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PCDD/Fs profile and risk assessment in water and sediments around a non-wood pulp and paper mill when a chlorine bleaching treatment is applied

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ABSTRACT

Non-wood pulp and paper mills (PMs) with chlorine bleaching, which was identified as a primary pollution source of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) in water environment, are still widely distributed around important rivers and lakes. The composition profiles and risk assessment of PCDD/Fs in water and sediments around a non-wood PM, in which a chlorine bleaching treatment is applied, were evaluated. PCDD/Fs concentrations in downstream water and sediments were 0.44 and 1.10×10^3 pg TEQ kg^{-1}, respectively, which were noticeably higher than these in upstream water and sediments. It is, therefore, important to take into account the cumulative effect of pollution by these effluent emissions from non-wood PMs. PCDD/Fs analysis provided further information about PCDD/Fs contamination from non-wood PMs. The environmental risk for fish in water and sediment was low, while for mammalian wildlife in water environment was high, with the risk quotient values higher than 7.00.

Keywords: PCDD/Fs; Congener profiles; Risk assessment; Non-wood pulp and paper mills

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) have been widely concerned due to their ubiquity, high toxicity and potential risk [1]. Non-wood pulp and paper mills (PMs) with chlorine bleaching, which was identified as a primary pollution source of PCDD/Fs in water environment [2], are still widely distributed in China, India and Southeast Asia [3–5]. It was reported that about 53% of the world's non-wood pulp in 2013 [6,7] was produced in China, while this was 80% in 1998 [8]. The freshwater consumption of non-wood PMs is huge. Therefore, almost all of the non-wood PMs in China were distributed around rivers or lakes, leading to serious pollution of the water and sediment environment around the non-wood PMs.

World widely, extraordinary work has been committed to studying the PCDD/Fs emission in PMs [1,9,10]. One of the important deliverables is the "UNEP Toolkit", which provided a method to assess the PCDD/Fs emission from wood PMs, especially to assess the PCDD/Fs emission from wood PMs in the countries or regions without direct data [11]. And in recent years a few studies have reported the PCDD/Fs release distribution from non-wood PMs with chlorine bleaching in China [12–16]. Wang et al. [14,16] described the PCDD/F emissions and kinetics formation from Chinese non-wood PMs. Fang et al. [15] recently reported

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PCDD/F concentrations and profiles from non-wood PMs with enzyme-aided bleaching processes. From the respect of environmental impact and risk assessment of non-wood PMs to water environment, more efforts were focused on the traditional water quality index such as chemical oxygen demand, ammonia nitrogen. Studies on the PCDD/Fs emission and risk assessment from non-wood PMs to water environment were rare, especially considering the persistence of PCDD/Fs in water and sediment.

In order to better understand the environmental fate, potential for long-range environmental transport, and risk assessment for the local inhabitants, the composition profiles and risk assessment of PCDD/Fs in water and sediments around a non-wood PM, in which a chlorine bleaching treatment is applied, were evaluated in this study.

2. Materials and methods

2.1. PM process

A non-wood PM located in Dongting Lake (Hunan province of China), in which chlorine–alkaline extraction–hypochlorite bleaching (CEH) process is applied, was selected as a case study. The designed yield and real yield of the mill was 6.00 × 10^4 tons of air-dried pulp per year (Adt/y) and 5.40 × 10^4 Adt/y, respectively. The core processes of the mill were as follows: (1) raw material preparation, (2) alkaline digestion to dissolve lignin and extraction with the help of white liquor (mixture of NaOH and Na_2S), (3) pulp bleaching with CEH process, and (4) paper product making with paper briquetting machine. The bleaching wastewater was finally sent to a wastewater treatment plant (WWTP) for further treatment, and then emitted to the Cao Wei river.

2.2. Sampling points and methods

Samples R2 and S2 were collected from the sample point 2# (Fig. 1). R2 consists of effluents from the WWTP and Sample S2 consists of sludge from the sample WWTP (Table 1).

To evaluate the environmental impact and risk for the local inhabitants, the sample point 1# was placed upstream and sample point 3# downstream of the Cao Wei river. Further, the Dongting Lake was set as a sample point 4# (Fig. 1), from where water sample R4 and sediment sample S4 were collected (Table 1). Water samples (samples of R1, R2, R3 and R4) were collected and concentrated using site-enrichment consumables with 0.45-μm glass fibre filter membrane and XAD-2 resin, and prior to liquid sample, a certain quantity of isotope-labeled PCDD/Fs would be spiked into XAD-2 resin. Sludge samples (S2) were collected using stainless steel grab or shovel. Sediment samples (S1, S3 and S4) were collected by Peterson grab. All of these samples were stored below 4°C and in brown wide-mouthed jars for further analysis.

2.3. PCDD/Fs analysis

The PCDD/Fs were analyzed with the methods of China National stander (CNS) of HJ 77.1-2008, HJ 77.3-2008 and HJ 77.3-2008, with an Agilent 6890N gas chromatography coupled with JEOL JMS-800D high-resolution mass spectrometer (HRMS). The analysis procedure was described in previous study [17], with main steps as follows: (1) about 10 g of dried sample spiked with 1 ng of 13C-labeled PCDD/Fs was soxhlet extracted for 16 h with 300 mL of toluene; (2) the extracts were concentrated and then purified through separating funnels, a multi-layer silica gel column and silica-gel dispersed carbon column in turns; (3) spiked with 13C-labeled internal standards (EDF-5431, Cambridge Isotope Laboratories, Andover, MA, USA) as syringe spike and concentrated to 50 μL for instrumental analysis. The temperature programs used for determination were as follows: the initial oven temperature was set at 130°C for 1 min, and then increased at 15°C/min to 210°C, at 3°C/min up to 310°C, and at 5°C/min up to 320°C with a final hold time of 10 min. The HRMS is operated in an electron impact (38 eV) and selected ion monitoring mode at a resolution R > 10,000 (10% valley).

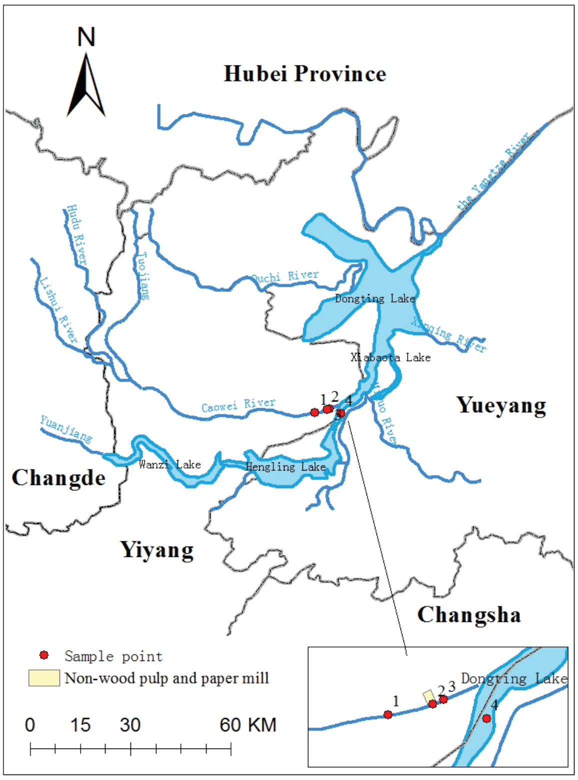

Fig. 1. Study area and sample points analyzed.

Table 1
Description of sample points and samples

Sample points	Water samples	Sediment samples	Sludge samples
Upstream of the Cao Wei river (1#)	R1	S1	–
WWTP (2#)	R2	–	S2
Downstream of the Cao Wei river (3#)	R3	S3	–
Dongting Lake (4#)	R4	S4	–

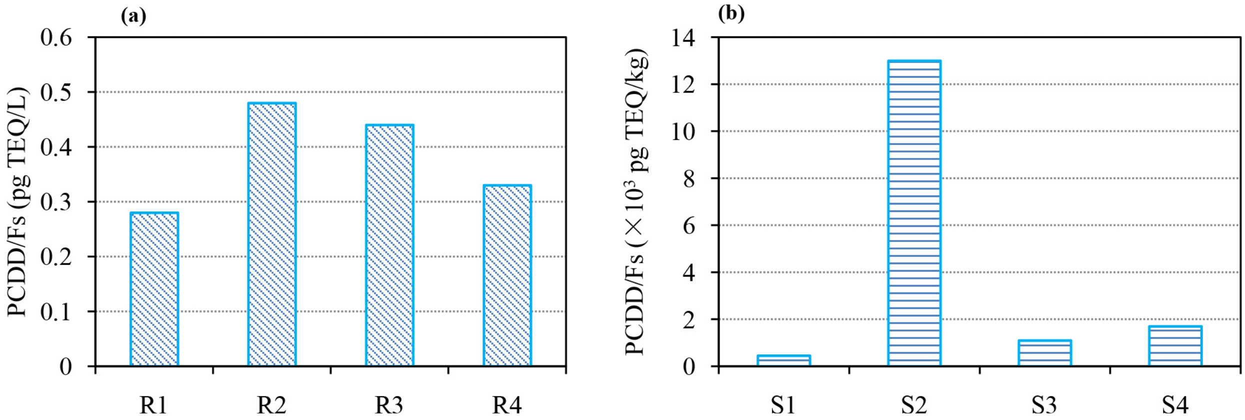

Fig. 2. PCDD/Fs concentration in (a) PCDD/Fs concentration in water—Cao Wei river water (R1 and R3), Dongting Lake water (R4) and WWTP effluent (R2); (b) PCDD/Fs concentration in sediment and sludge—Cao Wei river sediments (S1 and S3), Dongting Lake sediments (S4) and WWTP sludge (S2).

2.4. Quality assurance and quality control

Quality assurance and quality control were conducted in accordance with the requirement of USEPA method 1613 and Chinese national standard method. The recoveries of labeled surrogate, the sample detection limit and the sample quantity limit were controlled in accordance with the requirement of HJ 77.×-2008, and USEPA method 1613. The laboratory was also authorized with a Certificate of Accreditation for PCDD/Fs testing, and has often participated in interlaboratory PCDD/F analysis assessments.

2.5. Environment risk assessment

According to technical guidance on the environment risk assessment of the European Union, the risk quotient (RQ) was applied to assess the environment risk of the PCDD/Fs in Cao Wei river and Dongting Lake. The RQ is the ratio of the measured environmental concentration and predicted no effect concentration (PNEC) [18], which is shown in Eq. (1).

$$RQ = MEC / PNEC \tag{1}$$

where PNEC values are usually derived from dividing the experiment of acute and chronic toxicity data (LC50, EC50 and NOEC, etc.) by the assessment factors (AFs). The toxicity data can be obtained by ECTOX query, and the range of AF is from 10 to 1,000 [19]. According to the RQ values, environmental risk can be divided into three grades: (a) the low environmental risk, with RQ in the range of 0.01–0.10; (b) the medium environmental risk, with RQ in the range of 0.10–1.00; and (c) the high environment risk, with RQ greater than 1.00.

3. Results and discussion

3.1. TEQ values of PCDD/Fs in water and sediments

In a previously study [17], the PCDD/Fs concentrations in the bleaching wastewater were determined to be within the ranges of 3.50–5.30 pg TEQ L^{-1}. Then, the bleaching wastewater was treated by the WWTP. An activated sludge process followed by advanced treatment was applied in the WWTP to remove the organic matters and absorbable organic halide. Meanwhile this process was invalid for the removal of PCDD/Fs. However, the PCDD/Fs concentration of effluent of WWTP (R2) was 0.48 pg TEQ L^{-1} (Fig. 2), which was lower than that of the influent (i.e., bleaching wastewater). Due to the hydrophobic nature of PCDD/Fs [20], the difference of the PCDD/Fs between influent and effluent was mainly adsorbed by the sludge, with PCDD/Fs concentration of sludge in the WWTP (S2) reaching up to 1.30×10^4 pg TEQ kg^{-1} (Fig. 2).

The effluent of the WWTP was then discharged to the Cao Wei river. The PCDD/Fs concentration in the downstream water (R3) and sediment (S3) was 0.44 pg TEQ L^{-1} and 1.10×10^3 pg TEQ kg^{-1}, respectively, which was noticeably higher than in upstream water (R1, 0.28 pg TEQ L^{-1}) and sediment (S1, 0.45×10^3 pg TEQ kg^{-1}) (Fig. 2). It is, therefore, important to take into account the cumulative effect of the pollution by these effluent discharges from non-wood PMs. Considering the PCDD/Fs in sediment was characterized by cumulative pollution, the negative impacts to the environment from the mill are long term. It was reported that hundreds of thousands of noon-wood PMs were located around Dongting Lake during 1990s to early of 2000s, with most of these being small in scale with backwards technology and environmental protection facilities, leading to the serious pollution of the Dongting Lake. Therefore, to protect the environment, from 2005 to 2007, most of the small-scale mills were closed, with only a small amount of reserved mills were required to update their technology and environmental protection facilities to meet the environmental standards. However, due to the persistence of PCDD/Fs, the concentrations of PCDD/Fs in Dongting Lake were still higher with 0.33 pg TEQ L^{-1} in water and 1.70×10^3 pg TEQ kg^{-1} in sediment.

3.2. PCDD/Fs congener profiles in water and sediments

The PCDD/Fs congener profiles and mass concentrations in water and sediment are shown in Fig. 3. The total mass concentration of the 17 PCDD/Fs congeners in water varied from 4.10 to 5.90 pg L^{-1}, however, in the sediment samples, these concentrations reached values from 9.20×10^3 to 1.95×10^6 pg kg^{-1}. The mass concentrations of PCDD/Fs in S3 and S4

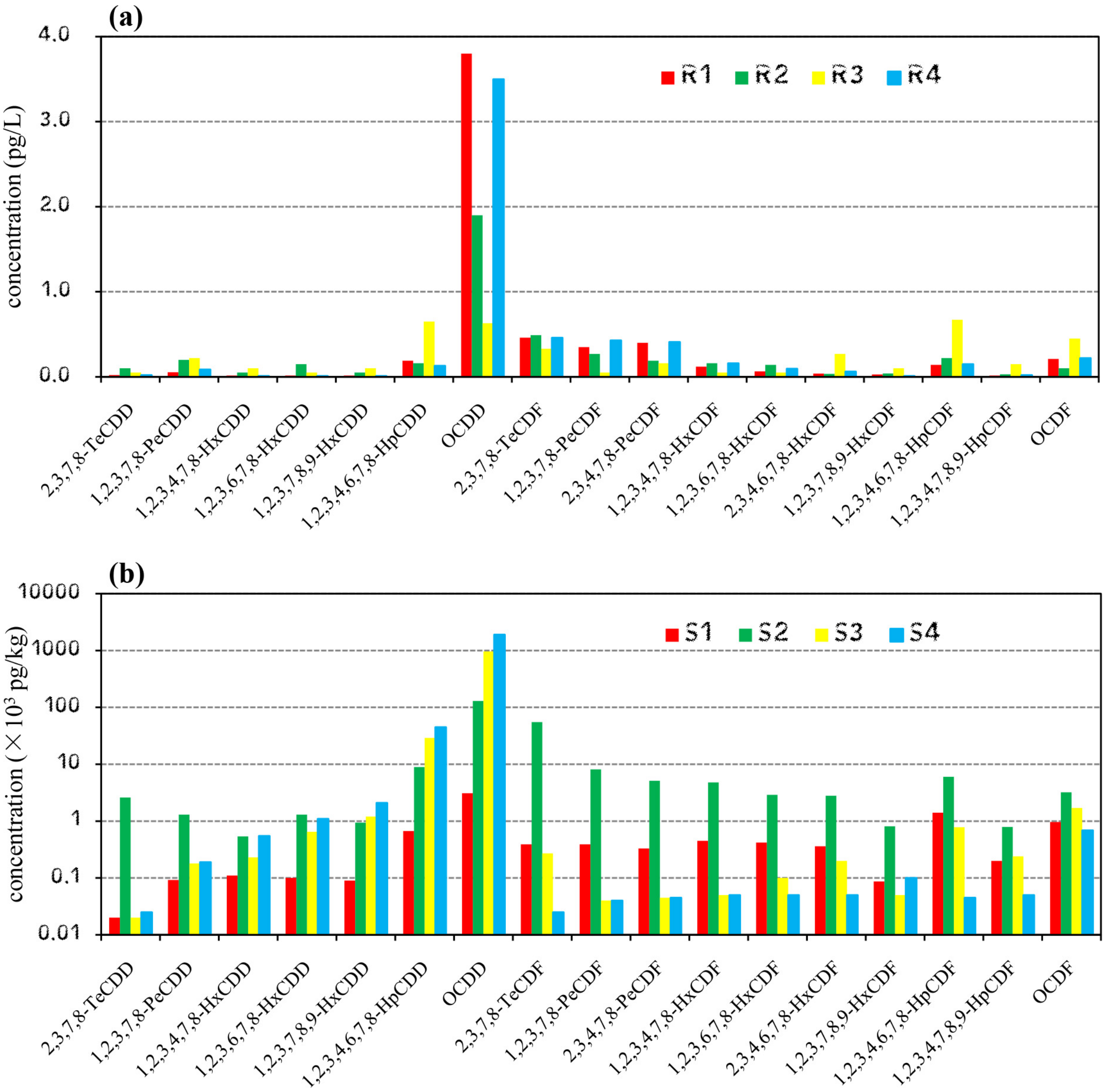

Fig. 3. PCDD/Fs congeners profile in (a) PCDD/Fs congeners profiles in water—Cao Wei river water (R1 and R3), Dongting Lake water (R4) and WWTP effluent (R2); (b) PCDD/Fs congeners profile in sediment and sludge—Cao Wei river sediments (S1 and S3), Dongting Lake sediments (S4) and WWTP sludge (S2).

were obviously higher than in S1, indicating a significant source of pollution from the PMs around Dongting Lake. For individual PCDD/Fs, the OCDD congener had the greatest concentration in the water and sediment, followed by 2,3,7,8-TeCDF; 1,2,3,7,8-PeCDF in water; and 1,2,3,4,6,7,8-HpCDD in sediment. Especially in S3 and S4, OCDD accounted for 96.50% and 97.40% of the total mass PCDD/Fs. This may be due to low-chlorinated PCDD/Fs were with smaller distribution coefficient (the logKow values), leading them relatively difficult to distribute to the sediment [21–23].

It was observed that the PCDD/Fs congeners profile of R1 and R4 were similar, while R2 and R3 were similar (see Fig. 4(a)), indicating a significant source of pollution from the WWTP effluent. However, due to the persistence of PCDD/Fs and its long-term cumulative pollution in sediment, the PCDD/Fs congener profiles of S3 and S4 were similar, but those of S3 and S1 were different (see Fig. 4(b)). Based on these results, there is further proof of the PMs being significant sources of pollution. It is surprising that the PCDD/Fs congeners profile of water and sediment in the same sampling point was all totally different from each other. A possible explanation is the intermolecular dispersive interactions and thus the more chlorine in the PCDD/F molecules, the greater the logKow values, leading PCDD/Fs congeners in water and sediment were different [23].

3.3. The risk assessment of PCDD/Fs

Based on US EPA's interim report on the data and methods for assessment of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin risks to aquatic life and associated wildlife [24], the minimum risk threshold value for fish and mammalian wildlife was listed

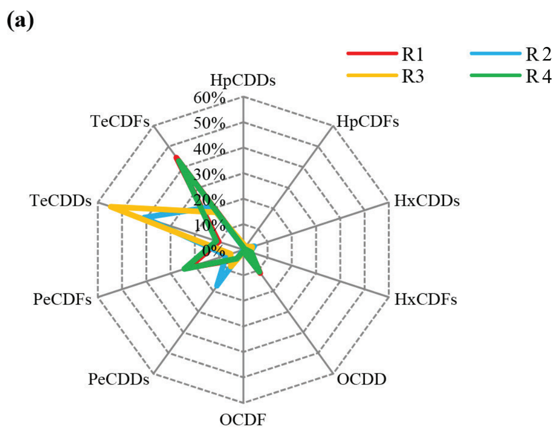

Fig. 4. Comparative analysis of PCDD/Fs congeners profile in (a) PCDD/Fs congeners profiles in water—Cao Wei river water (R1 and R3), Dongting Lake water (R4) and WWTP effluent (R2); (b) PCDD/Fs congeners profile in sediment and sludge—Cao Wei river sediments (S1 and S3), Dongting Lake sediments (S4) and WWTP sludge (S2).

Table 2
Environmental risk assessment associated with PCDD/Fs risk to fish and mammalian wildlife

Organism	Environment	PNEC	RQ in Sample 1#	RQ in Sample 3#	RQ in Sample 4#
Fish	Water	3.10	0.09	0.14	0.23
	Sediment	60.00	0.01	0.02	0.03
Mammalian wildlife	Water	0.04	7.00	11.00	17.50
	Sediment	2.50	0.18	0.44	0.68

in Table 2. The RQ values for fish in water environment were 0.09, 0.14 and 0.23, respectively, and in sediment environment, they were all below 0.10, suggesting a low environmental risk. However, considering the environmental risk to mammalian wildlife and human beings, it is essential to apply the PNEC for mammalian wildlife to calculate the RQ. The results showed that the RQ values for mammalian wildlife in water environment were 7.00, 11.00 and 17.50, respectively, while in sediment, they were 0.18, 0.44 and 0.68, respectively, suggesting a high environmental risk in water environment and medium environment risk in sediment environment. Therefore, in future, the mills around Dongting Lake should update their pulp bleaching process to reduce their dioxin emission levels, and convert pulp bleaching process from CEH to elemental chlorine free or totally chlorine free, which been proven to be an effective way to reduce dioxin emissions. Furthermore, to ensure the security of the drinking water for the people around Dongting Lake, a proper drinking water purification process that ensure the removal of PCDD/Fs should be considered.

4. Conclusion

PMs were one of the most significant emission sources of PCDD/Fs. There were numerous non-wood PMs in China, yielding 6.80 million tons in 2015 [6]. The freshwater consumption of non-wood PMs is huge. Therefore, almost all of the non-wood PMs in China were distributed around rivers or lakes, leading to serious pollution of the water and sediment environments around the non-wood PMs. We conducted a detailed survey of the PCDD/Fs concentrations and congener profile distributions in the water and sediment environment of Dongting Lake. Generally, PCDD/Fs concentrations in downstream water (R3) and sediment (S3) were 0.44 and 1.10 × 10^3 pg TEQ kg^{-1}, respectively, which were noticeably higher than in upstream water (R1) and sediment (S1), indicating that the WWTP effluent from the pulp mill could be a source of pollution. This possibility was further proven by analyzing the PCDD/Fs congener profiles in water and sediment. Among the individual PCDD/Fs, the OCDD congener had the greatest concentration in the water and sediment, followed by 2,3,7,8-TeCDF; 1,2,3,7,8-PeCDF in water; and 1,2,3,4,6,7,8-HpCDD in sediment. The RQ values for fish were below 0.30 and 0.10 in the water and sediments, respectively, suggesting a low environmental risk. However, the RQ values for mammalian wildlife were all higher than 7.00 in water environment, suggesting a high environmental risk in water environment. In the future, more efforts should be devoted to updating pulp bleaching process to reduce the levels of dioxin emissions from pulp mills.

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