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Level and characteristics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in feed and feed additives

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ARTICLE INFO

Article history:

Received 20 March 2016

Revised 13 June 2016

Accepted 29 July 2016

Available online 12 August 2016

Keywords:

PCDD/Fs

Chinese feed

Feed additives

Characterization

ABSTRACT

Feed security is a prerequisite for safe animal food products. In this study, 13 groups of feed and feed ingredients, totaling 2067 samples, were collected in the period of 2011 to 2014 from China. The highest mean level of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) was found in fish meals and shell powders, with a concentration of 60.35 ng/kg, followed by mineral origin materials. In terms of the toxicity equivalent concentration, the fish oil group showed the highest PCDD/F levels because of their bio-accumulation through the aquatic food chain, with an average concentration of 1.26 ng WHO-TEQ/kg, while the lowest level was observed in compound feed for chickens and pigs, with an average value of 0.16 ng WHO-TEQ/kg. OCDD and OCDF were the predominant congeners in all groups except fish oils, in which the primary congeners were 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF. For zinc chloride samples, different from other zinc-based compound samples, the main congeners were 1,2,3,4,6,7,8-HpCDF (17%), 1,2,3,4,7,8,9-HpCDF (15%), 1,2,3,4,7,8-HxCDF (12%) and OCDF (30%). Considering toxicity equivalency factors, the dominant congeners were 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 2,3,7,8-TCDF and 1,2,3,7,8-PeCDD, and the contribution to the total TEQ was 29%, 16%, 14% and 12%, respectively. Overall, 2.1% (43 out of 2067) of all the analyzed samples exceeded the different individual 'European Union maximum limited levels for PCDD/Fs. This study is beneficial for the determination of the status of contamination levels of feed and feed ingredients.

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Introduction

In China, like elsewhere in the world, the industrial revolution has been accompanied by a rapid rise in environmental contamination (Zhao et al., 2011), especially heavy metals and

persistent organic pollutants. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are classed as toxic and environmentally persistent compounds. They are formed as the by-products of many industrial and disposal processes and are a threat to the environment and to human health (Addeck et al.,

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2014; Bao et al., 2012; Chobtang et al., 2011). They are generally persistent in the environment because of their lack of microbial degradation and plant uptake (exclusive of some members of the cucurbit family) (Huelster et al., 1994). The concentrations of pollutants in animals depend on the environment where the respective species are living and feeding. Aquatic organisms such as fish and other marine animals can accumulate very large amounts of dioxins (Smith and Gangolli, 2002; Domingo and Bocio, 2007; Turyk et al., 2012). Land and agricultural animals accumulate dioxins through eating contaminated plants or feed, thereby entering the human food chain. China is one of the largest dioxin emitting counties in the world, with the annual dioxin emissions from various sources estimated at 10 kg toxic equivalent (TEQ), and the reported levels of PCDD/F contamination of many rivers, lakes, coastal areas, soil and sediment have been found to significantly exceed the safe limits (Bao et al., 2012; Zheng et al., 2008). These might be one of the reasons leading to the accumulation of dioxins in the food chain. In addition, the raw materials and production processes for feed and feed additives are another important source of contamination (Kim et al., 2011; Torres et al., 2013; Wang et al., 2014).

About 90% of human exposure comes from food, especially food of animal origin. Several studies have reported that contaminated animal feeds or feed additives could cause food contamination (Hayward and Bolger, 2005; Schulz et al., 2005). Moreover, several highly publicized incidents have occurred in the USA and in Europe during the past two decades, such as ball clay contamination in the United States (Ferrario et al., 2004), citrus pulp contamination in Germany (Malisch, 2000) and recycled fat pollution in Belgium (Bernard et al., 2002). In all cases, PCDD/Fs entered the food chain via animal feed. Since then, the general public has become concerned about PCDD/F levels in feed and feed ingredients. In China, with the developing economy and the improvement of people's living standards, the proportion of animal origin products in the diet has also increased. Therefore, it is necessary to control the safety of feed and feed additives in order to provide safe food of animal origin.

The European Food Safety Authority (EFSA) has launched and constantly updated Directives and Regulations laying down the official limits for levels of PCDD/Fs and polychlorinated biphenyls (PCBs) in food and feed (EFSA, 2010, 2012). In other countries, comprehensive reports on PCDD/F levels in feed are very limited (Eljarrat et al., 2002; Kim et al., 2007). In China, while the environmental levels of PCDD/Fs have been intensively studied (Deng et al., 2015; Li et al., 2008, 2010; Rong et al., 2010; Zhou et al., 2014), little data about the PCDD/F contents in feed has been reported, to the best of our knowledge. Therefore, this study was designed to determine PCDD/F levels in feed and feed ingredients obtained from different provinces in China.

Synthetic vitamins, as some of the most important nutritional supplements, are widely used for animal nutrition. China produced approximately 7.4×10^5 tons of vitamins in 2013 (China Feed Industry Association) and produced almost 40% of the world's vitamin E. Therefore, the safety of feed grade vitamins, especially vitamin E, has become very important. For this reason, we have analyzed many vitamin E samples at different stages of production.

In this study, seventeen 2, 3, 7, 8-substituted PCDD/Fs were determined in a total of 2067 samples using the high resolution gas chromatograph-high resolution mass spectrometer (HRGC-HRMS) platform according to the US EPA method 1613. This is the first comprehensive study on PCDD/Fs in feed and feed additives in China.

1. Materials and methods

1.1. Chemicals and materials

Solvents (acetone, *n*-hexane, dichloromethane, ethyl acetate, methanol, toluene for pesticide residue analysis) were purchased from J.T Baker, Co., Ltd. (USA). Calibration standard solutions, internal surrogate standards (EPA 1613-LCS) and injection standards (EPA 1613-IS) were obtained from Wellington Laboratories (Canada). Silica gel 60 (0.063–0.200 nm, AR grade) was purchased from Merck (Darmstadt, Germany) and was activated at 500°C for 6 hr before use. Sulfuric acid (95%–97%) was also purchased from Merck (Darmstadt, Germany).

1.2. Sampling

The sampling of feed categories was based on the main raw materials used to make feed and general feed compounds used for livestock and in fisheries. The samples were collected from different companies and markets located in different provinces in China from 2011 to 2014. The types and the amounts of compound feeds and feed additives are listed in Table 1. The samples were kept at 4°C or –20°C until analysis, according to the stability requirements of each sample.

1.3. Sample analysis

The analysis was carried out according to US EPA method 1613 B. All samples were spiked with surrogate standards (EPA 1613-LCS) before extraction. Fresh milk samples were freeze-dried before adding standards. Samples were extracted by an Accelerated Solvent Extractor (ASE 300, Dionex, USA) or Soxhlet extractor and purified used Fluid Management Systems (FMS). The method is reported elsewhere (Kim et al., 2007; Zhang et al., 2013). When

Table 1 – Number of samples from each feed category.

Feed group	Number
Materials of plant origin excl. oils	19
Materials of mineral origin	36
Other land animal products	52
Fish oils	34
Fish meals and shell powders	181
Anti-caking agents and binders	27
Trace elements	160
Pre-mixtures	35
Feed for chickens and pigs	23
Feed for fur animals, pets and fish	120
Vitamins	1089
Amino acids	133
Coloring agents	158
Total	2067

ASE was used, samples were extracted with *n*-hexane and dichloromethane (1:1, V/V) at 150°C and 1500 psi after spiking with internal standards. When the Soxhlet extractor was used, samples were extracted with toluene for 20 hr. After extraction, the solvent was evaporated and first purified using acid-modified silica-gel with *n*-hexane elution, followed by further purification using an automatic system (Power Prep, Fluid Management Systems, Waltham, MA, USA), comprised of multiple commercial silica-gel columns (PCBS-ABN-Std), basic alumina columns (PCBA-BAS-011) and carbon columns (PCBC-CCE-034). The PCDD/F fraction was separated and concentrated to approximately 25 µL. An injection standard (EPA 1613-IS) was added before instrumental analysis. Seventeen PCDD/F congeners were quantified using an isotopic dilution method by HRGC-HRMS (DFS, Thermo, USA/AutoSpec, Waters, USA) with a DB-5 MS capillary column (60 m × 0.25 mm i.d. × 0.25 µm). The instrumental conditions were similar to those reported by Zhou (Zhou et al., 2014).

1.4. Quality assurance and quality control

A blank sample was tested for each batch of six samples. The recoveries of internal standards were all in the range of 60%–120%. The laboratory has participated in international comparisons for the detection of PCDD/Fs and PCBs including in the food and feed field, which were organized by the Norwegian Institute of Public Health and European Union Reference Laboratory. TEQ of individual congeners was calculated by multiplying the concentration by the corresponding toxic equivalency factor (TEF) established by the World Health Organization in 2005 (Van den Berg et al., 2006), followed by the addition of the individual TEQs to obtain a total TEQ concentration for the mixture. The upper and lower bound values were calculated by setting the non-detectable congeners equal to the limit of detection and to zero, respectively.

2. Results and discussion

2.1. Level of PCDD/Fs in feed

The number of non-detected samples and the level of 17 PCDD/Fs in feedstuffs (Appendix A Table S1). The highest mean concentration was found in fish meals and shell powders (60.35 ng/kg), while the lowest group was compound feed for chickens and pigs (1.83 ng/kg). In the Korean report in 2007, the mass concentration of PCDD/Fs of fish origin was 4.60 ng/kg (Kim et al., 2007), which was much lower than that in China. In Egypt, the concentration in chicken feed was 2.32 ng/kg (Loutfy et al., 2007) and similar to that in China. Materials of mineral origin, trace elements, anti-caking agents and binders showed relatively higher concentrations of PCDD/Fs, with average levels of 40.44 ng/kg, 16.42 ng/kg and 10.62 ng/kg, respectively. Compared with compound feeds, pre-mixtures showed higher concentrations, with a mean value of 25.89 ng/kg. Plant origin and other land animal origin products showed similar levels (5.38 ng/kg and 7.75 ng/kg, respectively). For fish oil, the mass concentration of PCDD/Fs was 9.35 g/kg and was much lower than those reported in Japan (Hasegawa et al., 2007) and Korea (Kim et al., 2007).

Fig. 1 presents the TEQ distribution of individual feed sample and the mean levels of each feed group. An overall 2.1% (43 out of $N = 2067$) of the samples exceeded the different individual EU maximum limit levels for PCDD/Fs, which were set by the European Commission (Commission Regulation (EU) No 277/2012, 2012). This percentage was a little lower than results reported in Europe, in which the percentage was 8% (EFSA, 2010).

The highest level of PCDD/Fs was found in fish oils, in the range of 0.10–6.61 ng WHO-TEQ/kg, with an average of 1.26 ng WHO-TEQ/kg. Four of the fish oil samples (out of $N = 34$)

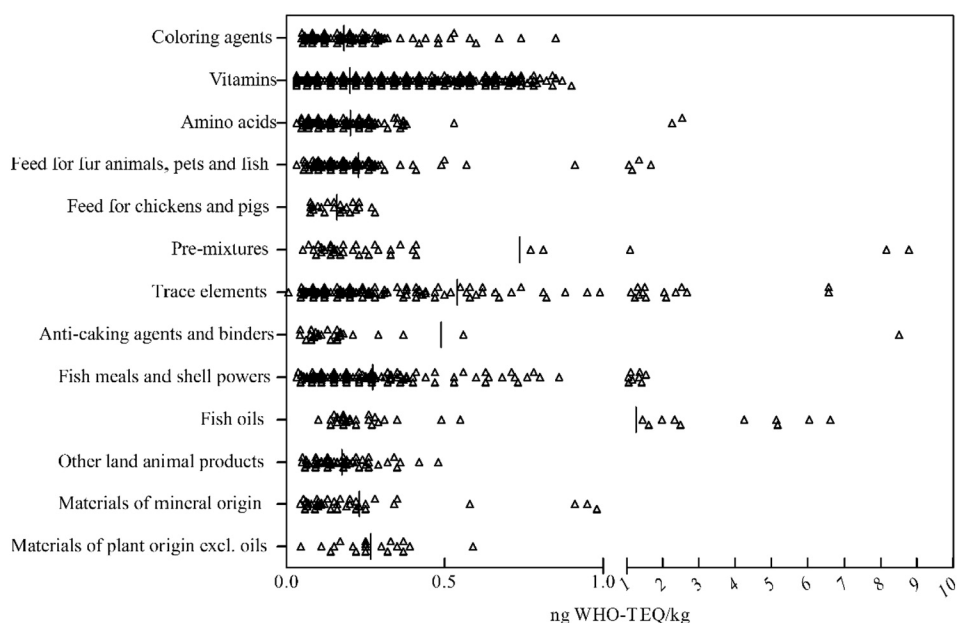


Fig. 1 – Toxic equivalent concentration (TEQ) distribution in individual feed sample and the mean concentration of each group. Upper bound value was applied.

exceeded the EU maximum limit level for the sum of PCDD/Fs (5.0 ng WHO-TEQ/kg). The result corresponds with previous studies that PCDD/Fs and DL-PCBs tend to bio-accumulate in fish oils through the aquatic food chain (Smith and Gangolli, 2002; Jacobs et al., 1998) and have relatively high concentrations. In Japan, the concentration of PCDD/Fs in the fish oil feed ingredient was 2.10 ng WHO-TEQ/kg (Hasegawa et al., 2007). In Europe, the concentration was 2.43 ng WHO-TEQ/kg (EFSA, 2010) and 3.25 ng WHO₉₈-TEQ/kg in Denmark, 3.9 ng WHO₉₈-TEQ/kg in Norway (Suominen et al., 2011). All were higher than those in this study.

The concentrations of PCDD/Fs in fish meals and shell powders ranged from 0.03 to 1.53 ng WHO-TEQ/kg, with average of 0.27 ng WHO-TEQ/kg. Four samples (out of $N = 181$) exceeded the EU maximum level (1.25 ng WHO-TEQ/kg). It was found that red fish meals (0.24 ng WHO-TEQ/kg) had higher PCDD/F concentrations than white fish meals (0.18 ng WHO-TEQ/kg). This might be caused by the use of different raw materials. In European reports, the average concentrations were 0.48 ng WHO₉₈-TEQ/kg (Suominen et al., 2011) and 0.73 ng WHO-TEQ/kg (EFSA, 2010), respectively. For other land animal products, including whey powder, animal liver powder and protein powder were found to contain under 0.5 ng WHO-TEQ/kg. In the European monitoring report, the concentration of PCDD/Fs in this group was 0.08 ng WHO-TEQ/kg (EFSA, 2010).

The second highest concentration of PCDD/Fs was found in pre-mixtures, with an average of 0.74 ng WHO-TEQ/kg. Two trace element pre-mixture samples showed higher levels of PCDD/Fs, which were 8.16 and 8.78 ng WHO-TEQ/kg. The average concentration of PCDD/Fs in pre-mixtures in Europe was 0.12 ng WHO-TEQ/kg (EFSA, 2010) and was lower than our results. Therefore, more attention should be paid to this kind of feed.

The concentrations of PCDD/Fs in mineral origin feed ingredients, including sodium bicarbonate, sodium carbonate, calcium phosphate, calcium chloride, calcium bentonite, mineral crystal and salt, were found to be in the range from 0.04 to 0.98 ng WHO-TEQ/kg, with an average of 0.22 ng WHO-TEQ/kg. Three samples exceeded the EU maximum level (0.75 ng WHO-TEQ/kg). This mean concentration was two times as high as previous reports (EFSA, 2010; Kim et al., 2007). Kaolin clay, which was reported to have extremely high levels of PCDD/Fs (Abad et al., 2002; Eljarrat et al., 2002), was not tested in this study.

Levels of PCDD/Fs in the group of trace elements (including chloride, sulfate, proteinate or amino acid complexes of trace elements such as chromium, copper, zinc, manganese and iron) were in the range of 0.01–2.67, with average of 0.37 ng WHO-TQ/kg. 8.8% of the samples in this group (14 out of $N = 160$) exceeded the EU maximum level (1.0 ng WHO TEQ/kg). Out of these fourteen samples, ten were zinc chloride samples. The average concentration of this group was higher than EU monitoring results, as was the over-limit ratio (EFSA, 2010). Therefore, this kind of additive is of continuing concern in China. Generally, additives of trace elements are one of major sources of feed PCDD/F contamination and there have been contamination incidents in many countries. For example, in 2003 in the USA, mineral mixture and premix contaminations were caused by copper oxide and zinc oxide (FDA, 2003), respectively, and the Chilean pork contamination in 2008 was caused by zinc oxide (Kim et al., 2011).

Because there was a reported contamination incident caused by ball clay in the USA (Hayward et al., 1999), this study also focuses on binders and anti-caking agents. The concentration of PCDD/Fs in this group, which includes kieselgur, silica, sepiolite, activated carbon, and white carbon black, was found to be in the range of 0.04–8.51 ng WHO-TEQ/kg, with an average of 0.50 ng WHO-TEQ/kg. Only one activated carbon sample exceeded the EU maximum level (0.75 ng WHO-TEQ/kg).

For the other three additive groups, vitamins, amino acids and coloring agents, the range of PCDD/Fs was 0.03–0.90, 0.05–0.85, and 0.03–0.53 ng WHO-TEQ/kg, respectively. The maximum level used to assess these three additive groups was set as 0.75 ng WHO-TEQ/kg, which was the lowest value of the EU maximum limit levels. The proportions of these three group samples that exceeded the maximum limit level were 1.1%, 1.5% and 0.6%, respectively. Choline chloride, which caused a PCDD/F contamination incident in Germany in 2000 (Llerena et al., 2003), was also studied. Eighty two choline chloride samples were analyzed and all samples were below 0.50 ng WHO-TEQ/Kg. There were no obvious differences between different formulations and carriers of choline chloride (data not shown). Since China is one of the main producers and exporters of vitamin E, this study analyzed vitamin E samples at different stages of production, such as the crude products, intermediate products and finished products, and all the samples showed relatively low levels of contamination (Fig. 2).

In feed for fur animals, pets and fish, the average PCDD/F concentration was 0.23 ng WHO-TEQ/kg, and none exceeded its individual EU maximum limit level. For fish feed, the average concentration was 0.22 ng WHO-TEQ/kg, and was higher than that in Ismailia city, Egypt (0.17 ng WHO₉₈-TEQ/kg) (Loutfy et al., 2007) and much lower than that in Finland (0.98 ng WHO₉₈-TEQ/kg) and Denmark (0.55 ng WHO₉₈-TEQ/kg) (Suominen et al., 2011). For pet compound feed, for example, for cats and dogs, the average concentration was 0.16 ng WHO-TEQ/kg and was a little lower than in fish feed.

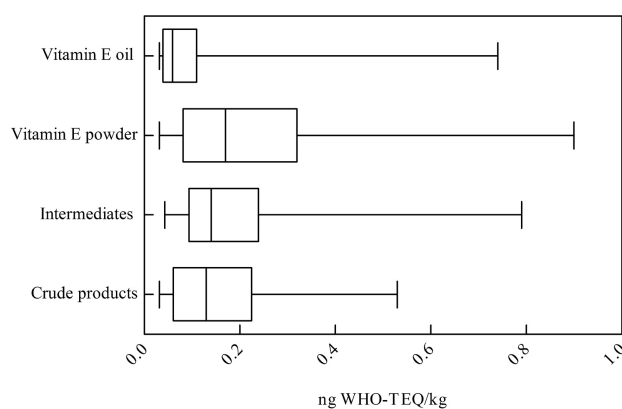


Fig. 2 – Box plot (whiskers at minimum and maximum, box at P25 and P75 with line at P50) of the overall concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in crude products ($n = 65$), intermediates ($n = 91$), vitamin E powder ($n = 523$) and vitamin E oil ($n = 137$) samples.

2.2. Homolog and congener profiles of PCDD/Fs in feed

It can be seen from Appendix A Table S1 that 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,7,8-HxCDF were detected at the highest frequency of all congeners in feed samples, with percentages of 67% and 63%, respectively. The congener detected at the lowest frequency was 1,2,3,4,7,8-HxCDD, which was only detected in 98 samples (out of $N = 2067$). This result is in disagreement with the EFSA reports (EFSA, 2010, 2012), in which Octa-CDD (OCDD) occurred at the highest frequency and 1,2,3,4,7,8,9-HpCDF at the lowest frequency.

For all groups, for PCDDs, HxCDD, 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD were detected at low frequencies and the total contribution to the sum of the PCDD/Fs of each group was less than 8%. In addition, HxCDF, except for 1,2,3,4,7,8-HxCDF, was also less detected. This indicated that hexa-chlorinated PCDD/Fs were not the main pollutants in feed and feed additives, and a similar situation was observed in the EFSA survey (EFSA, 2010). The reason may be that hexa-chlorinated compounds were less absorbed and bio-accumulated in feed ingredients, since the primary materials used in the ordinary production process could affect the finished products.

Overall, OCDD and Octa-CDF (OCDF) were the predominant congeners of all groups except fish oils, binders and anti-caking agents, with contributions from 41% (in coloring agents) to 93% (in other land animal products). These two congeners have previously been identified as the dominant ones in feed samples (Eljarrat et al., 2002). Moreover, contaminations in groups such as materials of plant origin, feed for chickens and pigs, other land animal products and amino acids, which showed high ratios for the sum of PCDDs/PCDFs ($R > 1.0$), were caused by relatively high OCDD levels. In these groups, PCDDs were the dominant congeners.

In fish oil, binder and anti-caking agent groups, 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF were the predominant congeners, with total contributions of 63% and 40%, respectively. This

characteristic of fish oil was similar to that in an earlier report (Hasegawa et al., 2007), but the results for binders and anti-caking agents were much different from previous studies (Abad et al., 2002). In the pre-mixture group, OCDD (44%) and 1,2,3,4,7,8-HxCDF (22%) were important constituents.

Fig. 3 shows the congener profile of fish meals. For red fish meals, OCDD and OCDF were the major compounds and contributed 96% of the sum of PCDD/Fs. For white fish meals, however, 2,3,7,8-TCDF (54%), OCDD (16%) and 1,2,3,7,8-PeCDF (15%) were more important. It can be seen that the relatively higher concentrations of PCDD/Fs in red fish meals were caused by OCDD and OCDF, although they had the lowest TEF values. In the Korean report, OCDD and OCDF were not detected in fish origin samples, in which the dominant congeners were 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF (Kim et al., 2007).

Since a relatively high percentage of zinc chloride samples exceed the EU maximum limit level, the distribution of PCDD/F congeners in zinc-based compound samples was studied (Fig. 4). For zinc chloride samples, the main congeners were 1,2,3,4,6,7,8-HpCDF (17%), 1,2,3,4,7,8,9-HpCDF (15%), 1,2,3,4,7,8-HxCDF (12%) and OCDF (30%). For the other zinc-based compound samples, OCDD (55%) and OCDF (26%) were definitely dominant ones. The predominant congeners in zinc chloride samples had relatively high TEF values, compared with other zinc-based compounds. This may be due to differences in production processes, and needs to be further studied.

The above results show that the sources of materials and different production processes could affect congener profiles even in the same group. Therefore, more detailed monitoring should be performed in further studies in order to obtain congener profile information for each category of feed and feed ingredient.

As can be seen, in this study OCDD was the most abundant congener. It has also been reported to dominate in some feeds, such as fish oil, feed materials of mineral origin including kaolin (Eljarrat et al., 2002), binding and anti-caking additives (Abad

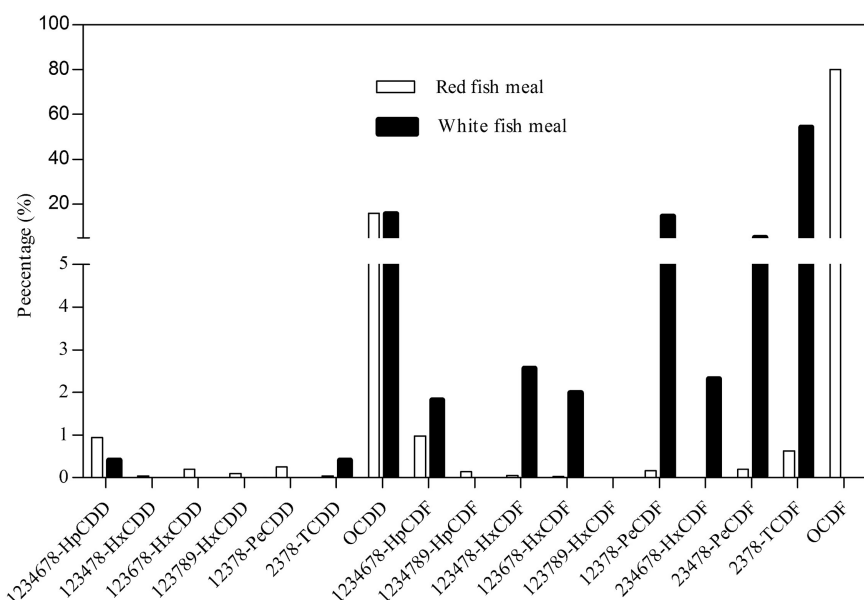


Fig. 3 – Percentage of 17 PCDD/F congeners to the sum of PCDD/Fs (mass concentration) in red fish meals and white fish meals.

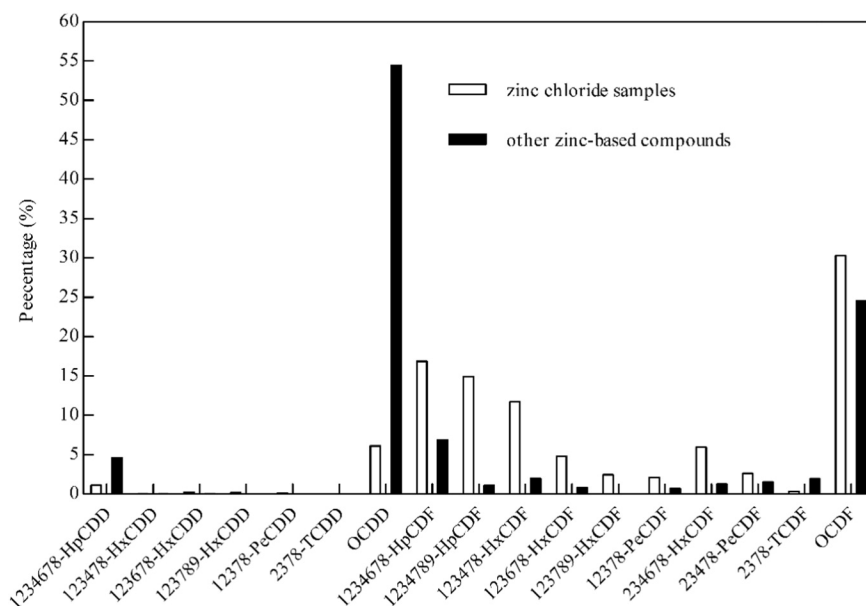


Fig. 4 – Percentage of 17 PCDD/F congeners to the sum of PCDD/Fs mass concentrations in zinc chloride samples and other zinc-based compounds.

et al., 2002) and feed compounds (Loutfy et al., 2007). This result was also found in food (Zhang et al., 2008), human breast milk (Tue et al., 2014), human blood and serum (Tohyama et al., 2011), air, soil, sediments, and emission resources from combustion (Zheng et al., 2008). Although OCDD has the lowest TEF (TEF = 0.0003), its widespread presence and high abundance make it worthy of our attention.

When considering toxic equivalents, typically, the overall main contributors were 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 2,3,7,8-TCDF and 1,2,3,7,8-PeCDD, contributing on average 29%, 16%, 14% and 12% of the total TEQ, respectively (Fig. 5).

These contributions reflect their high TEF values (Kim et al., 2007).

3. Conclusions

This study is the first relatively comprehensive survey of PCDD/Fs in feed in China. The results show that the overall situation of feed and feed ingredients is better than the EU monitoring results in 2010. We did not estimate the potential health risk caused by feed and feed additives of different

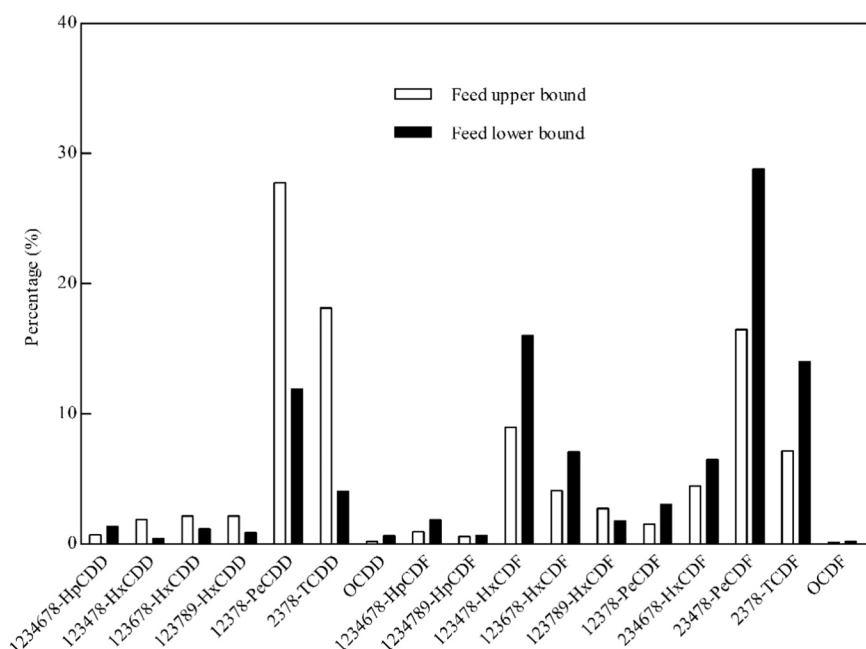


Fig. 5 – Percentage contribution of PCDD/F congeners to the total TEQ concentration of all analyzed feed samples.

provinces because of the distribution and sampling of products was imbalanced. In addition, due to the imbalance of sample numbers in each group and the vast area of China, further study should be carried out for PCDD/F levels in different feed ingredients and in different local areas. This study provides only general information about feed and feed ingredient contamination levels in China.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (No. 21525730) and the Strategic Priority Research Program of the Chinese Academy of Sciences (Nos. XDB14030401 and XDB14030402). The authors thank the staff of the dioxin lab of the China Inspection and Quarantine Institution for assistance in sample collection. Special thanks to Prof. Minghui Zheng for helpful revision and Dr. Marjorie A. Phillips from UC Davis for correction of English language problems.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2016.07.010>.

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