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Residues of organochlorine pesticides and polycyclic aromatic hydrocarbons in farm-raised livestock feeds and manures in Jiangsu, China

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HIGHLIGHTS

- Slightly higher mean residuals of OCPs were found in manures than in feeds.
- α-HCH was the most abundant compound in all kinds of animal feeds and manures.
- The predominance of p,p′-DDE and p,p′-DDT of total DDTs was clearly observed.
- Phenanthrene was the most dominant PAH species in each kind of animal manure.
- PAHs with 3 rings were the primary components in the tested manures.

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ABSTRACT

The residual levels of 8 organochlorine pesticides (OCPs) and 15 priority polycyclic aromatic hydrocarbons (PAHs) were determined in pig, chicken, and cow feed and manure samples collected from feedlots in Jiangsu province, China. The mean residuals of OCPs ranged from 25.35 to 65.62 ng g^{-1} in feeds and from 33.46 to 90.89 ng g^{-1} in manures. Among 4 hexachlorocyclohexanes (HCHs), α-HCH was the most abundant compound, with a high occurrence above 80% in all kinds of animal feeds and manures. For dichlorodiphenyltrichloroethanes (DDTs), the predominance of p,p′-DDE and p,p′-DDT of total DDTs was also clearly observed. Composite profiles of HCHs and DDTs in feeds indicated that the residuals of lindane and DDTs could be attributed to new inputs in the past several years. The mean residuals of all of the PAHs varied from 128.94 to 389.66 ng g^{-1} in manures. The mean concentrations of seven carcinogenic PAHs in manures varied from 16.80 to 79.70 ng g^{-1}. Of the 15 priority PAHs, phenanthrene was the most dominant PAH species and accounted for approximately 50% of the total PAHs in all animal manures. The distribution of PAHs with different rings showed that PAHs with 3 rings were the primary components in the tested manures.

1. Introduction

Hexachlorocyclohexane isomers (HCHs, including α-HCH, β-HCH, γ-HCH and δ-HCH) and dichlorodiphenyltrichloroethane and its metabolites (DDTs, o,p′-DDT, p,p′-DDT, DDD and DDE), the important components of organochlorine pesticides (OCPs), were extensively used in agriculture and vector control in China from the 1950s to the 1980s. During this period, the production of HCHs and DDTs was about 4.9 and 0.4 million tons, respectively, accounting for 33 and 20% of the total world production (Zhang et al., 2002). Although the application of OCPs has been banned from agricultural use since the early 1980s, for industrial HCHs, and early 1990s for DDTs and lindane (almost pure γ-HCH) (Chen, 1990), 3200 t of lindane continued in use until 2000 for the control of forest pests. DDT was also produced for export and/or for further production of dicofol, another pesticide (Li et al., 1999, 2001). After the ban on OCPs usage in 1983, residuals of HCHs and DDTs in various environmental media have declined considerably, but large amounts still remain in the environment due to high persistency, possible illegal use, or occurrence of DDTs as an impurity in widely applied dicofol (Chen et al., 2005a; Wu et al., 2005).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants formed from the combustion of fossil fuels and are always found as a mixture of individual compounds (Wilson and Joins, 1993). Sixteen PAHs have been identified as priority pollutants by both China and the United States Environmental Protection Agency and seven of them are considered as probably carcinogenic (Menzie and Potokib, 1992). The determination and monitoring of PAHs in environmental samples and foodstuffs are necessary and important to human health (García-Falcón et al., 2004,2006; Rey-Salgueiro et al., 2008a,b; Rey-Salgueiro et al., 2009).

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Because of high persistence, bioaccumulation and toxicity of OCPs and PAHs, pollution by them is still of wide concern. In recent years, a larger number of studies have reported OCPs and PAHs contamination in China; however, most studies examined the residuals of these pollutants in soils, foodstuffs, vegetables, organisms, water and sediments (Tao et al., 2004,2009; Zhang et al., 2004; Chen et al., 2005b; Song et al., 2006; Hu et al., 2009). On the other hand, commercial livestock production using similar facilities and commercial feeds has increased rapidly in recent years in China, and concomitantly large numbers of animal manures are produced during large-scale animal feeding operations. Animal manure is not only a source of valuable plant nutrients, but can also be a source of air pollution and a threat to aquifers and surface water because animal manure contains trace nutrient elements, viruses, heavy metals, veterinary antibiotics and other pollutants (Sager, 2007; Venglovsky et al., 2009). In addition, the animal manure can be used as feeds for the fish to reduce the requirement for expensive feeds and fertilizers (Salazar and Saldana, 2007). The residual of heavy metals and veterinary antibiotics have been well documented (Salazar and Saldana, 2007; Zhao et al., 2010; Pan et al., 2011); however, little attention has been paid to OCP and PAH residuals in feed and manure samples from farm-raised animals in China. Therefore, screening for persistent organic pollutants, such as OCPs and PAHs in farm-raised animal feeds and manures is imperative for food safety and environmental protection. In this study, the objective was to investigate OCPs and PAHs residual levels in animal feeds and manures at different livestock and poultry farms in Jiangsu province of China and evaluate a possible influence of the residual of OCPs and PAHs on the environment.

2. Materials and methods

2.1. Chemicals and standards

High-performance liquid chromatographic (HPLC) grade *n*-hexane, petroleum ether, dichloromethane, acetone, acetonitrile and methanol were purchased from Tedia Company Inc. (Fairfield, OH). Ultra pure water was provided with a Milli-Q Advantage A10 Water Purification System (US Millipore Co., Bedford, MA). All glassware was prewashed and rinsed with distilled methanol before use. Anhydrous sodium sulfate was dried at 450 °C for 6 h and stored in a sealed desiccator.

The reference standard mixtures of eight OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, o,p′-DDT, p,p′-DDT, p,p′-DDD and p,p′-DDE) at a concentration of 100 mg l^{-1} were purchased from the National Research Center for Certified Reference Materials, China. The standard mixtures of OCPs were diluted by petroleum ether for calibration standards in the range of 1.0–200.0 μg l^{-1}. Standard PAHs (16 compounds specified in EPA Method 610) in a mixture were obtained from Supelco (Bellefonte, PA). These compounds are as follows: naphthalene (Nap), acenaphthylene (Acl), acenaphthene (Ace), fluorene(Flu), phenanthrene (Phen), anthracene (Anth), fluoranthene (Flt), pyrene (Pyr), chrysene (Chry), benzo[a] anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (Inpy), benzo[g,h,i]perylene (B[ghi]P) and dibenzo[a,h]anthracene (D[ah]A). Working standards of PAHs were prepared by diluting the standard mixture with acetonitrile in the range of 0.01–10 mg l^{-1}.

2.2. Sample collection

Samples were collected from 12 feedlots that are located in Lianyungang, Huaian, Taizhou, Yangzhou, Nanjing, Dongtai, Haian, Rugao, Changzhou, Liyang, Wuxi and Suzhou, from the North to the South in Jiangsu province, in June, 2005. Eight pig feed samples and 15 pig feces samples were collected from 10 pig farms (70–5000 pigs in total at a farm). Eight feed samples and 12 manure samples were collected from 11 chicken farms (1200–1,000,000 chickens in total at a farm). Six feed samples and 8 manure samples were collected from 7 cow farms (100–700 cows in total at a farm).

Each manure sample was placed into a plastic container. All samples were air-dried at room temperature away from light after being taken to the laboratory. The samples were ground and sieved (60 mesh), and stored in closed vessels for further analysis.

2.3. Sample extraction, clean-up and analysis

2.3.1. OCPs

An aliquot (10 g) of feed or manure sample was weighed accurately and mixed with 10 g of copper powder (100 mesh) that was used as a desulfurating agent. The mixtures were extracted by Soxhlet-extraction in a 60 °C water-bath for 6 h with 60 ml 1:1 petroleum ether/acetone (V/V). The extracts were transferred to a 250 ml separatory funnel and sulfonated with 10 ml of concentrated sulfuric acid several times until the sulfuric acid layer became colorless. After the sulfuric acid layer was discarded, the petroleum ether layer was purged with 6% sodium sulfate solution until the pH value of the extraction system was greater than 5.0. Finally, the petroleum ether layer was dehydrated with anhydrous sodium sulfate and concentrated by a rotary evaporator to 25 ml for GC detection.

The concentrated extracts were analyzed by an Agilent 6890 N GC, coupled with a micro-electron capture detection (μ-ECD) system, 7683 auto-injector and chromatographic working station. The GC column was a DB-1701 fused silica capillary column (J&W Scientific Inc.) that was 0.32 mm × 30 m × 0.25 μm. The injection conditions were: injector temperature, 210 °C; μ-ECD temperature, 320 °C; and the oven temperature started at 165 °C (holding time 2 min) and then increased to 265 °C at 6 °C min^{-1} (holding time 2 min). The carrier gas was helium with a flow rate of 2 ml min^{-1}, and the make-up gas was nitrogen with a flow rate of 60 ml min^{-1}. The injecting volume was 1.0 μl, which was injected into a split/splitless inlet operated in the splitless mode. The calibration method was based on a six-point calibration curve for individual components (1.0–200.0 ng ml^{-1}). Linear fits were used for all analytes, and correlation coefficients were >0.99.

2.3.2. PAHs

Only four pig, two chicken and two cow manure samples collected from Nanjing farms were selected to determine the residuals of PAHs in manure samples. To extract PAHs from the manure samples, 10 g of dry sample were placed in Soxhlet-extraction thimbles and extracted for 24 h with 60 ml of dichloromethane: acetone (1:1) in a 60 °C water-bath. The extracts were then reduced to near dryness on a rotary evaporator. The extracts were redissolved in about 2 ml of cyclohexane and cleaned by a chromatography column filled with 10 mm of anhydrous sodium sulfate, 80 mm of silica gel, 60 mm of neutral alumina and 10 mm of anhydrous sodium sulfate. For the cleaning, 15-ml of hexane:dichloromethane (1:1) was added for elution at the rate of 1 ml min^{-1} and the 3-ml beginning of the elution fraction was discarded, then the remaining elution fraction was collected and concentrated to near dryness by a rotary evaporator and redissolved in 1 ml of acetonitrile for HPLC analysis.

Determinations of PAHs were performed using a 2695 Waters Alliance system (Milford, MA, USA) equipped with an autosampler-controlled binary gradient system. A Waters® PAH C18 column (4.6 × 250 mm, particle size 5 μm; Waters Corporation, Milford, MA) with a Waters C18 guard cartridge (4.0 × 3.0 mm) used to separate PAHs. A Waters 2475 fluorescence detector was used to measure PAHs. The native fluorescence of the PAHs was used for their detection and quantification, and PAHs were determined by their retention times calibrated by a mixed standard sample from Supelco Company containing 16 individual PAHs. Acenaphthylene was not included in this study because of its low fluorescence properties. The chromatographic method employed an injection volume of 10 μl, at 30 °C column temperature and