A Study on the Concentration Variation and Mass Balance of Dioxin in the Waste Water Processing Facilities for the Vinyl Chloride Monomer Factory

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Introduction

In the "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases" published by the United Nations Environment Programme (UNEP) in 2005[1], it explicitly pointed out that waste water produced in the manufacturing process of chlorine was one of the polluting sources of dioxin. In Japan, Ministry of the Environment conducted a survey on the dioxin concentrations in the waste water discharged from seven factories of vinyl chloride monomer (VCM) in 2005[2]; seven sets of data were obtained and the dioxin concentrations were in the range from 0.022 to 4.0 pg-TEQ/L. In 2007, EPA of Taiwan carried out a survey on the dioxin concentrations in the raw waste water and effluent of four factories of VCM in Taiwan[3]. Six sets of data were obtained in the raw waste water of these four factories and the dioxin concentrations were in the range from 38.5 to 1546 pg I-TEQ/L; eight sets of data were obtained in the effluent of these four factories and the dioxin concentrations were in the range from 0.211 to 9.53 pg I-TEQ/L. In this study, we determined the dioxin concentrations of waste water processing units of a factory of VCM to assess the variation of the dioxin concentrations of the waste water from these units and the distribution of the congener profile of the seventeen 2,3,7,8 chlorinated substituted PCDD/Fs; we also carried out a survey on the sludge in the waste water processing plant so as to assess the mass balance of dioxin contents in the waste water treatment facility.

Materials and Methods

The factory produced 0.35 million tons of VCM per year and discharged about 36,000 cubic meters of waste water per month; the factory produced about 50 tons of sludge (its water content was about 70%) per month. The factory used the technologies of activated sludge, coagulation-precipitation, and filtration to process the waste water. In this study, we collected waste waters from outlets of the equalization tank, the sedimentation tank after the activated sludge treatment, chemical precipitation tank, effluent and the sludge of the storage cake tank so as to obtain the dioxin concentrations.

Water samples were collected in pre-cleaned sampling bottles with large volume (about 25L). The amount of water sampled was 25-50 L. After samples were carried back to the laboratory, the pre-treatment would follow the procedure: water samples would first filter through the glass fiber membrane (Advantec GD-120), then the filtrate would pass through Polyurethane Foam (PUF) to adsorb the trace amount of PCDD/Fs in water with the trapping velocity less than 1.0 L/min, the PUF would put together with the glass fiber membrane in a clean area for air dry. Place the sludge sample on a piece of clean aluminum foil, then put it in a hood to be dried (it takes about 3 to 5 days). Grind the dried sludge to let it go through a standardized sieve of 18 mesh (that is a diameter $\leqq$1 mm). After that the mixture would put into a sample bottle. Then, the samples were analyzed according to USEPA Method 1613B, Samples were quantified by HRGC/HRMS (Thermo TRACE GC ULTRA/DFS) using a DB-5MS capillary column (60m × 0.25mm i.d. × 0.25μm film thickness). Toxic equivalents as 2,3,7,8-TCDD (TEQ) were calculated by using the international toxicity equivalency factors (I-TEFs). All samples of the seventeen congeners of dioxin can be detected in this study.

Results and Discussion

The dioxin concentrations of waste water were found respectively as 1546, 89.0, 28.0, 9.38 pg I-TEQ/L, for equalization tank, the sedimentation tank after the activated sludge treatment, chemical precipitation tank, and effluent and the dioxin concentration in the sludge was 2.26 ng I-TEQ/g. Facilities in the waste water treatment plant and the flow chart of treatment as well as the variation of dioxin concentration are shown in figure 1. It is obvious that dioxin concentration of waste water generated is high in the VCM process. However, the dioxin concentration will reduce gradually after treatments although dioxin concentration remains high in the sludge.

The congener profiles of the seventeen 2,3,7,8 chlorinated substituted PCDD/Fs of various treatment units is show in Figure 2. The profiles were calculated according to the fraction (%) of each congener to the total PCDD/F mass concentration. It shows from figure 2 that PCDD/F congener profiles of various treatment units did not change significantly. This is due to the fact that the PCDD/F congeners were not degraded throughout the entire treatment. The PCDD/F congener profiles of the VCM factory show that the most abundant congeners in waste water and sludge were OCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF, which are consistent with those found in other study[4].

This study is to investigate the mass balance of dioxin in the waste water treatment plant. Two tests were conducted for dioxin concentration on the raw waste water, effluent and sludge, the dioxin concentrations of the raw waste water are 1546 and 661 pg I-TEQ/L respectively; the dioxin concentrations of effluent are 9.38 and 0.667 pg I-TEQ/L respectively; the dioxin concentrations of the sludge are 2.26 and 1.78 ng I-TEQ/g respectively. The mass balance results are shown in Table 1. Different amounts of dioxin between raw waste water and effluent were 0.66746 and 0.28552 g I-TEQ/year respectively, and the dioxin amounts in the sludge were 0.40680 and 0.32094 g I-TEQ/year respectively. The balance are -0.261 and 0.035 g I-TEQ/year.

This study shows that the dioxins were not degraded throughout the entire waste water treatment. The different amount of dioxins between raw waste water and effluent through waste water treatment may transfer to the sludge.

Acknowledgments

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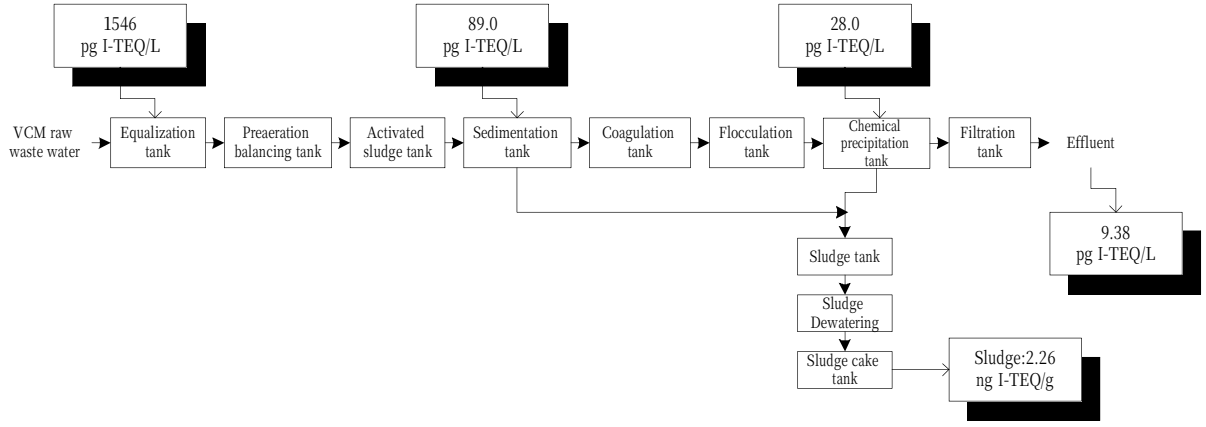

Figure 1: Facilities in the waste water treatment plant and the variation of dioxin concentration

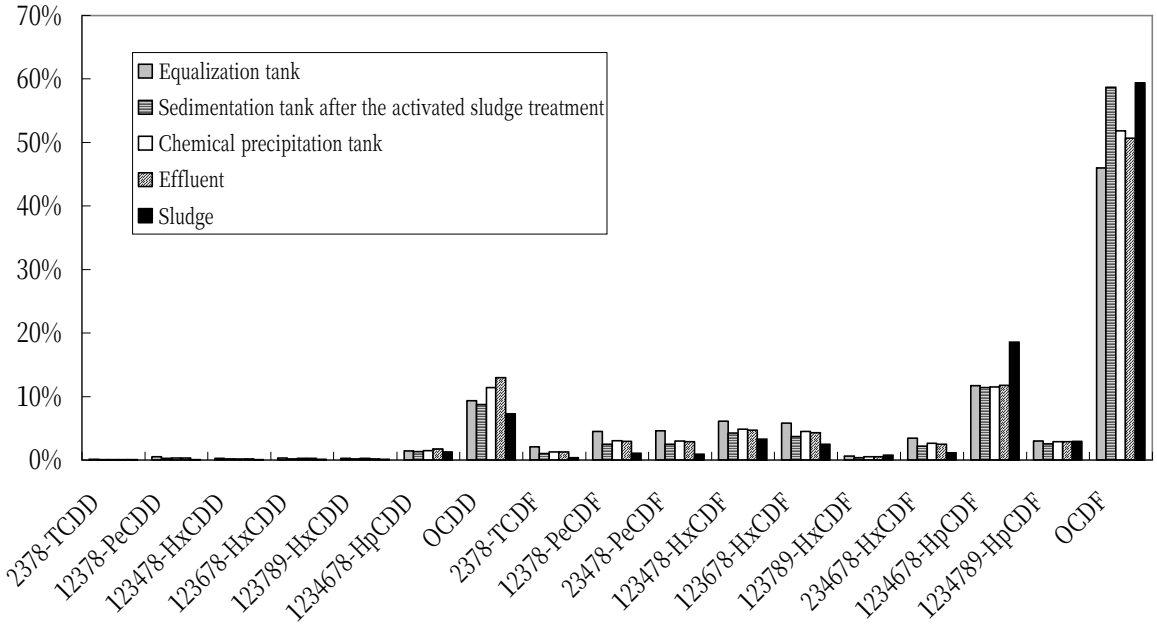

Figure 2: PCDD/Fs congener profiles of various treatment units

Table 1: Dioxin mass balance

	Dioxin amount in the raw waste water (g I-TEQ /year)	Dioxin amount in the effluent (g I-TEQ /year)	Different amount of dioxin between raw waste water and effluent (g I-TEQ /year)	Dioxin amount in the sludge (g I-TEQ /year)	Balance (g I-TEQ /year)
1st sample collection	0.66787	0.00041	0.66746	0.40680	-0.261
2nd sample collection	0.28555	0.00003	0.28552	0.32094	0.035