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Analysis of Phthalate Esters in Air, Soil and Plants in Plastic Film Greenhouse

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Abstract: The phthalate esters such as DMP, DEP, DBP and DEHP in air, soil and plant samples in plastic film greenhouse were clean up with fine silica gel column and determined with HPLC. It was found that the concentrations of PEs in air and soil samples in plastic film greenhouse are much higher than those of contrast samples. But concentrations of PEs in plants in plastic film greenhouse are not remarkably affected by the pollution of air and soil.

Keywords: Phthalate esters, plastic film greenhouse, analysis.

Phthalate esters (PEs) are abundant chemicals commonly used as plasticizer, especially in the manufacture of poly(vinyl chloride) (PVC). Global annual consumption of PEs is about 2×10^7 tons. Now PEs have been a kind of ubiquitous contaminants in the biosphere and have been found world-wide in atmosphere[1], water[2], sediment[3] , soil[4] and biota[5]. Although most PEs have a very low acute toxicity, it is reported that chronic exposure to some PEs, such as di-(2-ethylhexyl)phthalate (DEHP), could cause liver cancer in rats and mice and decrease human platelet function. Six PEs, *ie*. dimethyl-phthalate(DMP), diethylphthalate(DEP), dibutylphthalate(DBP), butylbenzylphthalate (BBP), dioctylphthalate(DOP) and DEHP are listed as priority pollutants by US EPA. More attention has been paid to analysis of PEs in environmental samples.

Nowdays, plastic film greenhouse are widely developed to grow vegetables. The air, soil and plants in plastic film greenhouse as a small environment system are seriously polluted by PEs, but the result has not been reported . This paper presented the analysis results of PEs in the air, soil and plants in plastic film greenhouse.

Experimental

All solvents used were of analytical grade and distilled before use. Dichloromethane, petroleum ether (30-60°C), diethyl ether, methanol and ketone were obtained from Jinan Chemical Works. Silica gel H(10--40μm) was obtained from Qingdao Ocean Chemical Works. Phthalate esters were of analytical grade and obtained from Jinan Chemical

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Works(DMP, DBP, DOP)and Shanghai Chemical Regent Works (DEP, DEHP) respectively. All glassware used were soaked in 5% chromic acid solution overnight, rinsed with redistilled water, ketone and petroleum ether successively.

The PEs in atmosphere were adsorbed on GDX-102 resin(60-80 mesh) by using air sampling pump, then extracted with dichloromethane for 6 h in a Soxhlet extractor. The extract was filtered and concentrated to 1 mL in a K-D concentrator at 50°C. The soil samples were collected both in-side and out-side of the plastic film greenhouse in different depths, then extracted with 20% acetone in petroleum ether for three times by using supersonication. The extract was filtered and concentrated to 1 mL. The plant sample was washed with water and homogenized with petroleum ether, extracted with 10% acetone in petroleum ether for three times by using supersonication. The extract was filtered and washed with water, dried over Na_2SO_4 and then concentrated to 1 mL.

2.5 g silica gel(10-40μm) was packed in a 1.0×10 cm glass column. The extract of the sample was adsorbed on 0.3 g silica gel(10-40μm) and added onto the top of the chromatographic column, eluted with 6.0 mL petroleum ether/diethyl ether (10/0.5, v), then with 10.0 mL petroleum ether/diethyl ether(10/3, v). The flow rate was 0.3-0.4 mL/min with vacuum suck. The initial 8 mL eluent was discarded and the following 8 mL eluate was collected as PEs fraction. The PEs fraction was concentrated nearly to dryness with N_2 stream and then redissolved in 1.0 mL methanol for HPLC analysis.

A Beckman model 344 HPLC equipped with a model 163 variable wavelength ultra- violet detector (Beckman, USA) was used for determination of PEs on a Dupont Zorbax- ODS C_{18} column (15cm×4.6mm ID). A mobile phase of 85% methanol in water was used at a flow rate of 1.0 mL/min. UV detection wavelength was 228 nm.

Result and Discussion

A major problem in the analysis of PEs in environmental samples is the high possibility of contamination from the reagents, solvents, equipments and other materials, as well as the air in the laboratory during the sample treatment,. So the method was required with minimum steps and the smallest quantities of solvents and adsorbents to minimize the risks of high procedural blanks and ensure reliable analysis results.

Conventional liquid solid chromatography using adsorbent with large particles (100-200μm) could not isolate sufficient PEs from pollutants. Dual column liquid solid chromatography with different adsorbents was developed to get more sufficient separation, but more operation steps and large volume of eluents were needed resulting in high procedural blanks. As we know that the column efficiency of liquid solid chromatography is in inverse proportion to the diameter of adsorbent particles, so the fine silica gel (10-40μm) was used to get more satisfactory separation. With which the column efficiency was raised remarkably and only small amount of the adsorbent and solvent were needed, and the procedural blank was avoided. **Table 1** shows the recoveries of some PEs standards spiked in soil and plant samples. From **Table 1** it can be seen that PEs in these samples were almost completely isolated from the pollutants (The average recoveries of PEs were found to be 86-98%).

Table 1 Average recoveries of PEs standards spiked in plant and soil samples

Compounds	DMP	DEP	DBP	DEHP	DOP
Plant sample(%)	89.2±5.6	90.4±3.8	95.7±5.2	98.4±4.2	96.0±3.1
Soil sample(%)	86.4±4.7	88.3±5.0	97.6±6.2	96.1±5.4	93.2±4.5

Plastic film greenhouse is a special closed environment. PEs used as plasticizer in plastic film can transfer into the environment and could be absorbed by plants. The plastic film greenhouse studied in this work has been used for two years. The air, soil and plants samples were collected in december, 2000. Six independent samples for each kind of samples were studied. **Table 2** and **Table 3** show the analytic results of PEs in air and soil samples. From the **Tables** it can be seen that the concentrations of PEs in air and soil in the plastic film greenhouse are much higher than those of contrast samples.

Table 2 Concentrations of PEs in air samples

Compounds	DMP	DEP	DBP	DEHP
Plastic film greenhouse samples(ng/m^3)	56±20	32±18	1910±480	550±210
Contrast samples*(ng/m^3)	ND	ND	224±46	56±18

*The contrast air samples were sampled in urban area of Jinan in december, 2000

Table 3 Analytic results of PEs in soil samples

Compounds	Concentrations (mg/kg)							
	Inside of plastic film greenhouse				Outside of plastic film greenhuose			
	5cm*	10cm	15cm	25cm	5cm	10cm	15cm	25cm
DBP	2.6±0.5	3.6±1.1	3.2±0.9	2.5±0.8	1.5±0.6	1.4±0.7	1.2±0.7	0.9±0.4
DEHP	2.7±0.6	3.4±0.7	2.9±0.9	1.8±0.6	1.2±0.5	1..3±0.8	1.3±0.6	0.8±0.4

*The depth of the soil sample collected.

The analytic results of PEs of plants grown in plastic film greenhouse are given and compared with PEs of those grown in field condition in **Table 4**. It showed that the concentrations of PEs in these two samples are not different so much. The concentrations of PEs in plants are not remarkably affected by the pollution of air and soil of plastic film greenhouse because the bioconcentration factors of PEs for various plants are very small (0.01-0.3)[5]. Since the plant leaves uptake PEs *via* air is more than fruits and root *via* soil[6], the concentrations of PEs in chinese cabbage (leaves) grown in plastic film greenhouse are higher than those in contrast samples.

Table 4 Analytic results of PEs in plant samples

Compounds	Concentrations (mg/kg)					
	Plastic film greenhuose samples			Contrast samples*		
	Chinese cabbage	Cucumber	Summer squash	Chinese cabbage	Cucumber	Summer squash
DBP	1.7±1.1	0.9± 0.5	1.3±0.7	1.2±0.8	1.0±0.8	0.9±0.7
DEHP	1.9±1.3	1.2± 0.7	1.0±0.6	1.4±0.7	0.8±0.7	1.1±0.9

*The contrast plant samples were grown in natural environment in July, 2000

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