

Occurrence of priority organic pollutants in the fertilizers, China

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Abstract

The use of large quantities of chemical fertilizers is usually associated with environmental problems. A lot of work has been done on the concentrations of heavy metals and radionuclides in chemical fertilizers, but little work has focused on the occurrence of semi-volatile organic compounds (SVOCs). In this study the occurrence of 43 SVOCs listed as priority pollutants in 22 widely used-fertilizers of China was determined by gas chromatography coupled with mass spectrometry. Twenty-six SVOCs were detected with different detection frequencies and concentrations. The most abundant compounds were phthalic acid esters (PAEs; ranging from 1.17 to 2795 $\mu\text{g kg}^{-1}$ dry weight, d.w.) and nitroaromatics (up to 9765 $\mu\text{g kg}^{-1}$ d.w.), followed by polycyclic aromatic hydrocarbons (PAHs; <140 $\mu\text{g kg}^{-1}$ d.w.) and halogenated hydrocarbons (<900 $\mu\text{g kg}^{-1}$ d.w.). Chlorobenzenes and haloethers occurred generally at low concentrations. There are large variations in concentrations of various compounds in different fertilizers, and the total concentrations of each class of contaminants varied widely, too. The highest levels of sum concentration for 16 PAHs, for 6 PAEs and for nitroaromatics were found in organic fertilizer containing pesticide and soil amendments. Concentrations of SVOCs in coated fertilizers (the controlled release fertilizer with coating) were considerably higher than those in the corresponding fertilizers without coating. The occurrence frequencies of SVOCs in the straight fertilizers (containing only one of the major plant nutrients) were lower than in the other fertilizers.

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1. Introduction

The exponentially increasing consumption of chemical fertilizers in China and other Asian countries during the last decades posed serious environmental problems. There were about 137 million tonnes of fertilizers consumed in the world in 2001, of which 72% was for the production of nitrogen fertilizer, 10% for phosphate fertilizer, 16% for complex fertilizer and only 2% for potassium fertilizer [1]. Statistics showed that China consumed 30% of the total chemical fertilizers of the world in 1997, with nitrogen, phosphate and potassium fertilizers being

up to 174, 31 and 21 kg ha^{-1} , respectively [2]. It was estimated that there is a strong demand for higher fertilizer application rates in order to keep high crop production, and this trend is expected to continue for the next 30 years. Overuse of chemical fertilizers in agriculture results in many environmental problems, because some fertilizers contain heavy metals (such as cadmium and chromium) and radionuclides at high concentrations [3–5], which later become a main source of heavy metals and radionuclides in the agro-ecosystems [6], and results in accumulation of inorganic contaminants in some vegetables [7].

Although much work has been done during the past decades on the concentrations of heavy metals and radionuclides in chemical fertilizers, little information is available regarding the occurrence of organic contaminants in fertilizers. Our previous investigation showed that fertilizer application contributed to the increase of PAH and PAE concentrations in soils and subsequently in vegetables [8,9]. PAEs were also detected in the tissues of sheep grazing pastures fertilized with inorganic fertilizer [10]. These facts make the authors speculate that there

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might be organic contaminants unknown in fertilizers, and it is necessary, therefore, to make a survey of fertilizers in terms of organic contamination. The objective of the present study was to investigate the priority organic pollutants in different fertilizers extensively used in China to provide lines of evidence for risk analysis of agricultural foods.

2. Materials and methods

2.1. Sampling and fertilizer classification

According to the nomenclature of European Commission (COM2001 0508), a straight fertilizer (SF) contains only one of the primary nutrients-N, -P, or -K, while a compound fertilizer (CF) contains two or more [11]. Compound fertilizers are usually labeled with three numbers, e.g., NPK 15–10–10, meaning 15% for nitrogen (as N), 10% for phosphate (as P₂O₅), and 10% for potassium (as K₂O). A mineral fertilizer contains nutrients in inorganic form, or as urea or cyanamide, and an organo-mineral fertilizer contains nutrients in both organic and inorganic form. Organic fertilizers (OF) are substances containing nutrients derived from the remains or by-products of an organism. The coated fertilizer is a controlled release fertilizer with coating.

In this study, 22 widely used-fertilizers in China were collected from different factories/companies. The fertilizers examined were categorized in three major groups: straight fertilizers (SF1–SF7), compound fertilizers (CF1–CF10) and other fertilizers (including Coated-SF, Coated-CF, OF1, OF2, MSF). The compositions of these fertilizers are presented in Table 1. Most of them are mineral fertilizers, except from OF1 and OF2 which are organo-mineral fertilizers.

2.2. Chemicals and materials

A composite stock standard solution (1000 µg ml⁻¹ in dichloromethane, 99.8% purity) was used, containing 43 USEPA priority organic pollutants, including 16 PAHs, 6 PAEs, 5 chlorobenzenes, 4 haloethers, 4 halogenated hydrocarbons, 3 nitroaromatics, and other compounds (*N*-nitroso-*N*-propylamine, azobenzene, 2-chloronaphthalene, diphenylamine, isophorone) (Table 2). Working standard solutions in dichloromethane were prepared by diluting appropriate volumes of the stock standard solution. Internal standard contained [²H₄]1,4-dichlorobenzene (1,4-dichlorobenzene-*d*₄), [²H₈]naphthalene (naphthalene-*d*₈), [²H₁₀]acenaphthylene (acenaphthylene-*d*₁₀), [²H₁₀]phenanthrene (phenanthrene-*d*₁₀), [²H₁₂]chrysene (chrysene-*d*₁₂) and [²H₁₂]perylene (perylene-*d*₁₂), and surrogate standard mixture contained nitrobenzene-*d*₅ and *p*-terphenyl-*d*₁₄, in a mixture solution of 4000 µg ml⁻¹, respectively. These standards were purchased from Ultra Scientific (North Kingstown, RI, USA).

Analytical grade dichloromethane (DCM), acetone and *n*-hexane were redistilled before use. Silica gel (80–200 mesh) and neutral alumina were Soxhlet-extracted with DCM for 48 h, activated at 180 and 250 °C, respectively, for 12 h, deactivated with 3% redistilled water, and kept in *n*-hexane prior to use.

Table 1
Compositions of 22 fertilizers analyzed from China

Sample name	Fertilizer	Content of nutrients (%)
Straight fertilizer (SF)		
SF1	(NH ₄) ₂ SO ₄	N: 21
SF2	NH ₄ Cl	N: 25.4
SF3	Urea	N: 46
SF4	Urea	N: 46.3
SF5	Ca(H ₂ PO ₄) ₂ ·H ₂ O	P ₂ O ₅ : 12
SF6	KCl	K ₂ O ≥ 57
SF7	KCl	K ₂ O: 21
Compound fertilizers (CF)		
CF1	(NH ₄) ₂ (H ₂ PO ₄)(HSO ₄)	N: 16; P ₂ O ₅ : 20; SO ₄ ²⁻ : 20
CF2	NH ₄ H ₂ PO ₄	N + P ₂ O ₅ ≥ 60
CF3	(NH ₄) ₂ HPO ₄	P ₂ O ₅ : 18
CF4	NPK 15–6–8	N: 15; P ₂ O ₅ : 6; K ₂ O: 8
CF5	NPK 15–15–15	N: 15; P ₂ O ₅ : 15; K ₂ O: 15
CF6	NPK 17–0–8	N: 17; K ₂ O: 8; Ca + Mg + S: 20%
CF7	NPK 15–15–15	N: 15; P ₂ O ₅ : 15; K ₂ O: 15
CF8	NPK 15–0–15	N: 15; K ₂ O: 15
CF9	NPK 17–5–15	N: 17; P ₂ O ₅ : 5; K ₂ O: 15
CF10	–	N + P ₂ O ₅ + K ₂ O: 36
Other fertilizer		
Coated-SF	Urea	N: 25.5
Coated-CF	14–16–16	N: 14; P ₂ O ₅ : 13; K ₂ O: 13
OF1	Organic fertilizer	N: 10; P ₂ O ₅ : 2.5; K ₂ O: 6; Ca + Mg + Zn + Fe + Mn + Cu + S + Mo + B: 12%. Also containing organic matter, pesticide and soil amendments
OF2	Pure organic fertilizer	–
MSF	MgSO ₄	MgSO ₄ ≥ 70%

Anhydrous sodium sulfate was dried at 450 °C for 6 h and stored in a sealed desiccator.

Special precautions were taken during sampling and further processed of the sample to avoid contamination as described by Cai et al. [12].

2.3. Analytical procedure

Sample extraction and silica gel cleanup were performed according to USEPA methods 3540C and 3630C with some modification, respectively. Fertilizer sample (approximately 20 g) was weighed on Whatman cellulose extraction thimbles (pre-extracted with *n*-hexane/DCM (1:1, v/v) for 24 h) and extracted in a Soxhlet-extractor for 24 h with 100 ml acetone/DCM (1:1, v/v) in a water bath at 73 °C. The extracts were concentrated, cleaned-up and further processed as described in details by Cai et al. [12].

The analysis of SVOCs was performed by gas chromatography (GC, Hewlett-Packard 5890 Series II, Agilent Technology) coupled with mass spectrometry (MS, Hewlett-Packard 5972, Agilent Technology) by a modification of USEPA method 8270C. A HP-1 25 m × 0.20 mm i.d., 0.11 µm film (Agilent Technology) fused silica capillary column was used. The GC oven temperature was programmed as follows: 45 °C hold for 1 min, raised at 6.0 °C min⁻¹ to 200 °C, then at 8.0 °C min⁻¹ to

Table 2
The detection limits and recoveries of organic contaminants

Compounds	Detection limit ($\mu\text{g kg}^{-1}$)	Recovery (%)
PAH compounds		
Naphthalene	0.21	62
Acenaphthylene	0.22	74
Acenaphthene	0.20	74
Fluorene	0.45	82
Phenanthrene	0.44	83
Anthracene	0.78	85
Fluoranthene	0.99	88
Pyrene	1.4	89
Benzo[<i>a</i>]anthracene	0.71	88
Chrysene	0.84	92
Benzo[<i>b</i>]fluoranthene	1.3	91
Benzo[<i>k</i>]fluoranthene	1.1	93
Benzo[<i>a</i>]pyrene	0.61	91
Indeno[1,2,3- <i>cd</i>]pyrene	0.75	82
Dibenzo[<i>a,h</i>]anthracene	0.68	83
Benzo[<i>ghi</i>]perylene	0.78	78
PAE compounds		
Dimethyl phthalate (DMP)	1.4	80
Diethyl phthalate (DEP)	0.91	81
Di- <i>n</i> -butyl phthalate (DBP)	0.60	82
Butylbenzyl phthalate (BBP)	0.39	94
Di- <i>n</i> -octyl phthalate (DOP)	0.57	95
Di(2-ethylhexyl) phthalate (DEHP)	0.49	93
CB compounds		
1,2-Dichlorobenzene	0.26	84
1,3-Dichlorobenzene	1.1	79
1,4-Dichlorobenzene	0.32	82
1,2,4-Trichlorobenzene	0.19	76
Hexachlorobenzene	0.34	78
Nitroaromatic compounds		
Nitrobenzene	0.33	81
2,4-Dinitrotoluene	0.22	79
2,6-Dinitrotoluene	0.19	76
Haloether compounds		
Bis(2-chloroethyl) ether	0.32	81
Bis(2-chloroisopropyl) ether	0.32	76
4-Chlorophenyl phenyl ether	0.36	68
4-Bromophenyl phenyl ether	0.36	70
Halogenated hydrocarbons		
Hexachloroethane	0.51	78
Bis(2-chloroethoxy) methane	0.42	82
Hexachlorobutadiene	0.14	70
Hexachlorocyclopentadiene	0.12	73
Other compounds		
<i>N</i> -Nitroso- <i>N</i> -propylamine	0.38	83
Isophorone	1.1	74
2-Chloronaphthalene	0.30	89
Diphenylamine	0.38	86
Azobenzene	0.97	77

(0–20 $\mu\text{g l}^{-1}$). This operation was performed automatically by the Hewlett-Packard MS chemstation. The detailed quantification method, the details of the quality assurance/quality control (QA/QC) have been presented elsewhere [12,13]. The detection limits and the recoveries of 43 SVOCs are listed in Table 2.

3. Results and discussion

3.1. Polycyclic aromatic hydrocarbons (PAHs)

The occurrence of PAHs in fertilizer samples is illustrated in Table 3. PAHs were detected in 10 out of 22 samples. Their total concentrations (Σ_{PAHs}) in 86% of samples ($n=22$) were less than 10 $\mu\text{g kg}^{-1}$ dry weight (all results of this study were expressed on a dry weight basis), but up to 77 $\mu\text{g kg}^{-1}$ in CF9 and 138 $\mu\text{g kg}^{-1}$ in OF1. The Σ_{PAHs} were considerably lower than those observed in vegetable soils within the Pearl River Delta, China [14]. The carcinogenic PAH compounds (including benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and dibenzo[*a,h*]anthracene) were detected in CF5, CF7, CF9 and OF1, and their sum concentrations ($\Sigma_{\text{PAHscarce}}$) were 6.15, 9.78, 71.6 and 69.0 $\mu\text{g kg}^{-1}$, respectively, and accounted for 50–93% of the Σ_{PAHs} .

As for individual PAHs, 12 PAH compounds were detected with different detection frequencies and various concentrations. Other PAHs including naphthalene, dibenzo[*a,h*]anthracene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene were all below the detection limits. Phenanthrene, anthracene, fluoranthene and pyrene were detected in four or five samples, while the other compounds only in one or three samples. Eight PAH compounds were detected in CF5, whereas only two to six compounds were detected in the other samples, when detected. The highest concentrations (69 $\mu\text{g kg}^{-1}$) were found for fluoranthene and chrysene in OF1, followed by benzo[*a*]anthracene and chrysene in CF9 with concentrations of 35.6 and 33.9 $\mu\text{g kg}^{-1}$, respectively. The concentrations of the other PAHs were <5 $\mu\text{g kg}^{-1}$.

When 16 PAHs were grouped following ring numbers, the dominant compounds in fertilizers were those with three- and four-ring (except from CF7) (Table 3). The low molecular weight PAHs (≤ 3 rings) were dominant in SF1, CF3, CF6 and Coated-SF, as it is shown from the ratios of sum concentration of low molecular weight PAHs (≤ 3 rings) to that of high molecular weight PAHs (≥ 4 rings) ($R_{\leq 3/\geq 4}$), ranging from 1.63 (SF1) to 4.69 (Coated-SF). The predominance of high molecular weight PAHs was observed in CF5, CF7, CF9, OF1 and OF2, with the ratio values of less than 0.1.

3.2. Phthalic acid esters (PAEs)

The occurrence of six PAEs is presented in Table 4. PAEs were detected in all samples. The total concentrations of six PAEs (Σ_{PAEs}) ranged from 1.17 to 2795 $\mu\text{g kg}^{-1}$ with a mean of 252 $\mu\text{g kg}^{-1}$, and were lower than 100 $\mu\text{g kg}^{-1}$ in 64% of samples. These results are comparable with those recorded in the artificial fertilizer and cow manure from Denmark [15], but far lower than those in sewage sludges and its composts [12,15,16].

300 °C (held for 1 min). Helium was the carrier gas, at a flow of 0.615 ml min⁻¹. Detection was conducted by a mass selective detector. MS transfer line temperature was at 280 °C. The MS was operated in full scan with an electron multiplier voltage of 2200 V. The mass scanning ranged from *m/z* 50 to 550. The internal calibration method for quantification was applied based on five-point calibration curve for individual component

Table 3
Occurrence of PAHs in fertilizers, China ($\mu\text{g kg}^{-1}$ dry weight)^a

Compounds	N ^b	SF1	CF3	CF5	CF6	CF7	CF8	CF9	Coated-SF1	OF1	OF2
Naphthalene	2	ND ^c	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthylene	3	ND	ND	ND	ND	ND	0.27	ND	ND	ND	ND
Acenaphthene	3	ND	ND	ND	0.57	ND	ND	ND	ND	ND	ND
Fluorene	3	ND	ND	ND	ND	0.98	ND	ND	1.95	ND	ND
Phenanthrene	3	2.31	1.04	0.29	0.57	ND	ND	ND	1.30	ND	ND
Anthracene	3	2.70	1.04	0.29	0.85	ND	ND	ND	1.30	ND	ND
Fluoranthene	4	1.54	0.70	0.29	0.57	ND	ND	3.76	0.32	69	0.42
Pyrene	4	1.54	0.35	0.29	0.57	ND	ND	1.74	0.65	ND	0.42
Benzo[a]anthracene ^d	4	ND	ND	1.17	ND	ND	ND	35.6	ND	ND	ND
Chrysene ^d	4	ND	ND	2.05	ND	ND	ND	33.9	ND	69	ND
Benzo[b]fluoranthene ^d	5	ND	ND	0.88	ND	2.28	ND	2.03	ND	ND	ND
Benzo[k]fluoranthene ^d	5	ND	ND	ND	ND	2.28	ND	2.03	ND	ND	ND
Benzo[a]pyrene ^d	5	ND	ND	2.05	ND	5.22	ND	ND	ND	ND	ND
Dibenzo[a,h]anthracene ^d	5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-cd]pyrene ^d	6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[ghi]perylene	6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
$\Sigma_{\text{PAHs}}^{\text{e}}$		8.09	3.13	7.31	2.28	10.8	0.27	77.0	5.52	138	0.84
$\Sigma_{\text{PAHscarce}}^{\text{f}}$		0	0	6.15	0	9.78	0	71.6	0	69	0
$R_{\leq 3/\leq 4}^{\text{h}}$		1.63	1.98	0.09	1.75	0.10	–	0	4.69	0	0

^a No PAHs was detectable in samples of SF2–SF7, CF1, CF2, CF4, CF10, Coated-CF1 and MSF.

^b Ring number of PAHs.

^c Not detectable.

^d Carcinogenic PAH compound.

^e Sum concentration of 16 PAHs.

^f Sum concentration of seven carcinogenic PAHs.

^h Ratio of sum concentration of low molecular weight PAHs (≤ 3 rings) to that of high molecular weight PAHs (≥ 4 rings).

The highest value was observed in OF1, being more than six-fold higher than those in the other samples. One of the explanations for this high value is that its ingredients, e.g., pesticide and soil amendments might contain these contaminants. It should be

noted that the Σ_{PAEs} in Coated-SF and Coated-CF were remarkably higher than those in the corresponding SF and CF, respectively, which might be partly attributed to the materials used as coating. Further investigation on this phenomenon is needed.

Table 4
Occurrence of PAEs in fertilizers, China ($\mu\text{g kg}^{-1}$ dry weight)

	DMP	DEP	DBP	BBP	DOP	DEHP	$\Sigma_{\text{PAEs}}^{\text{a}}$
SF1	5.78 (1.3) ^b	1.16 (0.3)	304 (66.5)	ND ^c	ND	146 (32.0)	457
SF2	15.7 (40.4)	ND	17.3 (44.5)	ND	ND	5.88 (15.2)	38.8
SF3	5.01 (16.9)	ND	18.1 (61.0)	ND	ND	6.56 (22.1)	29.7
SF4	8.28 (18.0)	ND	29.7 (64.7)	ND	ND	7.94 (17.3)	45.9
SF5	3.96 (18.9)	ND	12.5 (59.3)	ND	ND	4.53 (21.6)	21.0
SF6	86.8 (36.6)	ND	52.1 (22.0)	ND	ND	98.4 (41.5)	237
SF7	4.48 (56.3)	ND	1.74 (21.9)	ND	0.250 (3.1)	1.49 (18.7)	7.96
CF1	92.7 (22.6)	ND	618 (86.9)	ND	ND	ND	711
CF2	5.25 (12.2)	ND	21.9 (51.0)	ND	ND	15.8 (36.7)	42.9
CF3	ND	ND	176 (56.3)	ND	ND	136 (43.6)	312
CF4	1.10 (12.9)	ND	3.29 (38.7)	1.64 (19.3)	ND	2.47 (29.1)	8.50
CF5	ND	0.290 (24.8)	0.590 (50.4)	ND	0.290 (24.8)	ND	1.17
CF6	ND	0.280 (0.6)	25.0 (50.0)	ND	ND	24.7 (49.5)	49.9
CF7	3.59 (7.8)	0.330 (0.7)	21.5 (46.8)	0.650 (1.4)	1.30 (2.8)	18.6 (40.4)	46.0
CF8	11.7 (21.6)	ND	28.3 (52.2)	ND	ND	14.1 (26.1)	54.1
CF9	3.47 (5.6)	ND	24.6 (39.7)	1.45 (2.3)	3.47 (5.6)	29.0 (46.7)	62.0
CF10	4.57 (2.3)	ND	68.6 (35.0)	ND	ND	123 (62.7)	196
Coated-SF	0.980 (0.5)	0.65 (0.3)	94.1 (43.6)	ND	ND	120 (55.8)	216
Coated-CF	82.2 (42.8)	ND	27.4 (14.3)	ND	ND	82.2 (42.8)	192
OF1	ND	ND	1967 (70.4)	34.5 (1.2)	ND	794 (28.4)	2795
OF2	1.25 (50.0)	ND	0.420 (16.8)	ND	ND	0.83 (33.2)	2.50
MSF	ND	ND	22.7 (96.6)	ND	ND	0.754 (3.2)	23.5
Mean	15.3	0.12	161	1.74	0.24	74.2	252

^a Sum concentration of six PAE compounds.

^b Number in parentheses is the percentage of individual compound to total concentration.

^c Not detectable.

The concentrations of individual PAEs in different fertilizers varied greatly (Table 4). Among six PAE compounds of interest, di-*n*-butyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) were detected in most samples (except for DEHP in CF1 and CF5) and were the most abundant. The concentrations of DEHP, one of the more recalcitrant PAEs, ranged from not detectable (ND) to 794 $\mu\text{g kg}^{-1}$ (OF1) and, when detected, accounted for 15.2–62.7% of the Σ_{PAEs} (Table 4). The levels of DBP varied from 0.59 (CF5) to 1967 $\mu\text{g kg}^{-1}$ (OF1) and accounted for 16.8–86.9% of the Σ_{PAEs} . The average concentrations of DBP and DEHP (161 and 74.2 $\mu\text{g kg}^{-1}$) were five times higher than the other PAEs. A significantly positive correlation was observed between DBP concentrations and the Σ_{PAEs} ($R^2 = 0.99$, $P < 0.001$), between DEHP concentrations and the Σ_{PAEs} ($R^2 = 0.91$, $P < 0.001$), respectively. Dimethyl phthalate (DMP) was detected in 77% of samples, having a concentration of less than 100 $\mu\text{g kg}^{-1}$ and accounting for less than 50% of the Σ_{PAEs} (except for SF7). Diethyl phthalate (DEP), butylbenzyl phthalate (BBP) and di-*n*-octyl phthalate (DOP) were detected only in four different samples with concentrations of $< 5 \mu\text{g kg}^{-1}$. The concentrations of DBP in the present study were comparable or somewhat higher than those reported in the study from Denmark [15], but the concentrations of BBP, DOP and DEHP were far lower than those in the aforementioned study and in soils of vegetable field within the Pearl River Delta, China [17].

3.3. Other compounds

Five chlorobenzene compounds, nitrobenzene, bis(2-chloroethyl) ether, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether, hexachloroethane, *N*-nitroso-*N*-propanamine, 2-chloronaphthalene and isophorone were below detection limits in all examined fertilizer samples. Among the other SVOCs, 2,6-dinitrotoluene and hexachlorocyclopentadiene were the most frequently detected in 13 fertilizer samples, while the rest of SVOCs were detected only in one to eight samples (Table 5).

The concentrations of nitroaromatics, haloethers, halo-genated hydrocarbons, diphenylamine and azobenzene were generally $< 100 \mu\text{g kg}^{-1}$; Some samples, such as Coated-CF and OF1, contained high concentrations of 2,6-dinitrotoluene, being $> 200 \mu\text{g kg}^{-1}$, even up to 9764 $\mu\text{g kg}^{-1}$ (Table 5), which might be derived from certain specific components in this fertilizer. Moreover, the organic contaminants in fertilizers are expected to be highly bioavailable [8,9]. Special attention, therefore, should be given to organic contamination of the fertilizers.

As described above, among 43 SVOCs of interest, 26 SVOCs were detected in fertilizer samples. The concentrations of different classes of organic contaminants in the same fertilizer varied widely. The most abundant compounds in fertilizers analyzed were PAEs (except from CF9, Coated-CF, OF1 and OF2), followed by nitroaromatics, PAHs and halogenated hydrocarbons, while the other classes of SVOCs were the least abundant (Tables 3–5). In total, the concentrations of individual compounds were $< 100 \mu\text{g kg}^{-1}$, even $< 10 \mu\text{g kg}^{-1}$. But, there existed unexpectedly high concentrations (e.g., $> 1000 \mu\text{g kg}^{-1}$).

Table 5
Occurrence of other compounds analyzed in fertilizers, China ($\mu\text{g kg}^{-1}$ dry weight)^a

	SF1	SF2	SF3	SF4	SF5	SF6	CF2	CF3	CF5	CF6	CF7	CF8	CF9	CF10	Coated-SF	Coated-CF	OF1	OF2	MSF
2,4-Dinitrotoluene	ND ^b	ND	ND	ND	ND	ND	ND	ND	3.52	ND	ND	ND	ND	ND	10.4	ND	ND	ND	0.808
2,6-Dinitrotoluene	66.3	13.3	32.0	9.32	5.10	ND	8.75	ND	ND	ND	23.8	14.9	9.55	3.56	52.4	247	9765	7.49	ND
Bis(2-chloroisopropyl) ether	2.31	ND	ND	ND	ND	52.1	0.44	5.92	ND	ND	ND	3.53	ND	ND	5.54	ND	242	6.24	ND
Bis(2-chloroethoxy) methane	ND	2.35	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorocyclopentadiene	8.87	58.0	3.86	11.7	189.7	ND	ND	ND	108	7.09	5.22	ND	3.47	ND	8.79	438	897	8.32	ND
Diphenylamine	5.78	ND	0.77	ND	ND	ND	ND	31.0	ND	ND	8.16	ND	0.29	ND	18.2	ND	207	ND	ND
Azobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.35	ND	ND	ND	0.977	ND	ND	ND	ND

^a No target compound was detectable in samples of SF7, CF1 and CF4. The concentration was below the detection limit for five chlorobenzene compounds, nitrobenzene, bis(2-chloroethyl) ether, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether, hexachloroethane, hexachlorobutadiene, *N*-nitroso-*N*-propylamine, 2-chloronaphthalene and isophorone.

^b Not detectable.

The occurrence of different organic contaminants in fertilizers was related to their physico-chemical characteristics and their origins. PAEs are ubiquitous in the environment [18]. It is well documented that the environmental behaviour and fate of organic contaminants are related to their half-lives, and to their structure characteristics such as the length of the alkyl-side chains. For example, PAEs with shorter alkyl-chains, i.e. DEP, are very easily degraded while PAEs with longer alkyl-chains, i.e. DBP and DEHP, are slowly degraded, at rates up to two orders of magnitude lower under the same experimental condition [18]. This is in good agreement with their occurrence in fertilizer samples.

As for the different fertilizers, the higher detection frequencies of SVOCs were observed in both CF9 and Coated-SF, where 15 compounds were detected. The highest concentrations of Σ_{PAEs} , Σ_{PAHs} , nitroaromatics (2,6-dinitrotoluene), haloethers, halogenated hydrocarbons, diphenylamine all were observed in OF1. Similarly, heavy metal input by organic fertilizers is much higher than by mineral fertilizers [6]. This might be attributed to its ingredients. OF1 contains organic matter, pesticide, soil amendments, which might increase the concentrations of organic contaminants. Nevertheless, the contaminant concentrations in the pure organic fertilizer (OF2) were lower than in OF1 and most of the other fertilizers, when detected (Tables 3–5), and its PAE concentrations were even lower than those in cow manure [15]. The results demonstrated that OF2 tended to favor the soil and crop in view of organic contamination. On the other hand, the contaminant concentrations in coated fertilizers (e.g., Coated-SF and Coated-CF) (except from PAHs in Coated-CF) were markedly higher than those in the corresponding fertilizers without coating (e.g., SF3, SF4, CF4-CF10). This might be due to the materials of coating.

4. Conclusion

Twenty-six SVOCs were detected with various detection frequencies and concentrations in widely used 22 fertilizers in China. This finding suggested that more attention should be paid to potential hazards of organic contaminants associated with extensive application of the fertilizers, but further investigation needs to be done in the future in terms of comparative risk analysis and evaluation of organic contamination in various chemical fertilizers.

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