Survey of phthalate pollution in arable soils in China

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The problem of pollution by phthalates is of global concern due to their widespread occurrence, toxicity and endocrine disruption properties. The contamination by phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) in 23 arable soils throughout China was investigated to evaluate the present pollution situation. The survey results demonstrated that phthalates were ubiquitous pollutants in soils in China. The total concentrations of phthalates differed from one location to another, and ranged from 0.89 to 10.03 mg kg^{-1} with a median concentration of 3.43 mg kg^{-1}. Among the phthalates, DEHP was dominant and detected in all 23 soils. DEP and DBP were also in abundance, and DMP was rarely detected. Similar contamination patterns were observed in all 23 soils. A distinct feature of phthalate pollution in China was that the average concentration in northern China was higher than that in southern China. In addition, a close relationship was observed between the concentration of phthalates in soils and the consumption of agricultural film. The correlation showed that the application of agriculture film might be a significant pollution source of phthalates in arable soils of China. The potential risk of phthalates in soils was assessed on the basis of current guide values and limits.

Phthalates are a family of chemicals and some phthalates are used as ingredients in pesticide and various consumption products. Phthalates are known as plasticizers and this use has resulted in their omnipresence in the environment.

Initially, phthalates were considered as substances of low toxicity. However, further studies revealed the possible toxic, carcinogenic, mutagenic, and teratogenic effects of phthalates on animals[1] although their effect on humans is still uncertain. Recent reports on their endocrine disrupting properties concern long-term hazardous effects on the environment from various aspects. Acting as hormone mimics of antagonists or through indirect pathways, phthalates exhibit multiple dangers to human reproductive health.[2] A series of studies suggested that increasing exposure to phthalates might be partially responsible for the recent decline in the male ratio,[3,4] the premature breast development in young Puerto Rican girls,[5] and the development of breast cancer in humans.[6] Therefore, the Japan Environmental Agency designated phthalates as endocrine disruptors.[7] The U.S. Consumer Product Safety Commission in 1998 called for the manufacturers of toys, baby pacifiers, and medical supplies to remove the most toxic phthalates from their products. Although phthalates are less persistent in the body and in the environment than many other synthetic organic compounds, the continuous release of large quantities of phthalates into the environment ensures that concentrations and exposures remained substantial. Some researches suggested that phthalates might persist in human body tissues for longer periods than previously assumed.[8]

Due to this environmental behavior phthalates in the environment have been widely surveyed, such as in the atmosphere,[9] in surface fresh water and marine water,[10,11] in soils,[12] in organisms,[13] and in humans.[14] However, there was little information about the contamination in arable soils throughout China.

China is a developing country and agriculture occupies an important position. Plastic film is applied extensively in Chinese agriculture. The national consumption of plastic film is estimated to exceed 1.1 million tons per year and the agricultural land covered by film was estimated to be about 36.2 million acres, resulting in a film residue in the agricultural soils, which was reported to be as much as 108.5 kg $acre^{-1}$. The soil is the main organic pool, which receives phthalates *via* atmospheric deposition, precipitation from wastewater and infiltration from cast off and film residue. Considering the agricultural situation in China, the pollution by phthalates in agricultural soils might be of considerable significance.

In the present survey dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) were chosen as representative phthalates, which the U.S. Environmental Protection Agency recognized as priority pollutants.[15] The purpose of this survey was to investigate the current state of phthalate pollution and possible pollution sources in arable soils in China and to assess their ecotoxicological potential effect on the environment.

1. Materials and methods

1.1 Sampling

Field culture surface soil samples were collected from 23 sites, which were located in an extensive geographical region in China (Fig. 1). The sampling sites were far away from cities to avoid the influence of factories as much as possible. The surface layer of soil (0–5 cm) was sampled using a vertical corer, and packed in aluminium foil and deep frozen for storage. Before chemical analysis, soil samples were air-dried in a clean laboratory and mixed thoroughly. Any foreign objects such as sticks, leaves, and rocks were discarded and then samples were screened through a 2 mm sieve.

1.2 Chemicals

Phthalate reference standards DEHP, DEP, DBP and DMP were purchased from AccuStandard Inc, USA. The surrogate standard, dicyclohexyl phthalate (DCP), 2 mg, was dissolved in 100 ml hexane. The internal standard, benzyl benzoate, which was suggested by the EPA, was prepared by spiking benzyl benzoate in hexane at 5 mg ml^{-1}. All reagents were pesticide

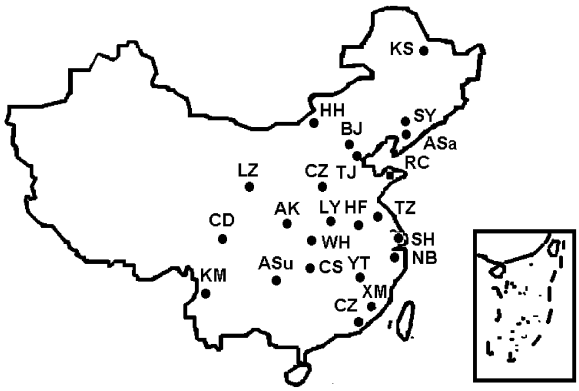

Fig. 1 Sampling sites.

grade. The laboratory glassware was cleaned with acid and detergent, rinsed with distilled water and acetone, and then heated to 400 °C overnight prior to use. Silica gel (60–80 mesh) was rinsed with dichloromethane, and then heated to 180 °C for 16 h to activate. When cooled 3% of organic-free reagent water was added to silica gel and mixed thoroughly by rolling for 10 min, and finally let it stand for at least 2 h. Glass wools, sodium sulfate and filter papers used in the sample preparation procedures should be thoroughly cleaned with dichloromethane in order to avoid contamination of phthalates before use.

1.3 Analysis

A portion of 10 g soil sample was placed into a thimble filter and extracted with 100 ml mixture of hexane and dichloromethane (1 : 1) for 24 h at 5–6 min cycle^{-1}. The extract was carefully concentrated to 2 ml by rotary evaporator. The residue was transferred to column (1 cm id × 10 cm) prepared by packing silica gel (60–80 mesh), covered by a 2 cm layer of sodium sulfate, which was used to clean up the extracts. Next, the column was washed with 30 ml hexane and 30 ml dichloromethane. The eluate was reduced to an adequate volume for analysis. The concentrations of phthalates in the extract were monitored with a gas chromatograph equipped with an electron capture detector (GC-ECD) (Hewlett Packard 6890, USA) and a HP-5 fused silica capillary column (film 0.25 μm, id 0.32 mm, length 30 m) (J&W, USA). 1 μl of each extract was injected into the GC system for separation of the phthalates. The column temperature increased from 40 °C to 70 °C at a rate of 30 °C min^{-1}, and was then programmed to a final temperature of 280 °C at 5 °C min^{-1}, and held at that temperature for 1 min. The injector and detector temperatures were kept at 250 °C and 310 °C, respectively. Nitrogen was used as carrier and makeup gas at a flow rate of 2.0 ml min^{-1} and 58 ml min^{-1}, respectively. Soil pH was measured using a 1 : 1 (w : v) soil : water ratio and organic matter was determined by the Walkley–Black procedure.[16] The properties of field soils are listed in Table 1.

1.4 Quality control

To assure quality of the proposed analytical method, the method blank, matrix spike and sample were successively analyzed in each analytical batch. A sextuple of each sample was analyzed. The blank values of the analytical procedure were determined by extracting an empty cellulose thimble by the same method as the real samples. Only the chromatographic peak of DBP was found in chromatograms of the procedural blanks. The mean concentration of DBP in the procedure blanks is 4.90 ng g^{-1} and RSD (n = 7) is 32.6%. Therefore, the blank values of phthalates are subtracted to correct the experimental values. A typical gas chromatogram of phthalates in Beijing soil is shown in Fig. 2. It can be seen clearly that DEHP, DEP, DBP and DMP were detected in Beijing soil. GC peak identification was conducted by comparing the gas chromatographic retention time with that of an authentic standard. Benzyl benzoate was used as internal standard to quantitatively evaluate the amounts of phthalates. Recoveries of all phthalates were in the range of 75.2–111.9% and RSD (n = 7) was 7.1–25.6%. To monitor the performance of the extraction, cleanup, and analytical system and the effectiveness of the method, each sample and blank were spiked with the surrogate standard, dicyclohexyl phthalate. The recoveries of the surrogate standard varied from 82–100%. Under the standard gas chromatographic conditions the detection limits of the recommended procedure were 5.79, 4.43, 3.04 and 1.56 ng g^{-1} for DMP, DEP, DBP, and DEHP, respectively, on the basis of a signal/noise ratio of 3. These

Table 1 Properties of soils and concentrations of phthalates in soils (mg kg^{-1}, dry soil)

Sample location		pH	OM[b] (%)	DMP/ mg kg^{-1}	DEP/ mg kg^{-1}	DBP/ mg kg^{-1}	DEHP/ mg kg^{-1}	ΣPAEs[c]/ mg kg^{-1}
East China	Rongcheng (RC)	6.08	0.68	ND	0.91±0.12	0.98±0.09	3.55±0.25	5.44
	Taizhou (TZ)	7.33	1.60	ND	ND	0.28±0.02	1.06±0.05	1.34
	Ningbo (NB)	4.86	4.89	ND	0.09±0.01	0.25±0.03	2.24±0.20	2.58
	Shanghai (SH)	7.62	3.02	ND	ND	1.16±0.07	5.98±0.41	7.14
	Hefei (HF)	5.58	2.09	ND	1.29±0.02	0.41±0.01	0.20±0.03	1.9
	Yintan (YT)	5.49	1.53	ND	0.21±0.02	1.38±0.13	5.38±0.77	6.97
	Xiamen (XM)	7.24	1.76	ND	0.05±0.01	0.21±0.02	2.67±0.39	2.93
Northeast China	Keshan (KS)	7.34	6.86	ND	0.91±0.20	0.16±0.02	3.34±0.39	4.41
	Shenyang (SY)	5.85	1.32	ND	1.36±0.11	1.56±0.13	7.11±0.91	10.03
	Anshan (ASa)	4.70	4.15	ND	0.18±0.04	0.37±0.01	5.15±0.32	5.7
North China	Huhehaote (HH)	7.21	13.02	ND	0.15±0.01	0.98±0.02	2.15±0.52	3.28
	Beijing (BJ)	8.28	1.35	0.20±0.04	2.61±0.63	0.27±0.08	0.70±0.13	3.78
	Tianjin (TJ)	7.17	1.89	ND	1.11±0.07	0.14±0.05	0.51±0.02	1.76
	Changzhi (CZi)	7.29	1.15	ND	0.20±0.04	0.8 3±0.02	2.18±0.42	2.38
Northwest China	Lanzhou (LZ)	7.42	0.31	ND	0.25±0.04	0.39±0.02	2.17±0.40	2.81
	Ankuang (AK)	7.30	2.1	ND	0.18±0.01	0.38±0.02	1.67±0.14	2.23
South China	Luoyang (LY)	7.48	1.40	ND	0.09±0.02	0.26±0.01	0.54±0.07	0.89
	Wuhai (WH)	6.65	2.37	ND	ND	0.17±0.03	0.98±0.12	1.15
	Changsha (CS)	5.20	2.28	ND	ND	0.21±0.05	2.04±0.26	2.25
	Chaozhou (CZu)	7.56	1.37	ND	0.17±0.02	ND	3.42±0.33	3.16
Southwest China	Chengdu (CD)	6.50	1.03	ND	ND	0.59±0.08	1.26±0.10	1.85
	Kunmin (KM)	4.71	4.22	ND	0.19±0.03	0.64±0.03	1.02±0.23	1.85
	Anshun (ASu)	6.30	6.76	ND	0.37±0.01	0.51±0.04	2.08±0.37	2.96

[a]ND: not detected. [b]OM: organic matter. [c]PAEs: phthalates.

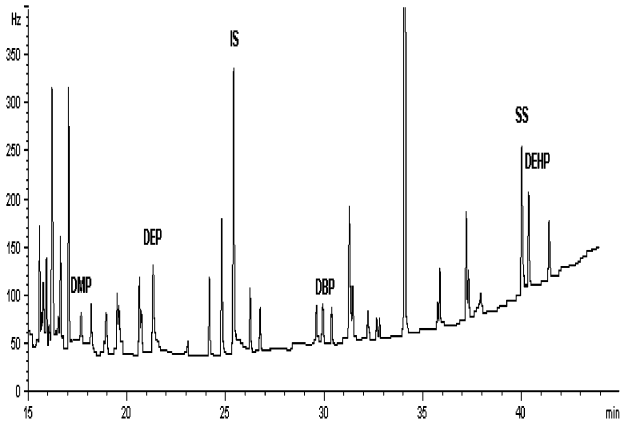

Fig. 2 GC/ECD chromatogram of phthalates in Beijing soil.

detection limits were low enough for the determination of phthalate residues in soils.

2. Results and discussion

2.1 Pollution of phthalates in arable soils

The phthalate pollution in different locations was surveyed and the results are summarized in Table 1. The total concentrations of phthalates in arable soils of China varied from 0.89 to 10.03 mg kg^{-1}. The mean concentration of phthalates was 3.43 mg kg^{-1}. The highest concentration of phthalates was found in Shengyang (SY) soil and the lowest was in Luoyang (LY) soil. As far as the distribution of various phthalates in soils was concerned, a quite similar contamination pattern was observed in different arable soils. DEHP was the most abundant phthalate in all soils, whereas DBP and DEP always occurred in lower concentrations. DEHP concentrations in arable soils were in the range of 0.20 to 7.11 mg kg^{-1}. No DEP and DBP were detected in some of soil samples, however, the highest levels of 1.56 mg kg^{-1} DBP and 2.61 mg kg^{-1} DEP were detected in Shengyang (LY) and Beijing (BJ) soils, respectively. DMP was only detected in Beijing soil and its concentration was 0.20 mg kg^{-1}. Fig. 3 illustrated the detection frequencies of phthalates in 23 field soils. Among the phthalates detected in field soils, DEHP was the most frequently detected one in all 23 field soils (100%), followed by DBP (96%) and DEP (78%).

These data suggested that phthalates were ubiquitous pollutants in arable soils in China mainly due to the production and consumption of phthalates. It was quite difficult to conceive any human activity free from the use of plastic materials. Plastic production is estimated to exceed 1.4 hundred millions of tons per year worldwide, and it is expected to increase continuously in the near future. Phthalates are the most commonly used plasticizer.[17] There is about 20–30% phthalates by weight in plastics which does not bind chemically with other ingredients in the matrix. As a consequence, phthalates are easily released from the plastics during manufacture, usage and disposal, resulting in environmental pollution.[18]

Exogenous contamination by anthropogenic pollution inputs might result in an accumulation of phthalates in soil. The retention, transformation, and transport processes govern the fate of phthalates in the soil environment. Many factors, such as properties of the soil and the particular phthalates, the population and activities of the microorganisms and weather, can affect the distribution of phthalates in the soil. Phthalates or their degradation products are retained and bound with soil organic matter or soil clay. Degradation processes are characterized by breakdown of the phthalate molecule by chemical, photochemical, or biological processes. Transfer processes, which are characterized by the phthalate molecule remaining intact, include movement from soil into surface water, sediments, and air. These processes affect the distribution of phthalates in soil. The distribution of various phthalates among the different locations was similar and could be explained by their similar pollutant sources and substance-specific properties. In all field soils, DEHP had the highest concentrations, followed by DBP and DEP, respectively. The longer the alkyl chain length of phthalates, the lower the water solubility and vapor pressure are, whereas their lipophilicity increases. Meanwhile, their degradation rates in soil decrease and half-life increases with increasing molecular weight of phthalates. This explains why low molecular weight phthalates of DMP, DEP and DBP were found to be at lower concentration levels in soils. In addition, the levels of phthalates in soils were also largely due to greater exposure. DEHP accounted for almost 50% of overall phthalate production, which may lead to its higher concentration in field soils than the other phthalates. Consequently, the high molecular weight phthalates resulted in more serious contamination in soils.

As shown in Fig. 4 the average concentration of DEHP, DBP and DEP in the northern area (northeast, north and northwest regions) of China was higher than that in southern area. A possible explanation for this might be the lower temperature in northern China. Consequently, less degradation of film residue in field soils occurred in northern China than in southern China.

2.2 Pollution source

An important task of the present survey was to search for the potential pollution sources of phthalates in arable soils in China. To address this, local consumption of agricultural film was collected. Soil pH and organic matter were also measured, and are listed in Table 1. Correlation between the various phthalate concentrations in the soils and soil properties were conducted with a linear regression analyses. The results showed

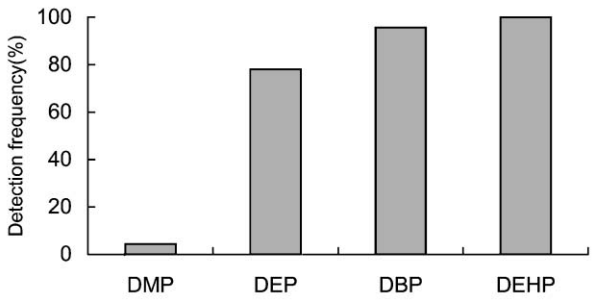

Fig. 3 Detection frequencies of phthalates in 23 sampling sites.

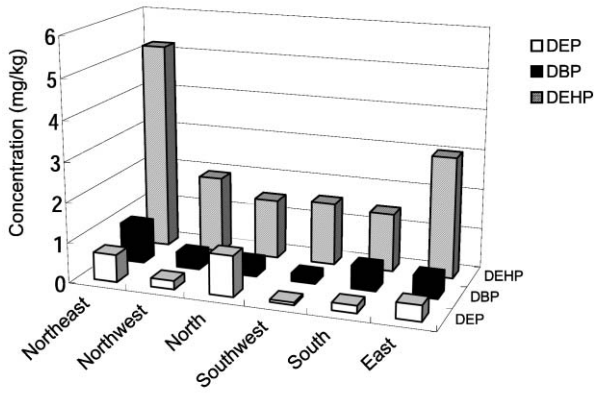

Fig. 4 Average concentrations of phthalates in different area of China.

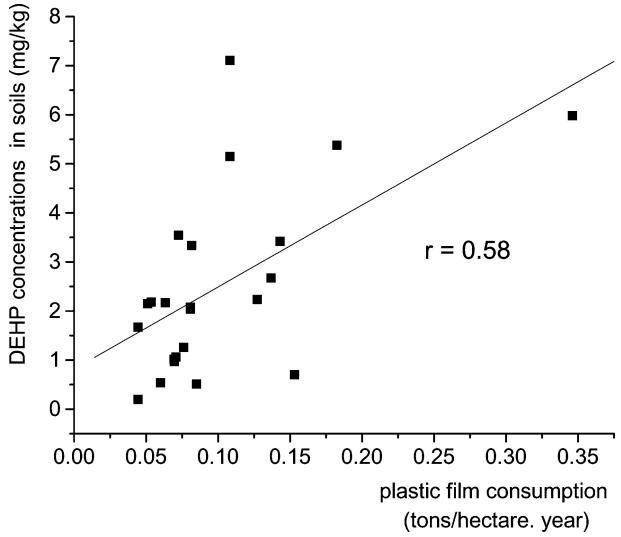

Fig. 5 Relationship between the concentrations of DEHP in soils and the consumption of plastic film.

that the concentrations of phthalates in soils had no significant correlation with soil properties, such as soil organic matter and soil pH. However, the concentration of DEHP in soils increased with increasing consumption of local agricultural film (Fig. 5), and a close relationship was obtained between the DEHP content in arable soils and consumption of agricultural film ($r = +0.58$, $P < 0.004$). However, there was no significant correlation between DBP or DEP contents in arable soils and consumption of agricultural film. The reasons for this are that DEHP is the most commonly used plasticizer of agricultural film, and moreover, DBP and DEP in soil are more easily degraded and transferred than DEHP is. This correlation analysis indicated that the greater concentration of DEHP in the soils is probably due to the greater amount of plastic film applied. These facts demonstrated that a point pollution source of DEHP in arable soils was the application of plastic film in Chinese agriculture.

2.3 Ecotoxicological evaluation of phthalate pollution in arable soils with the current guide values or environmental risk limits

The ecotoxic potential of phthalates was assessed on the basis of current guide values and limits. Because there was still no soil quality criterion of phthalates in China, our results were evaluated according to guide values and limits of soils from other countries. The total concentrations of phthalates in field soils of China were 10–100 times higher than the reference values in the Dutch list.[19] According to the Dutch values, the existing contents of phthalates in arable soils of China might affect the natural properties of the soils. The concentrations of DBP and DEHP in Chinese arable soils also exceeded the recommended Danish soil quality criteria of 100 μg kg^{-1} of DBP and 1000 μg kg^{-1} of DEHP, respectively.[20] Phthalates are often recognized as endocrine disrupters. Therefore, we should take their endocrine disruptive properties into account. Wezelare *et al.*[21] derived the environmental risk limits for DBP and DEHP with special emphasis on endocrine disruptive properties. The environmental risk limits in soil and sediment were 0.7 mg kg^{-1} of DBP and 1 mg kg^{-1} of DEHP, respectively, normalized based on 10% organic matter. According to these environmental risk limits, the concentrations of DBP in the arable soils of China were around the limits, while the concentrations of DEHP were higher. Based on the data mentioned above, a conclusion can be drawn that phthalates in arable soils of China, especially DEHP, could cause long-term ecotoxicological problems.

Vikelsøe[12] addressed the phthalate problem in agricultural soil in Denmark. The results revealed that DEHP was the most abundant phthalate, whereas relatively low concentrations of DBP were detected in all samples. The levels of DBP and DEHP in the field soils of Denmark were 0.3–453 μg kg^{-1} and 12–1900 μg kg^{-1}, respectively. Compared with Vikelsøe's results, the phthalate pollution in field soils of China was more serious. It should be pointed out that our results were also in agreement with other reports on DBP and DEHP contamination of 0.23–59.80 mg kg^{-1} in Beijing soil, 0.38-86.00 mg kg^{-1} in Shenyang soil and 1.84–2.54 mg kg^{-1} in Jinan soil.[22–24]

3. Conclusion

To our knowledge this is the first survey of phthalate pollution in arable soils throughout China. Our results indicated that the concentrations of phthalates in soils were different from site to site. DEHP was the most frequently detected phthalate. However, DBP and DEP were present at lower concentrations, and DMP was rarely detected. The phthalate levels in northern China were commonly higher than those in southern China. A correlation between the concentrations of DEHP in soils and the consumption of agricultural film was observed, which indicated that an anthropogenic pollutant input was a significant contamination source. The contamination levels of phthalates in soils were higher than many environmental risk limits recommended by other countries, and the potential hazardous environmental effect was worth studying in the future. Up to now, there have been no soil quality criteria for phthalates in China. Our results are useful for the establishment of soil quality criteria and provide data on phthalates in our living environment to understand their biological effects on humans. The contents of phthalates in arable soils in China are enough high to cause long-term ecotoxicological problems. Therefore, the local governments should take steps to control and to minimize the threats of phthalates to ecosystems and human health.

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