamic variations of PAE concentrations in a stadium with new plastic track (a), new cars (b), and a farming plastic film shed (c)

the 30th day test, due to air diffusion and dilution, the PAE concentrations decreased and gradually reached the background values (no plastic track). Exposure to

higher levels of PAEs would have adverse effects on athletes, so it was suggested that they avoid activities in the first month of the new field track (Toda et al. 2004).

Air quality in new cars

In China, the population of cars is increasing rapidly. Synthetic leather is used in most cars to upholster the seats and dashboard. Thus, the air quality inside cars is a great concern (Cadogan 1999). Nine new cars (Santana 3000) were selected as research objects. Air samples were collected at the first day of every month. Figure 2b showed that the PAE concentrations were relatively high, originating from internal painting materials and car interiors. Due to the interior temperature of cars and the natural air exchange, after 6 months, the PAE concentrations inside the cars slowly decreased to background levels. It could be suggested that passengers who drove new cars should pay attention to open car window frequently to circulate fresh air and avoid inhaling the air containing more PAEs. The measurable PAE concentrations were useful for car manufacturers to reduce possible PAE emission inside cars (Koch et al. 2004). The evaluation of PAE effects on passengers was important since automobile drivers could spend a considerable time in their cars (Koch et al. 2003).

In a farming plastic film shed

The consumption of farming plastic film in China now ranks the number one in the world. Large amounts of PAEs have been entered into agricultural ecosystem and caused serious environmental problems (Fromme et al. 2004). Therefore, a study on PAE pollution and accumulation in tomatoes inside a farm film greenhouse was carried out. We continuously determined the indoor and outdoor PAE concentrations from December 2009 to January 2010. Figure 2c showed that in the airtight greenhouse, PAEs released from farming plastic film and emitted into inside air and the indoor PAE concentrations were incredibly high, which differ greatly with the outdoor PAE concentrations. Meanwhile, we synchronously collected the tomatoes planted in the greenhouse and tested PAE concentration in them. The analytical data were: DMP $0.2 \pm 0.1 \mu\text{g g}^{-1}$, DBP $0.4 \pm 0.1 \mu\text{g g}^{-1}$, and DEHP $0.3 \pm 0.1 \mu\text{g g}^{-1}$, which

exceed $0.008 \mu\text{g g}^{-1}$ limit of DEHP in drinking water. There is no doubt that the DEHP contamination can influence vegetable quality (Kim et al. 2002; Sung et al. 2003).

Vertical variations of PAEs at specific site

Due to many multi-story buildings, especially in metropolitan Nanjing, the habitable heights have changed from the ground floor level to higher levels. Many people live in high-rise apartment buildings, and the indoor air pollutant concentrations are quite similar to those of outdoor air, which told us that the vertical profile of outdoor pollutants is important (Janhäll et al. 2003). The indoor air quality depends on air exchange rates, outdoor pollutant concentrations, and penetration efficiency of particles. The penetration efficiency is a function of particle size (Tripathi et al. 2004). The concentrations of pollutants change at different sites and different heights (Janhäll et al. 2003). The vertical distribution of PAEs described herein helps us to understand PAEs air pollution at different heights (Vitali et al. 1997). The vertical variations of averaged PAE concentrations in TSP at daytime were measured at S10. There were no significant anthropogenic sources in the immediate surroundings. The particulate concentration is approximately spatially constant over the study region. Although the present sampling does not cover a larger field of view, bulk data in this work show scientific representation of Nanjing urban area. Figure 3

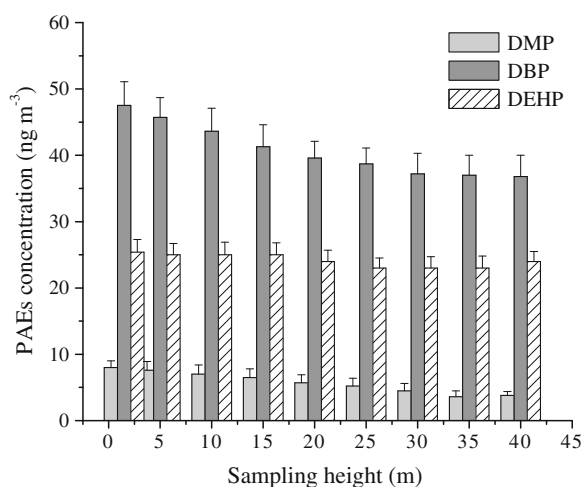


Fig. 3 Dynamic variation of PAEs in the air at different sampling heights

presents that there are slight decreases in DMP, DBP, and DEHP concentrations, as the height above the ground increases. At a height of 30 m, the daytime averaged DBP and DMP concentrations decayed to 7.6% and 45.0% of the maximum occurring at 1.5 m above the ground. As the height increased from 1.5 to 40 m, the attenuation of DBP concentration slowed down relatively. However, no significant changes on DEHP concentration over the measured height were observed. The reasons could relate to airborne particle size mode (Swartz et al. 2003) since the particles in the coarse mode have the much higher settling velocity than the fine mode at a low height level (from 1.5 to 40 m above the ground). Other factors, such as the physical properties of air particles, meteorological conditions of sampling spot, and chemical properties of PAEs, also contribute to this trend.

Conclusions

This paper systematically provided various detailed profiles of PAE concentrations at a wide range of sites across the city of Nanjing, China. The profile is important for us to understand the distributions of PAEs in air. DMP, DBP, and DEHP associated with TSP were monitored in the Nanjing atmosphere. The characteristics of sampling sites influence regional levels of PAEs. Quantitative data directly acquired from the three special environments showed that higher PAE levels present in polymeric material contributed to huge amounts of PAE emissions as a major source of these pollutants. The PAE concentrations in new cars and a stadium with a new plastic track were reduced to their background levels after 6 months and 1 month, respectively. The levels of PAEs in a farming plastic film greenhouse were relatively high, and small amount of PAEs accumulated in vegetables. No significant vertical variations were observable. The particulate PAE mass concentrations exhibited unique vertical variations, with little concentration gradient. The airborne PAEs may be accumulated in TSP. Atmospheric PAEs exist from many point sources over the studied urban atmosphere. The sources are mainly industrial, commercial, and personal emissions. These results would be a useful reference to generate control strategies of PAEs.

Acknowledgments This work was financially supported by the Natural Science Foundation of China (no. 30771696) and the Priority Academic Program Development of Jiangsu Higher Education Institutions. We would like to thank Guanghui Shen and Yaodong Yu for their help in providing chemical analyses for this study.

References

- Adams, W. J., Biddinger, G. R., Robillard, K. A., & Gorsuch, J. W. (1995). A summary of the acute toxicity of 14 phthalate esters to representative aquatic organisms. *Environmental Toxicology and Chemistry*, *14*, 1569–1574.
- Afshari, A., Gunnarsen, L., Clausen, P. A., & Hansen, V. (2004). Emission of phthalates from PVC and other materials. *Indoor Air*, *14*, 120–128.
- Arcadi, F. A., Costa, C., Imperatore, C., Marchese, A., Rapisarda, A., Salemi, M., et al. (1998). Oral toxicity of bis(2-ethylhexyl)phthalate during pregnancy and suckling in the Long-Evans rat. *Food and Chemical Toxicology*, *36*, 963–970.
- Battle, R., & Nerín, C. (2004). Application of single-drop microextraction to the determination of dialkyl phthalate esters in food simulants. *Journal of Chromatography. A*, *1045*, 29–35.
- Becker, K., Seiwert, M., Angerer, J., Heger, W., Koch, H. M., Nagorka, R., et al. (2004). DEHP metabolites in urine of children and DEHP in house dust. *International Journal of Hygiene and Environmental Health*, *207*, 409–417.
- Bornehag, C. G., Sundell, J., Weschler, C. J., Sigsgaard, T., Lundgren, B., Hasselgren, M., et al. (2004). The association between asthma and allergic symptoms in children and phthalates in house dust: A nested case-control study. *Environmental Health Perspectives*, *112*, 1393–1397.
- Cadogan, D. F. (1999). Health and environmental effects of phthalate plasticizers for poly (vinyl chloride)—an update. *Plastics Rubber and Composites*, *28*, 476–481.
- Cadogan, D. F., Papez, M., Poppe, A. C., & Scheubel, J. (1993). An assessment of the release, occurrence and possible effect of plasticizers in the environment. *Progress in Rubber and Plastics Technology*, *10*, 1–19.
- Cai, Y. Q., Jiang, G. B., Liu, J. F., & Zhou, Q. X. (2003). Multi-walled carbon nanotubes packed cartridge for the solid-phase extraction of several phthalate esters from water samples and their determination by high performance chromatography. *Analytica Chimica Acta*, *494*, 149–156.
- Casajuana, N., & Lacorte, S. (2003). Presence and release of phthalic esters and other endocrine disrupting compounds in drinking water. *Chromatographia*, *57*, 649–655.
- Chen, H., Wang, Y., & Zhu, R. H. (2006). Analysis of phthalates in plastic food-packaging bags by thin layer chromatography. *Chinese Journal of Chromatography*, *24*, 69–72.
- Clausen, P. A., Hansen, V., Gunnarsen, L., Afshari, A., & Wolkoff, P. (2004). Emission of di-2-ethylhexylphthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ. *Environmental Science and Technology*, *38*, 2531–2537.
- Colón, I., Caro, D., Bourdony, C. J., & Rosario, O. (2000). Identification of phthalate esters in the serum of young Puerto Rican girls with premature breast development. *Environmental Health Perspectives*, *108*, 895–900.
- CSTEE (Scientific Committee on Toxicity, Ecotoxicity and the Environment). (2004). EU Scientific committee on toxicity, ecotoxicity and the environment—opinion on the results of a second risk assessment of: bis(2-ethylhexyl) phthalate (DEHP) human health part expressed at the 41th CSTEE plenary meeting, Brussels, 08 January 2004.
- Fromme, H., Lahrz, T., Piloty, M., Gebhart, H., Oddoy, A., & Rüdén, H. (2004). Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany). *Indoor Air*, *14*, 188–195.
- Fujii, M., Shinohara, N., Lim, A., Otake, T., Kumagai, K., & Yanagisawa, Y. (2003). A study on emission of phthalate esters from plastic materials using a passive flux sampler. *Atmospheric Environment*, *37*, 5495–5504.
- Gao, R. Y., Guo, X. H., & Huang, R. D. (2005). Determination of phthalate ester in environmental samples by HPLC. *Technology Development of Chemical Industry (in Chinese)*, *34*, 34–37.
- Gavala, H. N., Alatraste-Mondragon, F., Iranpour, R., & Ahring, B. K. (2003). Biodegradation of phthalate esters during the mesophilic anaerobic digestion of sludge. *Chemosphere*, *52*, 673–682.
- Guo, W. L., & Wang, X. K. (1997). Analysis of phthalate esters in urban air and plastic greenhouse air. *Chinese Journal of Environmental Chemistry*, *16*, 382–386.
- Hartmann, P. C., Bürgi, D., & Giger, W. (2004). Organophosphate flame retardants and plasticizers in indoor air. *Chemosphere*, *57*, 781–787.
- Jakobsen, H. B., Nørrelykke, M. R., Christensen, L. P., & Edelenbos, M. (2003). Comparison of methods used for pre-concentrating small volumes of organic volatile solutions. *Journal of Chromatography. A*, *1003*, 1–10.
- Janhäll, S., Molnár, P., & Hallquist, M. (2003). Vertical distribution of air pollutants at the Gustavii Cathedral in Göteborg, Sweden. *Atmospheric Environment*, *37*, 209–217.
- Jonsson, S., & Baun, A. (2003). Toxicity of mono- and diesters of o-phthalic esters to a crustacean, a green alga, and a bacterium. *Environmental Toxicology and Chemistry*, *22*, 3037–3043.
- Kim, E. J., Kim, J. W., & Lee, S. K. (2002). Inhibition of oocyte development in Japanese medaka (*Oryzias latipes*) exposed to di-2-ethylhexyl phthalate. *Environment International*, *28*, 359–365.
- Koch, H. M., Drexler, H., & Angerer, J. (2003). An estimation of the daily intake of di(2-ethylhexyl)phthalate (DEHP) and other phthalates in the general population. *International Journal of Hygiene and Environmental Health*, *206*, 77–83.
- Koch, H. M., Drexler, H., & Angerer, J. (2004). Internal exposure of nursery-school children and their parents teachers to di(2-ethylhexyl)phthalate (DEHP). *International Journal of Hygiene and Environmental Health*, *207*, 15–22.
- Lamb, S. I., & Adin, N. E. (1983). Polar organic pollutants in air: A review of collection and analysis. *Environment International*, *9*, 225–243.

- Nanjing Environmental Monitoring Station. (2011). Environmental quality report-Nanjing, 2006–2010, Nanjing, China.
- National Bureau of Environmental Protection. (1992). *Study on the methods to preferentially control the potential and toxic chemicals* (pp. 116–122). Beijing: China Environmental Science Research Institute.
- Peijnenburg, W. J. D. M., & Struijs, J. (2006). Occurrence of phthalate esters in the environment of the Netherlands. *Ecotoxicology and Environment Safety*, *63*, 204–215.
- Peñalver, A., Pocurull, E., Borrull, F., & Marcé, R. M. (2001). Comparison of different fibers for the solid-phase microextraction of phthalate esters from water. *Journal of Chromatography. A*, *922*, 377–384.
- Prokúpková, G., Holadová, K., Poustka, J., & Hajšlová, J. (2002). Development of a solid-phase microextraction method for the determination of phthalic acid esters in water. *Analytica Chimica Acta*, *457*, 211–223.
- Psillakis, E., Mantzavinos, D., & Kalogerakis, N. (2004). Monitoring the sonochemical degradation of phthalate esters in water using solid-phase microextraction. *Chemosphere*, *54*, 849–857.
- Rhodes, J. E., Adams, W. J., Biddinger, G. R., Robillard, K. A., & Gorsuch, J. W. (1995). Chronic toxicity of 14 phthalate esters to *Daphnia magna* and rainbow trout (*Oncorhynchus mykiss*). *Environmental Toxicology and Chemistry*, *14*, 1967–1976.
- Sheldon, L., Whitaker, D., Kever, J., Clayton, A., & Perritt, R. (1993). Phthalates and PAHs in indoor and outdoor air in a Southern California Community. *Proceedings Indoor Air*, *3*, 109–114.
- Staples, C. A., Peterson, D. R., Parkerton, T. F., & Adams, W. J. (1997). The environmental fate of phthalate esters: A literature review. *Chemosphere*, *35*, 667–749.
- Sung, H. H., Kao, W. Y., & Su, Y. J. (2003). Effects and toxicity of phthalate esters to hemocytes of giant freshwater prawn, *Macrobrachium rosenbergii*. *Aquatic Toxicology*, *64*, 25–37.
- Swartz, E., Stockburger, L., & Gundel, L. A. (2003). Recovery of semi-volatile organic compounds during sample preparation: Implications for characterization of airborne particulate matter. *Environmental Science and Technology*, *37*, 597–605.
- Tan, G. H. (1995). Residue levels of phthalate esters in water and sediment samples from the Klang River basin. *Bulletin of Environment Contamination and Toxicology*, *54*, 171–176.
- Tanaka, T., Yamada, K., Tonosaki, T., Konishi, T., Goto, H., & Taniguchi, M. (2000). Enzymatic degradation of alkylphenols, bisphenol A, synthetic estrogen and phthalic ester. *Water Science and Technology*, *42*, 89–95.
- Teil, M. J., Blanchard, M., & Chevreuil, M. (2006). Atmospheric fate of phthalate esters in an urban area (Paris-France). *Science of the Total Environment*, *354*, 212–223.
- Thurén, A., & Larsson, P. (1990). Phthalate esters in the Swedish atmosphere. *Environmental Science and Technology*, *24*, 554–559.
- Toda, H., Sako, K., Yagome, Y., & Nakamura, T. (2004). Simultaneous determination of phosphate esters and phthalate esters in clean room air and indoor air by gas chromatography–mass spectrometry. *Analytica Chimica Acta*, *519*, 213–218.
- Tong, Q., Feng, S. Y., Ruan, Y. Y., Zhao, T. J., Yang, F., & Wang, Z. G. (1999). Phthalic esters in atmospheric particulate of different diameter in Huhehaote urban area. *Acta Science Circumstantiae*, *19*, 159–163.
- Tripathi, R. M., Vinod Kumar, A., Manikandan, S. T., Bhalke, S., Mahadevan, T. N., & Puranik, V. D. (2004). Vertical distribution of atmospheric trace metals and their sources at Mumbai, India. *Atmospheric Environment*, *38*, 135–146.
- Vitali, M., Guidotti, M., Macilenti, G., & Cremisinic, C. (1997). Phthalate esters in freshwaters as markers of contamination sources—a site study in Italy. *Environment International*, *23*, 337–347.
- Wang, J. L., Chen, L. J., Shi, H. C., & Qian, Y. (2000). Microbial degradation of phthalic acid esters under anaerobic digestion of sludge. *Chemosphere*, *41*, 1245–1248.
- Wensing, M., Uhde, E., & Salthammer, T. (2005). Plastics additives in the indoor environment—flame retardants and plasticizers. *Science of the Total Environment*, *339*, 19–40.