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Phthalate Residues in Greenhouse Soil from Beijing Suburbs, People's Republic of China

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Phthalate esters are widely used as additives in the polyvinyl chloride (PVC) (60%, w/w) and the total annual production is estimated around several million tons globally and continues to increase. Since phthalate esters are only physically bound to the plastic structure, they can leach out from the products during use and after disposal. Due to the high production quantities and widespread application, phthalate esters have become ubiquitous contaminants (Staples et al. 1997). Some of them were listed as priority pollutants by both the U.S. Environmental Protection Agency (EPA) and China National Environmental Monitoring Center. Di-n-butyl phthalate (DnBP) was also classified as a high-priority chemical for study by the National Institute of Occupational Safety and Health (Moorman et al, 2000). Although the acute toxicity was low, many studies showed that some phthalate esters, especially the most commonly used DnBP and di-(2-ethylhexyl) phthalate (DEHP), had carcinogenic as well as mutagenic and reproductive toxicity (Davis et al. 1994; Ema et al. 2000; Mylechreest et al. 1998; Tickner et al. 2001). Recently, there has been an increasing concern regarding the suspected endocrine disrupting potential of phthalate esters (Catherine et al 2001; Colon et al. 2000). As highly lipophilic compounds, phthalate esters exhibited a strong potential for adsorption onto the particles, and when remained in the soil, they not only affected the crop growth and production quality (Herring et al. 1988; Virgin et al. 1981) but also could leach from soil into the ground water, thus becoming a threat to the aquatic environment. They also could accumulate in human body via the food chain. In fact, phthalates and their metabolites were common contaminants found in human urine samples (Hoppin et al. 2002).

Beijing, as the capital, is located in the north of China and greenhouses are widely developed on its outskirts. However, up to now, little information is available on the phthalate contamination in soil, especially in greenhouse soil, of Beijing. The aim of this paper is to determine the phthalate residues in greenhouse soil of Beijing suburbs. We expect that our study will contribute to more complete comprehension of the city soil quality.

MATERIALS AND METHODS

The standards of phthalate esters (dimethyl phthalate (DMP), diethyl phthalate

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(DEP), di-iso-butyl phthalate (DIBP), DnBP, DEHP, di-n-octyl phthalate (DnOP)) were purchased from Supelco. All solvents were of analytical purity (Beijing Chemical Factory, China). Florisil (60-100 mesh, Supelco.) was activated at 140 ℃ for 16 hr. Anhydrous sodium sulfate (Beijing Chemical Factory) was heated at 600℃ for 12 hr to remove all the organic compounds. In order to avoid contamination by phthalate esters during the experiment, plastic tubing and containers were abstained and the solvents were redistilled in all-glass system before use. Glassware was treated successively in the following order: washed with acetone and water, soaked in 5% $K_2Cr_2O_4$ sulfuric acid solution overnight, washed with water and distilled water, dried in oven and rinsed with acetone just before use.

Eight sites at different locations on the outskirts of Beijing were chosen in April 2001. The samples S1 to S6 were collected from greenhouses and S2' and S3' were two film mulch soil samples collected near the sites of S2 and S3, respectively. A control sample was collected from farmland where no plastics were used. In each site, ten cores were sampled at an approximate depth of 0~20 cm with a stainless-steel spoon. The soil was air dried at room temperature, thoroughly mixed, ground to 30 mesh and stored in glass bottles at -4℃ until further processing. The remaining water content in the soil was determined gravimetrically after drying individual subsample in an oven at 105℃ for 12 hr. All the results were reported as dried weight.

About 5 g of soil was ground with anhydrous sodium sulfate into free flowing powder. The sample was ultrasonically extracted in centrifuge tube with 30 mL of 1/1 (v/v) acetone/hexane for 5 min and then the extract was separated by centrifugation. The process was repeated for three times. The solvents in combined extract were evaporated by K.D. apparatus with a gentle stream of nitrogen, and then hexane was added as solvent. The concentrated extract was transferred to a chromatograph column (30 cm×10 mm id) containing 5 g of activated Florisil and about 1 g of anhydrous sodium sulfate on the column top. The first fraction eluted by 100 mL of 91/9 (v/v) n-hexane/diethyl ether contained pesticides and was described in separate paper. The second fraction eluted by 60 mL of 50/50 (v/v) n-hexane/diethyl ether contained all the phthalates analyzed. The solvent was evaporated by K.D. apparatus with a gentle stream of nitrogen, and then the solvent was adjusted to 0.2 mL for GC analysis.

The identification and quantification of phthalate esters was carried out on a Hewlett Parkard 6890GC/5973 MSD system with a fused silica capillary HP-5 column (30 m × 0.25 mm id, 0.25 μm film thickness). The carrier gas was helium with a flow of 1 mL/min. 1μL of sample was injected in splitless mode. The injector and detector temperature were 280℃ and 300℃, respectively. The ion source temperature was 230℃. The mass spectrometer was operated in full scan mode (from 50 to 500D) using electron impact ionization (70 ev). The temperature program was as follows: initial temperature 50℃ held for 2 min, followed by a 4℃/min ascent to 280℃, maintained for 10 min.

The limit of detection (LOD) for the phthalate esters, estimated as three times response of signal-to-noise of 3:1 in blank sample, ranged from 0.01 mg/kg for DMP to 0.22 mg/kg for DnBP. The average recovery experiments of three times were done by spiking known concentration standards (2.0 mg/kg) in uncultured soil (previously found containing very low amounts of phthalate esters), ranged from 86% for DMP to 114% for DnOP and the relative standard deviation was 7-12%.

RESULTS AND DISCUSSION

The full scan chromatogram of phthalate esters in one greenhouse sample is shown in **Figure 1**, in which every phthalate ester was completely separated. Similar chromatograms were obtained from other samples. Six phthalates including DMP, DEP, DIBP, DnBP, DEHP and DnOP were detected. Of nine samples, concentrations of DnOP were all below the LOD, DMP was found in one sample (S2') and DEP was detectable in two samples (S1 and S2'). DIBP, DnBP and DEHP were the most frequently identified compounds in all samples.

The concentration and distribution patterns of residual phthalates in the soil are presented in **Figure 2**. It seemed that there was no significant difference in the distribution patterns between greenhouse and film mulch samples. Similar conclusion has also been reported by other authors (Tang et al. 1993). The total concentrations of phthalate esters in the greenhouses varied from 1.34 to 2.80 mg/kg, which are higher than those in the control. The highest residual phthalate concentration was in the film mulch sample S2'. DIBP, DnBP and DEHP were the major phthalates accounting for more than 97% of total phthalates studied. No previous data about DIBP in soil have been reported, while the compound was found in all of our samples amounting to 18-35%. A survey (Tienpont et al. 2000) of phthalate esters residues in the greenhouse atmosphere showed that the sum of the three compounds accounted for about 90% and DIBP made up about 30% of total phthalates studied. Its distribution pattern is similar to our results.

The trend of high DIBP, DnBP and DEHP values in soil is consistent with their high production. As for the different amounts of individual phthalate, the residual level of DEHP in the sample was much lower than that of DnBP despite the fact that DEHP was the most widely employed phthalate in PVC and its degradation rate in soil was higher than that of DnBP (Shanker et al. 1985). The reason may be that the higher solubility and vapor pressure make DnBP easily volatilized from PVC. The results of Wang et al. (2002) that concentration of DEHP in greenhouse atmosphere was also lower than that of DnBP supported our explanation.

There are few investigations on phthalate esters in the greenhouse soil in China. In Jinan (Wang et al. 2002), a city in the east of China, phthalate esters in greenhouse soil and air were higher than those of control samples. The mean concentrations of DnBP and DEHP in greenhouse soil were 2.96 mg/kg and 2.70 mg/kg, respectively, while those outside the greenhouse were 1.25 mg/kg and 1.15 mg/kg,

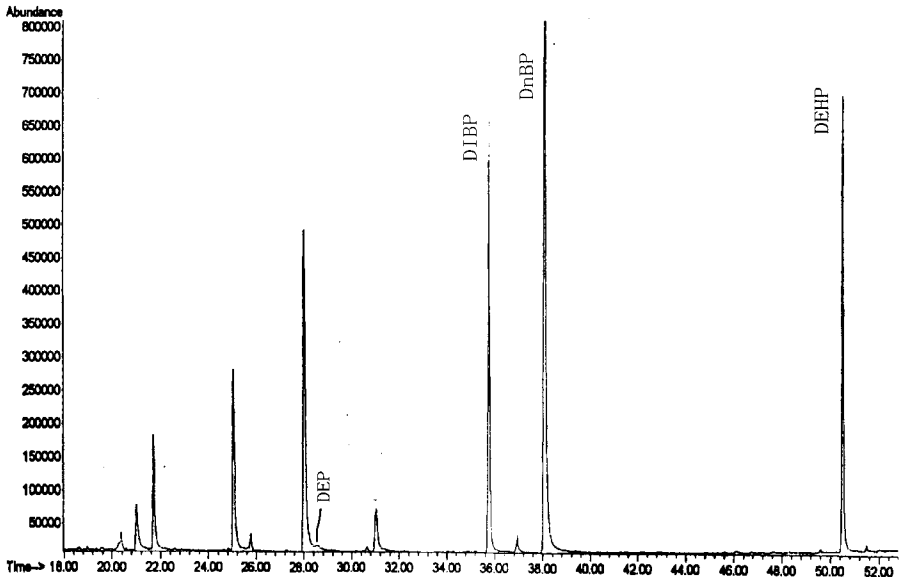

Figure 1. Total ion scan of phthalate esters in the greenhouse soil sample. DEP=diethyl phthalate, DIBP=di-iso-butyl phthalate, DnBP=di-n-butyl phthalate, DEHP=di-(2-ethylhexyl) phthalate.

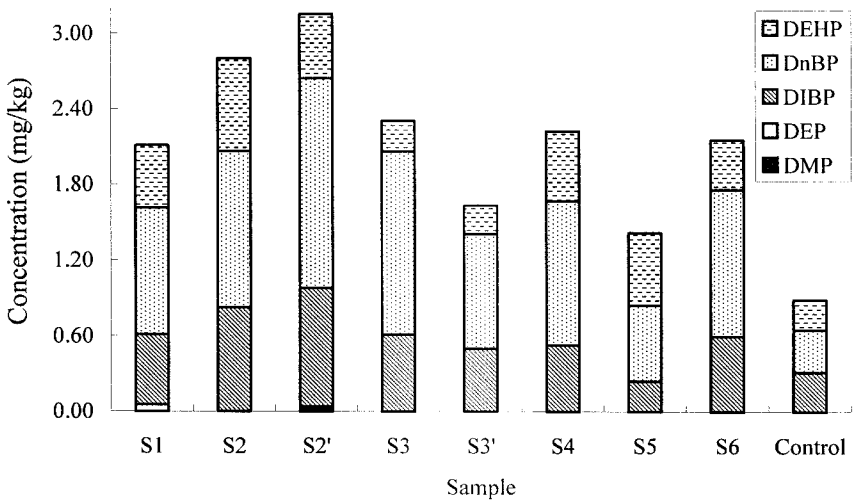

Figure 2. Concentration and distribution patterns of residual phthalate esters. S1, S2, S3, S4, S5 and S6 are six greenhouse samples; S2' and S3' are two film mulch samples.

respectively. In a northeast city Shenyang (Tang et al. 1993), the mean value in the

greenhouse soil was 0.60 mg/kg for DnBP and 0.63 mg/kg for DEHP. Compared with the data above, phthalate esters residue in Beijing greenhouse soil are lower, except DnBP is slightly higher than those in Shenyang city. Up to now, we have not found studies about phthalate esters in greenhouse soil in other countries. Compared to the reported concentrations for soils and sediments (0.001-10 mg/kg) (Ritsema et al. 1989), the residues of phthalate esters in Beijing greenhouse soil are not serious.

Phthalate esters exhibit harmful effects on plants as mentioned before, however the damage occurs only at considerably higher concentrations. The study of Wang et al. (2002) also showed that plants were not remarkably affected by the phthalate esters at low concentration. Therefore the level of phthalates found in Beijing suburbs will not result in harmful effects on vegetables.

Besides the leaching from plastics, other possible pathways of phthalate esters entering greenhouse soil system are via application of sewage sludge as agricultural fertilizer (Rhind et al. 2002), irrigation by polluted water (Zhao et al. 1982), or application of some pesticides using phthalates as ingredients. To define the real major sources needs further investigation.

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