



# Dioxin sources to the aquatic environment: Re-assessing dioxins in industrial processes and possible emissions to the aquatic

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## ARTICLE INFO

### Article history:

Received 19 October 2020

Received in revised form

21 January 2021

Accepted 27 January 2021

### Keywords:

PCDD/PCDF

Water pollution

Industrial sources

Acetylene manufacturing

Caprolactam manufacturing

Pattern

Unintentional POPs

## ABSTRACT

Releases of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs) from industrial or thermal processes to the aquatic environment are considered small compared to emissions to air today. However, industrial processes have occasionally released PCDD/PCDFs into local aquatic environments. PCDD/PCDF formation and releases were re-examined based on investigations conducted before the introduction of water quality regulations in Japan. Emphasis was given to PCDD/PCDF formation in various industrial processes such as the manufacture of acetylene and caprolactam.

In acetylene production, PCDD/PCDFs are formed in the oxidative process using chlorine to remove impurities, with PCDFs formed with the particular chlorine pattern with 1,2,7,8-TetraCDF, 2,3,7,8-TetraCDFs and 1,2,3,4,7,8-HexaCDF as major congeners and low PCDDs levels. This indicates that acetylene production residues contain organochlorines.

In caprolactam production, formation of PCDD/PCDFs in the cyclohexane photolactamization process has been confirmed and the emission factor for PCDD/PCDF releases to water from caprolactam manufacture was estimated with an emission factor for releases to the aquatic environment of  $0.25 \pm 0.04 \mu\text{g-TEQ/t}$ .

A range of additional processes with PCDD/PCDF release were also found during the Japanese survey. Overall, the formation processes were placed in two categories: A) chemical synthesis processes and B) flue gas treatment of high temperature processes. The final effluent water met the PCDD/PCDF limits by applying advanced treatment for PCDD/PCDF removal such as activated carbon treatment. The survey shows that industrial processes involving elemental chlorine or other processes that facilitate chlorination or use chlorinating chemicals should be assessed and controlled for PCDD/PCDFs and other unintentional POPs releases to water. In such surveys, chemicals from the chlorine and organochlorine industry should also be assessed for PCDD/PCDFs and other unintentional POPs contamination as proposed by the UNEP Toolkit. The current study can contribute to the Stockholm Convention implementation of Article 5 of the Stockholm Convention to take measures to reduce the release of UPOPs from anthropogenic sources with the goal of their continuing minimization and, where feasible, ultimate elimination.

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## 1. Introduction

In the past, releases of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF) from industries to rivers have contaminated entire river systems. In Germany, the release of

PCDD/PCDF from titanium and magnesium production in the 1940s contaminated 400 km of the Elbe River and related flood plains that continues impacting grazing cattle today [1–3]. Similarly, in Finland a chlorophenols manufacturer released approx. 30 kg dioxin toxic equivalents (TEQ) (8000 kg total PCDD/PCDFs) into the Kymijoki River. The PCDD/PCDFs have migrated slowly into the Baltic Sea over the decades so that more than 12.4 kg TEQ (approx. 40%) have reached the Baltic Sea today [4]. In these sediments of the Kymijoki River, PCDD/PCDFs were recently assessed and no

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Peer review under responsibility of KeAi Communications Co., Ltd.

evidence of dechlorination/degradation was detected. It was concluded that concentrations of weathered PCDD/PCDFs in these sediments are expected to remain stable for decades or centuries with further migration towards the Baltic Sea [5].

PCDD/PCDFs from different sources accumulate in fishes. Today herring and other oily fish from the Baltic Sea still exceed EU regulatory limits so they cannot be sold on the European market, and the PCDD/PCDF levels in the fish are relatively stable [6]. Also Australia's Sydney harbor has been contaminated by the release of PCDD/PCDFs from 2,4,5-T and 2,4-T and PCP production from 1949 to 1976. As a consequence, fish in the harbor have PCDD/PCDF levels too high for human consumption, and commercial fishing is banned [7,8]. Such cases demonstrate the importance of having policies and regulations to restrict releases of PCDD/PCDFs and other POPs to surface waters in order to prevent pollution of sediments and aquatic fauna.

Since the 1980s and 1990s, PCDD/PCDF releases have been reduced and controlled by improving and stopping production processes and applying best available techniques (BAT) and best environmental practice (BEP) in industrial countries. On the other hand, potentially problematic industries such as organochlorine, leather, and textile industries have largely moved to China, India or Bangladesh where lower standards were in place in the past [9].

A wide range of countries have regulatory limits for PCDD/PCDFs in air emissions from incinerators and metal industries so that emissions are monitored, abundant data are collected, studies are conducted, and control measures are in place [10–13]. However, few systematic studies of sources of PCDD/PCDF releases to the aquatic environment have been conducted [14], and often no specific regulations exist. However, Japan restricts releases of PCDD/PCDFs in industrial water to 10 pg TEQ/L and has a surface water quality standard of 1 pg-TEQ/L. The Japanese dioxin inventory [15], indicates an aquatic release of 1.5 g-TEQ/y for the fiscal year 2010 compared to a total release to air of 158–160 g TEQ/y from major sources that include approx. 1100 municipal waste incinerators, 1500 industrial waste incinerators, and large metal industries.

In the pulp and paper industry, it is generally known that, the bleaching process using chlorine is a source of PCDD/PCDF releases to water [16–19]. However, studies of PCDD/PCDF releases to water from other industries are rare [20]. Nonetheless, PCDD/PCDFs releases to the aquatic environment may well occur on local scales. In Japan, PCDD/PCDFs exceeding the national water quality standard have been found [21]. In many cases, PCDD/PCDFs detected in aquatic environments have been attributed to organochlorine pesticides. In particular the use of pentachlorophenol (PCP) and the herbicide chlornitrofen (CNP; banned 1995 in Japan) is estimated to have resulted in the release of more than 450 kg TEQ to Japanese rice fields where it is slowly migrating over decades to surface waters and sediments [22,23].

On the other hand, there are confirmed cases in Japan where PCDD/PCDFs were unintentionally produced by other industrial processes that had not been previously recognized as sources of PCDD/PCDFs. This was recognized by a pollution event where 25 pg-PCDD/PCDF TEQ/L were detected in river water in Nagoya city at February 2000. The levels exceeded Japan's water quality standard (1 pg-TEQ/L) by a factor of 25 and the cause was investigated [24]. The source was found to be a caprolactam manufacturing facility - which is an intermediate product for nylon - that was discharging its wastewater into the river. Triggered by this event other facilities and manufacturing processes with potential emission risk were assessed.

In the current study, findings of PCDD/PCDF formation in those manufacture processes are described based on the data obtained in the survey of Japan [25]. The survey included the manufacturing processes of caprolactam, chlorobenzene, acetylene, alumina fibers,

and crude pigments among others. PCDD/PCDFs as well as other unintentional POPs formed in these processes can be released into open waters along with wastewater from such facilities. The UNEP Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on Persistent Organic Pollutants recommend the use of PCDD/PCDF as indicators for other unintentional POPs (UPOPs) where appropriate [26a] and also PCDD/PCDF are the main regulated UPOPs in Japan and internationally. Therefore selected manufacture processes were investigated and evaluated for PCDD/PCDF formation and release to water. Chemical characteristics based on composition analyses of PCDD/PCDFs congener distributions are also examined. Through these investigations, for the first time findings on releases of PCDD/PCDFs to aquatic environment of these processes are described and their control discussed.

## 2. Materials and methods

### 2.1. Selection of facilities

The basis for considering and examining the discharge of PCDD/PCDFs to the aquatic environment and its regulation in Japan is the Law Concerning Special Measures against Dioxins established in 1999 and discharge regulations for PCDD/PCDFs are stipulated in the law [27]. In conducting related investigations for this purpose, some cases of pollution of the aquatic environment have been clarified. Some facilities were selected because elevated PCDD/PCDFs were detected in surface water. Also facilities of the organochlorine industry (chlorobenzenes, certain pigments) and facilities using chlorine in a process (acetylene process) were investigated similar to the suggested approach later published in the UNEP Toolkit in the section on "Guidance on Identifying Sources of PCDD/PCDFs" [26b].

### 2.2. Sampling of process discharge water and wastewater

In 2001, the Ministry of the Environment of Japan conducted a detailed survey with regard to industrial sources of PCDD/PCDFs releases to aquatic environments. The survey data was compiled by the Japan Environmental Sanitation Center in March 2003 [25]. In the survey report, written in Japanese, PCDD/PCDF emissions were investigated in water and wastewater samples from various industrial processes. As a result, industrial sources of PCDD/PCDFs to the aquatic environment were identified and regulated by the Government of Japan. In order to obtain detailed measurement data, a number of samples of aqueous waste streams in the purification processes and also final effluents were collected and analyzed for PCDD/PCDFs from different facilities manufacturing each of the desired chemicals. In the production process of one facility, 4 to 5 samples were collected. The samples were collected by an analytical institution in the presence of facility officials and the environmental administration department of the competent authority. Investigated manufacturing processes were the production of acetylene, caprolactam, chlorobenzene, alumina fibers and crude pigments among others. Initial information was presented in a conference [28].

### 2.3. Analysis

PCDD/PCDF analyses were conducted for both dissolved and suspended constituents in wastewater samples, using the methods determined by the Japanese Industrial Standards (JIS) Committee [29]. Wastewater samples were collected in the amount necessary for measurement - tens of liters - in order to reach the necessary

detection limits. The analyses were conducted at accredited laboratories in Japan.

In pretreatment, the aqueous sample was first separated into suspended solids and soluble components using a glass fiber filter having a pore size of 1  $\mu\text{m}$ . The pretreatment method for the analysis of aqueous samples is as follows: after adding the internal standard substances,  $^{13}\text{C}$ -PCDD and PCDF and also DL-PCB as cleanup spikes, to the sample, the sample was filtered through a 1  $\mu\text{m}$  glass fiber filter paper, then shaken and extracted with dichloromethane three times. The filtrate residue was air-dried and extracted for 16 h by the Soxhlet method using toluene. After combining these extracts, column cleanup was performed after dehydration and concentration. Then, after hexane extraction was performed by multilayer silica gel column chromatography, cleanup was performed by activated carbon column chromatography. Finally, the hexane extract was concentrated, and, after adding syringe spikes, analyzed using GC-HRMS. Regarding the recovery rate of the internal standard substance, The Japanese Industrial Standard (JIS) [29] stipulates that the recovery rate of the internal standard substance for cleanup spikes is 50–120%, which was also within this range in this measurement.

In addition to determining the total concentration of each homologue, this measurement also included the 1,2,7,8-TCDF isomer, which can be an indicator of elemental chlorination, and several isomers –1,3,6,8-TCDD and 1,3,7,9-TCDD—that do not have toxic equivalency factors (TEFs).

For quality control purposes, each sample was analyzed simultaneously by three different laboratories. Since the PCDD/PCDF survey included three kinds of water samples – industrial water, wastewater from industrial production processes and comprehensive effluent water mixed with various process effluents, the concentration range was thought to be significantly different. Therefore, for quality control, samples were collected and evaluated from all three types. In addition to the quality control survey, all samples were analyzed by three laboratories.

#### 2.4. Evaluation of quality control

All measurements have been conducted according to the JIS national standard which includes severe QA/QS like blank tests and calibration of instruments.

The results for the quality control of measurements of PCDD/PCDFs in the same samples in different participating laboratories are shown in Table S1. From the numeric range of 0.1 pg-TEQ/L for clean industrial water to highly polluted wastewater containing close to 100,000 pg-TEQ/L for the wastewater from the rinsing tower using sodium hypochlorite in the acetylene production facility the PCDD/PCDF levels in the water samples spread over 6 orders of magnitude. The measured data of the participating laboratories showed that the data of all concentration levels were in good agreement with a deviation reasonable for different laboratories. Hence, it was considered that the quality of the participating accredited laboratories was appropriate and the generated data reliable.

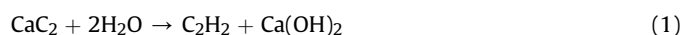
### 3. Results and discussion

#### 3.1. Formation of PCDD/PCDFs in calcium-carbide acetylene manufacturing

Acetylene is a highly reactive, commercially important gas used throughout the world in the synthesis of organic raw materials for manufacturing vinyl chloride, trichloroethylene, acetic acid and acrylonitrile etc. and also is used in oxyacetylene welding. In most of developed countries such as the United States, the calcium

carbide process has been replaced by alternate methods of acetylene manufacture. However, it remains an important source of acetylene in countries such as China, India, and Japan where there is ready access to inexpensive coal as the source of coke for calcium carbide production [30].

Acetylene is mainly manufactured by the partial oxidation of methane or the chemicals that appear as side products in the ethylene production stream from cracking of hydrocarbons. In 2017, the annual production amount of acetylene in Japan was 9717 tonnes dissolved in acetone or similar solvent for shipping and industrial and medial use. Production has decreased slightly [31]. However global production has significantly decreased from 10 million tonnes in 1960 to a current rate of only a few hundred thousand tonnes, mostly from sources other than coal [32]. The chemical was traditionally prepared by the hydrolysis of calcium carbide, a reaction discovered by F. Wöhler in 1862 in Germany and industrialized by Canadian inventor T. Willson in 1890s [33].



Calcium carbide production requires extremely high temperatures of around 2000 °C, necessitating the use of an electric arc furnace. In the US, this process was an important part of the late-19th century revolution in chemistry enabled by the massive hydroelectric power project at Niagara Falls.

A traditional manufacture process has been employed in Japan. Manufacturers produce acetylene by using either the dry or wet calcium carbide process to avoid explosion and polymerization of acetylene. In the next stage, dusts generated in the acetylene gas are removed and then some impurities such as phosphine and hydrogen sulfide are removed in gas purification processes using hypochlorite or sodium hypochlorite ( $\text{HClO}$  or  $\text{NaClO}$ ); chlorine water ( $\text{Cl}_2$ ); ferric chloride ( $\text{FeCl}_3$ ) and copper chloride ( $\text{CuCl}_2$ ) etc. An example of the dry process is shown in Fig. 1 and the process

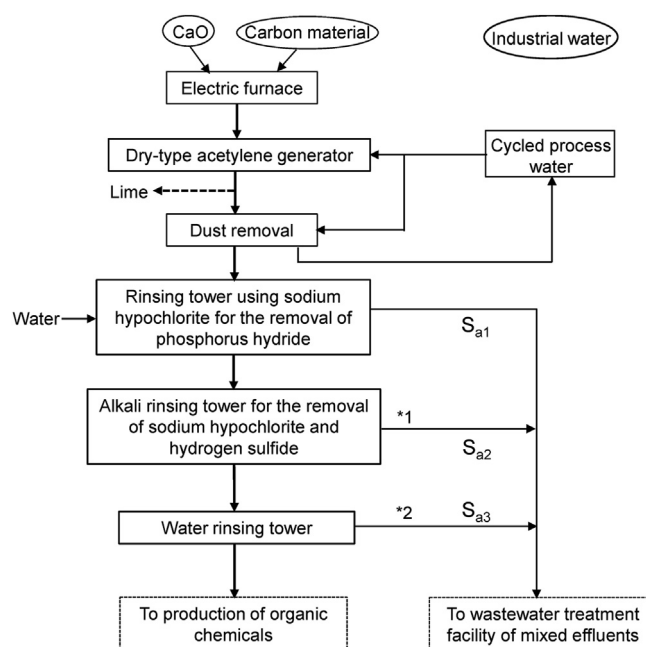


Fig. 1. Acetylene manufacturing process and water sampling points in an investigated facility ( $S_{a_i}$  means water sampling point. \*1: The water is changed when the alkalinity is lowered and sodium hydroxide is added. \*2: The rinse water is used repeatedly and changed once a day.).

flow is illustrated based on a Japanese textbook on pollution control management with regard to PCDD/PCDF [34]. The water sampling points in this study are also shown in Fig. 1.

Calcium carbide is produced from the high-temperature reaction of calcium oxide and coke in an electric arc furnace as mentioned above. The chemical is subsequently reacted with water to form acetylene, yielding calcium hydroxide as a waste product. Acetylene's major impurities are phosphine and hydrogen sulfide which are removed in various oxidative purification processes that introduce chlorine. This may allow/PCDFs to be generated, as shown by the detection of PCDD/PCDFs in waste streams of industries producing acetylene in Japan [28], Taiwan [35], Brazil [36,37], and Korea [38]. In these cases, the detailed PCDD/PCDF formation processes were not investigated. For example, in the Brazilian case, only the mixed wastes of the landfill was investigated and the major PCDD/PCDF source in the mixed wastes was the waste from the EDC process in particular the spent catalyst disposed at the same landfill [37].

Total PCDD/PCDF concentrations in purification wastes from ten different Japanese acetylene manufacturing facilities varied over a very broad range, from a low of 3.6 pgTEQ/L to high of 58,271 pg-TEQ/L, as shown in Table 1. It may be that the differences in the PCDD/PCDF concentrations released from the facilities can be attributed to differences in the reactivity of the chlorinating agents used. It is also possible that PCDD/PCDF were contaminants in the chlorinating agents. In all cases, PCDD/PCDF concentrations in background water samples were very low (Table 1), but concentrations in many samples of waste streams that included wastes from purification processes were high (Table 1) demonstrating PCDD/PCDF formation in the process. The distribution of PCDD and PCDF congeners in wastewater samples from acetylene manufacturing facilities is shown in Fig. 2 (a) and 2 (b), respectively. The two figures indicate that 1,2,7,8-TetraCDF and 2,3,7,8-TetraCDFs are the predominant TetraCDF in acetylene purification waste samples from the ten facilities and 1,2,3,4,7,8-HexaCDF is the predominant HexaCDF. This PCDF pattern is known from the chlor-alkali process where it was formed by chlorination of dibenzofuran present in tar/graphite [39,40]. It is likely that the PCDD/PCDF precursors including dibenzofuran were formed during acetylene synthesis, then chlorinated during purification, and resulting PCDD/PCDF were released in wastewater. Also other

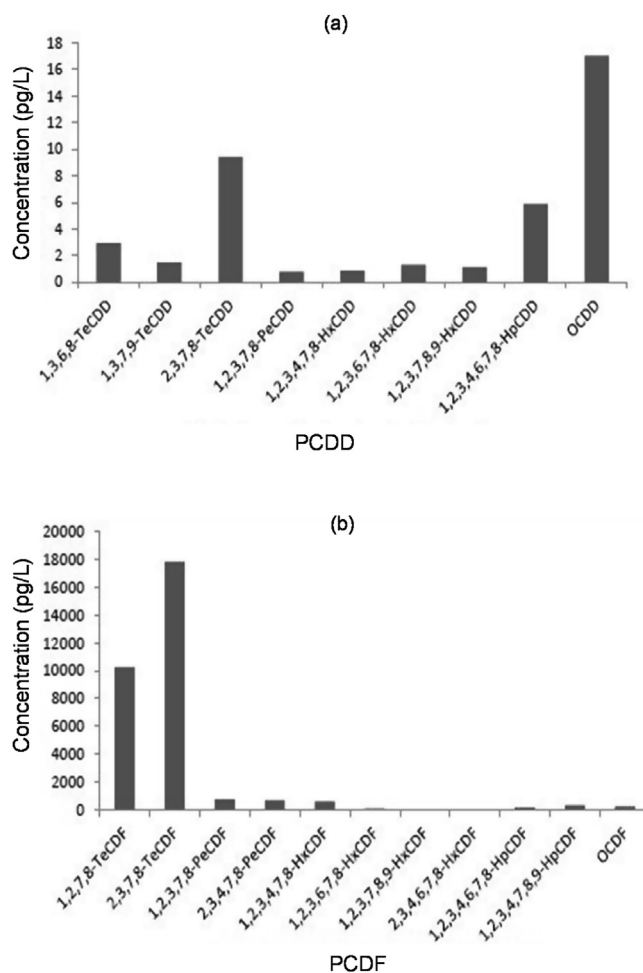


Fig. 2. PCDD (a) and PCDF (b) congener distribution example measured in acetylene purification waste stream samples.

organochlorines were likely formed by chlorination similar to other processes [40], and released from the process, but not measured. For example, polychlorinated naphthalene (PCNs) and biphenyl

**Table 1**  
Concentration of PCDD/PCDFs (pg TEQ/L) in wastewater samples of calcium carbide-based acetylene manufacturing facilities using different purification technologies.

Type of purification	Source water	Waste stream 1	Waste stream 2	Waste stream 3	Waste stream 4	Total <sup>a)</sup>
HClO - 1	0.19	13,000–21,000	13,000–15,000	240–470	0.38–0.70	26,240–36,470
	Industrial water	HClO purification tower	NaOH washing tower	Water washing tower	Overall discharge	
HClO - 2	0.1	2.3	8.4–15	4.5	N/A	15.2–21.8
	Well water	HClO purification tower	Acid washing tower	NaOH washing tower		
NaClO	0.1	0.0035–0.16	130–240	0.58–11	1.0–1.3	131.1–252.5
	Well water	Dust removal	HClO purification tower	Water discharge	Overall discharge	
FeCl <sub>3</sub> , CuCl <sub>2</sub> - 1	0.1	26,000–58,000	210	N/A	N/A	3.6–6.1
	Industrial water	Bleaching tower	Water washing tower			
FeCl <sub>3</sub> , CuCl <sub>2</sub> - 2	0.13	5.7–31	0.0013	N/A	N/A	5.7–31
	Well water	FeCl <sub>3</sub> - purification tower	H <sub>2</sub> SO <sub>4</sub> tower			
FeCl <sub>3</sub> , CuCl <sub>2</sub> - 3	0.098	1.7–2.7	2.3	N/A	N/A	4–5
	Industrial water	FeCl <sub>3</sub> - purification tower	NaOH washing tower			
Cl <sub>2</sub> - 1	0.14	1800	0.082	530–2200	130	2460–4130
	Industrial water	Cl <sub>2</sub> water sink	H <sub>2</sub> SO <sub>4</sub> tower	Cl <sub>2</sub> water tower	NaOH washing tower	
Cl <sub>2</sub> - 2	0.084–0.11	700	0.18	240–320	7.9	948–1028
	Industrial water	Cl <sub>2</sub> water sink	H <sub>2</sub> SO <sub>4</sub> tower	Cl <sub>2</sub> water tower	NaOH washing tower	
Ca(ClO) <sub>2</sub> - 1	0.13	26,000–58,000	210	26–56	5.1	26,241–58,271
	Industrial water	Bleaching tower	Water washing tower	Activated carbon sink	Overall discharge	
Ca(ClO) <sub>2</sub> - 2	0.11	0.099–3.4	150–270	210	N/A	360–483
	Industrial water	Cooling tower	Bleaching tower	NaOH washing tower		

b) N/A indicates not applicable or not available.

<sup>a)</sup> Total means the measured value for the combined water sample of all streams.



(PCBs) were likely formed as well as other UPOPs.

PCDFs were produced in much higher amounts than PCDDs (Fig. 2). This can be explained since dibenzofuran is formed in thermal processes in much higher concentrations compared to dibenzo-p-dioxin [41]. The 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) was produced in 7 of 10 facilities) and at generally low concentrations (from non-detected to 129 pg/L). Also 1,3,6,8-TCDD and 1,3,7,9-TCDD were formed to some extent but at lower levels (Fig. 1). This indicates that PCDDs were formed from phenol precursors which are chlorinated to 2,4-dichlorophenol and 2,4,6-trichlorophenol. These form by condensation the detected 1,3,6,8/1,3,7,9-TCDD as well as the not-monitored 1,3,7/1,3,8-TriCDDs and 2,7/2,8-DiCDDs [42]. The PCDDs are then further chlorinated preferably in the 2,3,7,8- positions resulting in formation of 2,3,7,8-TCDD from the 2,7 and 2,8-DiCDD. The ratio of the congeners of 1,3,6,8/1,3,7,9-TCDD versus 2,3,7,8-TCDD indicates the extent to which chlorination took place in the phenol or later in the formed PCDDs which showed for some process particular higher share of 2,3,7,8-TCDD (Fig. 1) indicating that initially the 2,7/2,8-DCDD were formed which were further chlorinated.

The large differences in concentration (Table 1) could not be explained by the purification method or waste stream type since both high and low PCDD/PCDF levels were found in wastewater from different facilities using the same technology. For example, wastewater samples from two facilities, both of which used the hypochlorite process had PCDD/PCDF concentrations as high as 21,000 pg/L in one factory and as low as 15 pg/L in the other (Table 1). Also two facilities using FeCl<sub>3</sub>/CuCl<sub>2</sub> processes had a similarly large difference with to 58,000 pg TEQ/L in the wastewater of one and 31 pg TEQ/L in the other (Table 1). These broad disparities could have resulted from PCDD/PCDF impurities in the chemicals used or by a higher input of precursors in the processes (e.g., use of waste water versus clean water). With no further assessment, the cause of the high variability in PCDD/PCDF production remains undetermined.

It should be noted that also further treatment of wastes can result in PCDD/PCDF releases from other sources. For example, residual carbide slag produced in the calcium-carbide acetylene manufacturing process can contribute to releases of unintentional POPs from cement production when it is used as a raw material, as evidenced by the occurrence of PCDDs/PCDFs, PCBs and polychlorinated naphthalenes (PCNs) in the stack gas of cement kilns using carbide slag as a raw material [43,44]. This particularly depends on the feeding point at the cement plant [45].

### 3.2. Formation of PCDD/PCDFs in the caprolactam manufacturing process

The compound caprolactam (C<sub>6</sub>H<sub>11</sub>NO) or ε-caprolactam is well known as an important raw material for the production of nylon 6 [46]. A variety of processes have been developed for producing caprolactam since it was first produced in 1943. An estimated 90% of caprolactam is synthesized from cyclohexanone which is converted to its oxime that, when treated with acid, undergoes the *Beckmann rearrangement* to form caprolactam. Caprolactam is also produced by 1) the cyclohexane photonitrosation method developed in Japan and 2) the cyclohexane oxidation method.

Fig. 3 shows caprolactam manufacture by the cyclohexane photonitrosation process. The process begins with the synthesis of nitrosyl chloride (NOCl) as follows [22]:

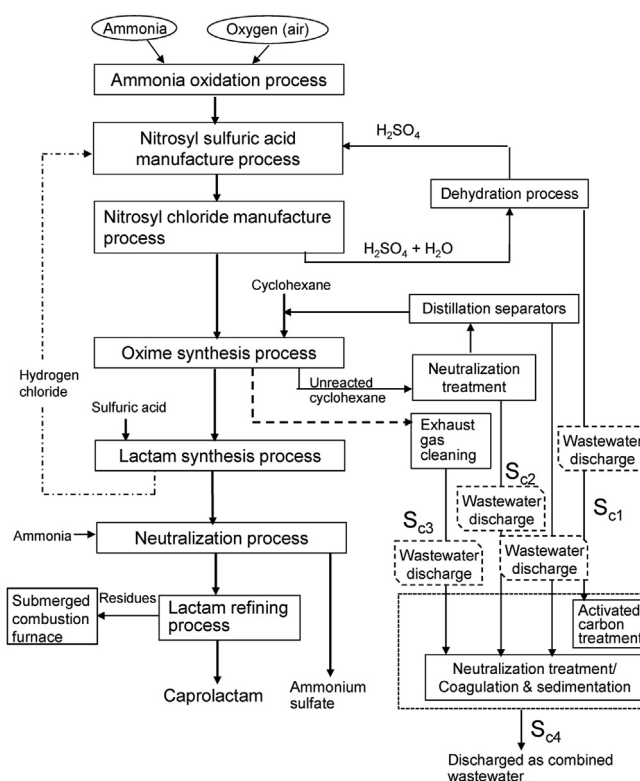
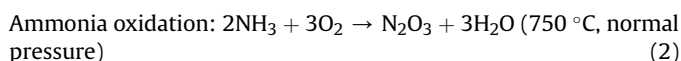
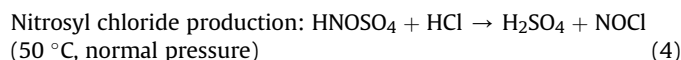
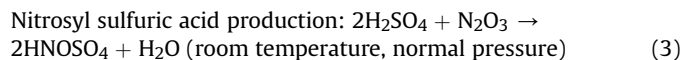


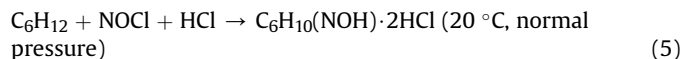
Fig. 3. Caprolactam manufacturing process and water sampling points in an investigated facility ( $S_{ci}$  means water sampling point).



A dehydration process for recycling of sulfuric acid is a sub-process. The water content of the sulfuric acid is evaporated by heating under reduced pressure (130 °C, 4000 Pa) in a dehydrating tower, and then it is condensed and eliminated.

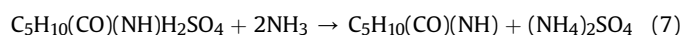
The synthesis of oximes proceeds according to the following reaction:

Oxime synthesis process:



For the recovery of unreacted cyclohexane, hydrochloric acid is eliminated from the unreacted cyclohexane by neutralization. Purge gas, primarily N<sub>2</sub> and HCl, from the reaction vessel is treated in an exhaust gas cleaning unit. Next, the following reactions are utilized in the caprolactam synthesis process, and the HCl gas is reused in the nitrosyl chloride manufacture process;

Caprolactam synthesis:



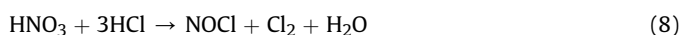
Thus, there is no direct elemental chlorine sources that may play a role in the formation of PCDD/PCDFs at this low temperature. However, PCDD/PCDF at the concentration of 120 pg-TEQ/L were measured in a wastewater sample from a caprolactam production

facility where the cyclohexane photonitrosation method was used. In response, the Ministry of the Environment of Japan (MEJ) collected and analyzed wastewater samples from other caprolactam facilities using this same manufacturing process, and confirmed the formation and release of PCDD/PCDFs from this process. The MEJ findings led to the enactment of regulatory limits on PCDD/PCDF releases from facilities using the cyclohexane photonitrosation process in the first decade of 2000. Further, the MEJ findings for the caprolactam production process confirm that PCDD/PCDF formation can take place in chemical manufacture processes at low temperature even for processes where HCl is the only chlorinating agent under certain oxidative reaction conditions (see below).

Table 2 shows the average concentrations of PCDD/PCDFs in wastewater samples collected from a caprolactam production facility. As shown, the PCDD/PCDF concentration was very low in sample a) Industrial water. However, high concentrations of PCDD/PCDF were measured in wastewater from the dehydration process (Sc1 in Fig. 3) and in wastewater from the neutralization treatment process (Sc2 in Fig. 3) within the oxime synthesis process, 620 - 770 pg-TEQ/L and 77 - 100 pg-TEQ/L, respectively. The PCDD/PCDF homologue distribution in the wastewater samples (Sc1 and Sc2) from the dehydration process and neutralization treatment are shown in Fig. 4 for both dissolved and suspended solids. As shown, most of the components were tetra-, penta- and hexachlorinated PCDFs, which is also the case for the wastewater sample Sc1. In sample Sc2, TeCDFs were a dominant congener. The formation of chlorinated by-products is presumed to occur when HCl reacts with cyclohexane and degradation products (Fig. 3). However, impurities in the HCl need also to be taken into consideration. Unfortunately relevant analyses have not yet been carried out.

The PCDD/PCDF contents of dissolved and suspended solids did not differ greatly which seemed to be due to the nature of SS. On the other hand, the isomer distribution pattern shown in Fig. 4 (b) was similar to (a). However, the pattern of Sc2 showed the existence of several PCDD isomers. The two differences may reflect differences in the processes of nitrosyl chloride synthesis and oxime synthesis but the details remained unknown and further assessment is needed. The combined wastewater (Sc4) was finally sufficiently purified to meet regulatory limits. Similar results were also obtained from the measurements of other facilities with the same type of caprolactam manufacturing process.

Shown in Table S2 are PCDD/PCDF congener concentrations measured in wastewater samples from three processes used in a caprolactam production facility. Since high concentrations of PCDD/PCDFs were detected in wastewater from the dehydration process, the primary source of PCDD/PCDFs was most likely the synthesis of nitrosyl chloride which involves the use of HCl in a pre-synthesis process. Also, nitric acid was thought to be produced as a by-product of the ammonia oxidation process and the synthesis of nitrosyl sulfate, and chlorine was thought to be produced in the production of nitrosyl chloride by a reaction such as the following;

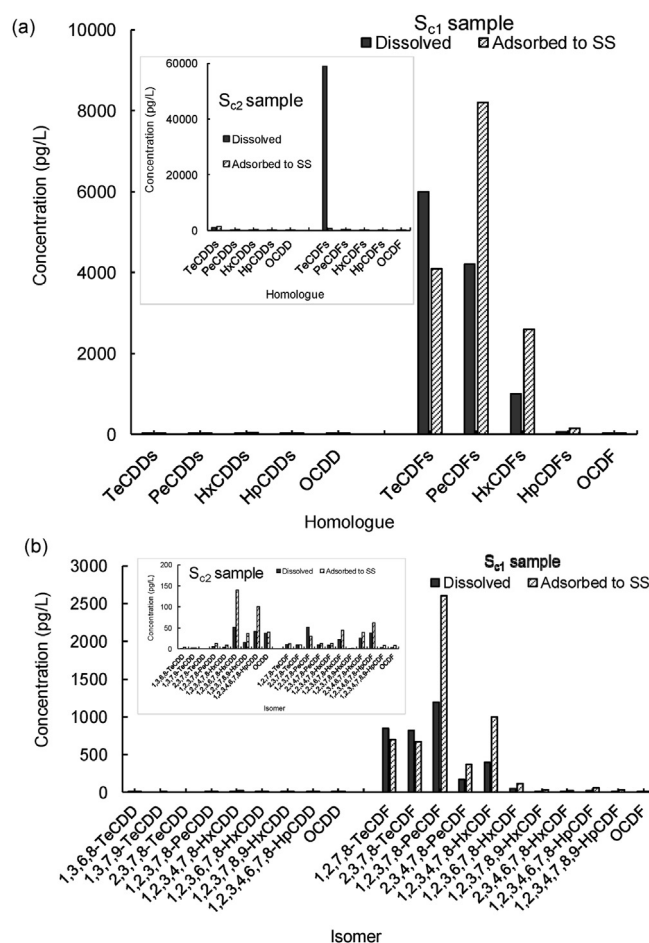


**Table 2**

Average PCDD/PCDF concentrations (in pg TEQ/L) in wastewater samples from selected processes of a caprolactam production facility.

Sample	Dissolved state	Suspended state	Total
a. Industrial water	0.080	0.094	0.17
b. Wastewater from dehydration process: Sc1 <sup>a)</sup>	240	440	680
c. Wastewater from neutralization process: Sc2	26	64	90
d. Wastewater from exhaust gas cleaning process: Sc3	1.8	2.5	4.3
e. Combined wastewater: Sc4	0.33	1.3	1.6

<sup>a)</sup> The mark corresponds to the sampling point number in Fig. 3.



**Fig. 4.** PCDD/F (a) homologue and (b) congener distribution patterns in the wastewaters from the dehydration process (Sc1) and neutralization treatment (Sc2) in caprolactam manufacturing (SS indicates suspended solids).

In the above process step, PCDF with a “chlorine pattern” with high contribution of the marker congeners 1,2,7,8- and 2,3,7,8-TetraCDFs and 1,2,3,4,7,8-HexaCDF was formed along with very low PCDD levels (Fig. 4; Table S1).

The source of the dibenzofuran, the precursor of the “chlorine pattern” [39,40], was not determined. Gaseous HCl from the caprolactam synthesis process contained 5% (v/v) unreacted cyclohexane and perhaps other carbon species that may be the source of carbon in each of the processes. But it was unclear if and by which process cyclohexane reacted to form the aromatic dibenzofuran structure or if contaminated HCl contributed to the PCDD/PCDFs or precursors.

It was assumed that a part of the PCDD/PCDFs formed in the manufacture of nitrosyl chloride was transported to the synthesis process together with the nitrosyl chloride gas. However, since

sources of carbon and chlorine exist in each of the synthesis processes, it cannot be excluded that PCDD/PCDF were also formed in these processes. Interestingly PCDD concentrations increased and with lower share of PCDF (Fig. 4; Table S2). This evidence of additional PCDD formation indicates that chlorophenols were produced in the preceding chlorinating processes and were condensed in the neutralization step. However, chlorophenols were not measured in this survey. A more comprehensive monitoring of aromatic chlorinated and non-chlorinated precursors as well as the potential contaminations in the HCl used in the process is needed for better elucidation of the overall formation mechanism of PCDD/PCDFs and other unintentional POPs.

The MEJ assessment discovered and confirmed at different facilities that the cyclohexane photolysis process for caprolactam manufacturing is a source of PCDD/PCDF. Subsequently on December 1, 2001, the three caprolactam manufacturing facilities that use nitrosyl chloride, namely the sulfuric acid condensing facility, the cyclohexane separation facility, and the exhaust gas cleaning facility, have been identified as “specified facilities” (facilities subject to water quality standards) of the Law concerning Special Measures against Dioxins.

Sufficient data were available to calculate PCDD/PCDFs per tonne of caprolactam produced, commensurate with the UNEP Toolkit methodology. Annual releases of PCDD/PCDF in each of three wastewater streams were calculated based on accompanying data shown in Table 3. Based on annual releases shown in Table 3 and an estimate of annual production of caprolactam in the examined facility at the time of survey (ca.  $1.2 \times 10^5$  tonnes/y), it is estimated that the caprolactam manufacturing facility has an emission factor for releases to the aquatic environment ( $EF_W$ ) of  $0.25 \pm 0.04 \mu\text{g-TEQ/t}$  and a total annual release to the aquatic environment of  $0.030 \text{ g-TEQ/y}$  at the relevant business establishment as shown in Table 3. The current status of large-scale production of caprolactam in Asian-Pacific countries shows growing use of caprolactam in the production of nylon 6 fibers and resins that are used in the manufacture of carpets, textiles, and industrial yarns [47]. Further assessment of the production processes used in the Asian-Pacific countries and releases of PCDD/PCDF and possibly other unintentional POPs by individual factories in the Asian region are recommended.

### 3.3. Formation of PCDD/PCDFs in the pigment violet manufacturing process

Some production processes of organic pigments were found to be sources of PCDD/PCDF releases. For example, Fig. 5 illustrates the

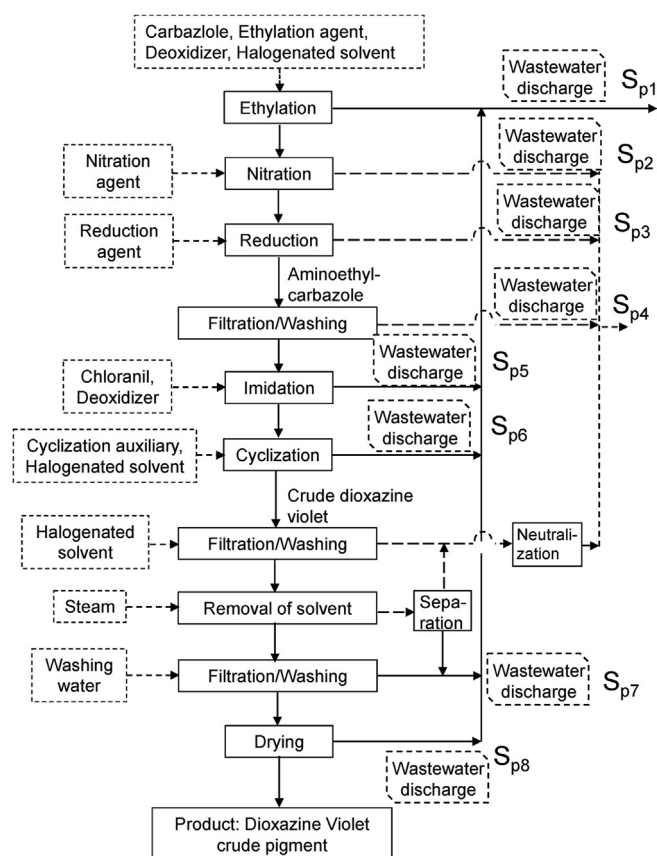


Fig. 5. Dioxazine Violet crude pigment production process and wastewater sampling points ( $S_{pn}$ ).

manufacturing process for Dioxazine Violet, one of the pigment manufacture processes that known to be a source of PCDD/PCDF releases, as well as several wastewater sampling points used in an investigation of PCDD/PCDF releases. The structural formula of this substance is also shown in Fig. S1 of the supplementary material. The synthesis of the Dioxazine Violet begins with the ethylation and nitration of carbazole which is ethylated and nitrated, and the resulting product is catalytically reduced to aminoethylcarbazole. This chemical is cyclized to crude dioxazine violet. In the next step, the crude dioxazine violet is rinsed by solvent and then by water. Finally, the dioxazine violet crude pigment is obtained after drying

Table 3  
Estimated total PCDD/PCDF releases in wastewater from a caprolactam production facility.

Sample	Discharge amount ( $\text{m}^3/\text{d}$ )	Average PCDD/PCDF concentration* ( $\text{pg-TEQ/L}$ )	Total PCDD/PCDF release in wastewater ( $\text{g-TEQ/y}$ )
Factory A shown in Fig. 3			
Industrial water	52,000	0.175	0.0033
Dehydration process wastewater	2000	683	0.499
Neutralization process wastewater	170	89	0.0055
Exhaust gas cleaning process wastewater	55	4.33	$8.70 \times 10^{-5}$
Combined wastewater	52,000	1.60	0.030
Factory B			
Industrial water	51,000	0.255	0.0047
Dehydration process wastewater	1500	567	0.310
Neutralization process wastewater	170	250	0.0155
Wastewater before activated carbon treatment	1700	560	0.347
Combined wastewater	51,000	1.64	0.030

\* Same samples were measured in three different laboratories.

around 150 °C. In the long synthesis process, PCDD/PCDFs might form both in the nitration and reduction processes and also in the rinsing and drying processes as shown in Table 4 and Fig. 5. These observations suggest that PCDD/PCDFs could form in cyclization processes and it is possible that a possible source of PCDD/PCDF releases is the cleaning process for the solid residue generated when the reaction mixture is filtered following cyclization. Many wastewater samples were analyzed for PCDD/PCDF, and the PCDD/PCDFs were detected in every sample. Of these, higher concentrations were found in the nitration and drying processes, respectively (samples of  $S_{p2}$  and  $S_{p8}$  in Fig. 5). PCDD/PCDF homologue and isomer distribution patterns of the two processes are shown in Fig. 6 and Table S2. From the results, the only abundant homologue of  $S_{p2}$  nitration process was TeCDFs with a minor contribution of 2,3,7,8-TeCDF (ca. 5%) indicating that the PCDFs were not formed from chlorination of dibenzofuran but from other chlorinated aromatic compounds present in the pigment production process. PCDD were not present in  $S_{p2}$ . Also after the drying process PCDDs including TeCDDs to OCDD were detected in high concentrations ( $S_{p8}$  in Fig. 6). The most prominent homologue in the drying process was also TeCDFs in even higher concentration compared to  $S_{p2}$  also with a minor share of 2,3,7,8-TeCDF (ca. 1%). Also for this process further assessment of the precursor chemicals and other unintentional POPs in this pigment production is needed to better understand the PCDD/PCDF formation mechanism.

Prior to final wastewater treatment and discharge, PCDD/PCDFs can be removed by processes such as coagulation-sedimentation, advanced oxidation using ozonation and ultra-violet light, and activated carbon adsorption process.

### 3.4. Other investigated industrial processes discovered as sources of PCDD/PCDF release to water

Other industrial processes that have been identified in Japan as PCDD/PCDF sources and subsequently regulated are as follows:

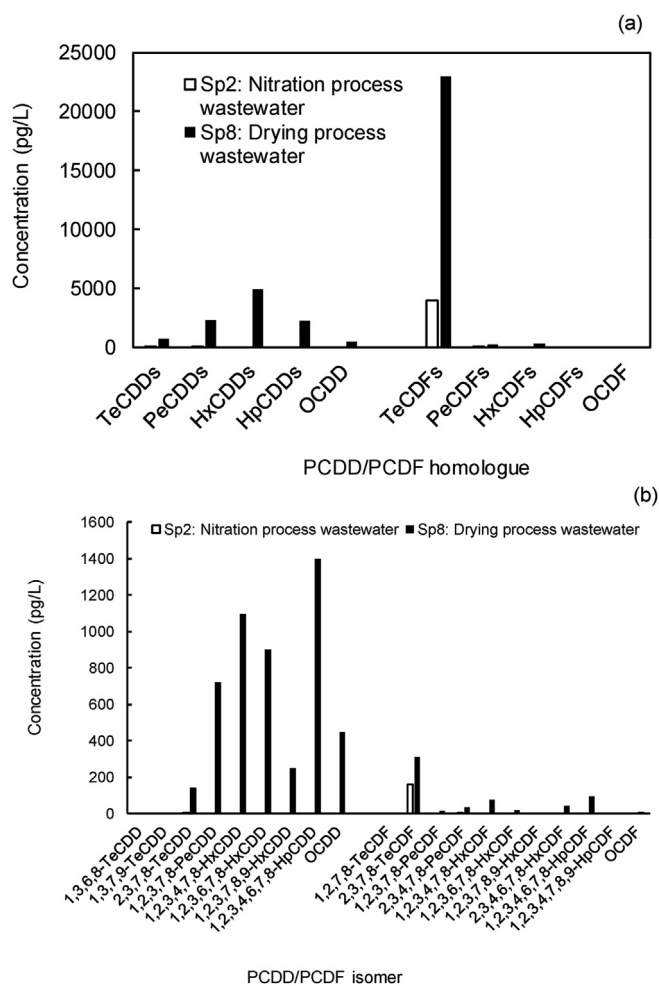
- chlorine bleaching during sulfate pulp manufacture,
- dichloroethylene rinsing processes for the manufacture of vinyl chloride monomer,
- filter and wet scrubber for the manufacture of 2,3-dichloro-1,4-naphthoquinone
- washing facilities and wet scrubber for chlorobenzene and dichlorobenzene manufacture,
- nitration derivative separation facilities and reduced derivative separation facilities etc. for dioxazine violet pigments manufacture,
- wet scrubber for flue gas from roasting furnace of aluminum alloy,
- wet scrubber in potassium sulfate manufacture,
- wet scrubber in aluminum fiber manufacture,
- purification facility and wet scrubber for zinc recovery,

**Table 4**

Measurement result of dioxins in the Dioxazine Violet crude pigment production processes.

Sample <sup>a)</sup>	Concentration (pg-TEQ/L)
$S_{p1}$	0.016–14
$S_{p2}$	160–1900
$S_{p3}$	82
$S_{p4}$	41
$S_{p5}$	2.3
$S_{p6}$	0.84
$S_{p7}$	5.5–36
$S_{p8}$	350–1200

<sup>a)</sup> Symbols indicate those in Fig. 5.



**Fig. 6.** PCDD/F congener distribution patterns in wastewaters ( $S_{p2}$  and  $S_{p8}$ ) from the Dioxazine Violet crude pigment production process.

Table 5 summarizes facilities and processes where PCDD/PCDF formation and release have been detected other than the three industrial processes described in 3.1–3.3. PCDD/PCDF concentrations measured in the Ministry of the Environment survey as well as the consideration of possible formation mechanisms are also included. The processes are placed in two categories: A) Chemical synthesis and B) flue gas treatment of high temperature processes.

It needs to be stressed that within a decade after PCDD/PCDF releases to aquatic environments from industrial facilities were regulated, certain manufacturing processes were changed to alternative processes or discarded. This course of events serves as an example to other countries for phasing out or modifying PCDD/PCDF generating processes in line with the requirement of Article 5 of the Stockholm Convention to take measures to reduce the release of UPOPs with the goal of their continuing minimization and, where feasible, ultimate elimination.

## 4. Conclusion

This study examined PCDD/PCDF formation in industrial processes in the context of releases to the aquatic environment based on the survey conducted by the Ministry of the Environment of Japan in 2001 against the background of the enforcement of the Law Concerning Special Measures against Dioxins in Japan. The major findings and conclusions are as follows:



**Table 5**  
Industrial processes and facilities were PCDD/Fs in wastewater from.

Process	Major processes of confirmed formation and/or discharge	Concentration (pg-TEQ/L)	Possible formation mechanism
Rinsing and exhaust gas cleaning facilities for chlorobenzene or dichlorobenzene manufacturing	Chlorination process of benzene	Wastewater from rinsing of crude chlorobenzene: 110–440	Organic chemistry reaction because of one-sided distribution of specific PCDF isomers and the reaction condition of low temperature and short process time. The presence or absence of impurities in the raw material remained an issue to be clarified in the future.
Ethylene dichloride cleaning facility in vinyl chloride manufacturing	Sub reactions in oxidation and chlorination process of raw materials including ethylene, air, hydrochloride acid etc.	Wastewater from rinsing process of ethylene dichloride synthesized by chlorination and oxidation processes: 4.6–990	Formation in the combustion process of process exhaust gas, flue gas of wastewater combustion process and effluent water of wastewater treatment facility
Filtration and exhaust gas cleaning facilities in 2,3-dichloro-1,4-naphthoquinone manufacturing	Chlorination process of naphthoquinone that is a raw material of 2,3-dichloro-1,4-naphthoquinone synthesis	Hydrochloric acid recovering equipment effluent: 28,000–38,000	It is estimated that specific isomers of PCDF generate by the chlorination reaction of naphthoquinone. Depending on the application of activated carbon treatment etc., the final effluent water quality meet the criteria.
Filtration, drying and exhaust gas cleaning facilities in 4-chloro sodium hydrogen phthalate manufacturing	Chlorination process of disodium phthalic acid that is the raw material of 4-chloro sodium hydrogen phthalate	Filtrate after the chlorination process: 470–660	It was estimated that the specific isomers of PCDF generate by the chlorination reaction of disodium phthalic acid. Depending on the application of activated carbon treatment etc., the final effluent water quality meet the criteria.
Exhaust gas from the cleaning equipment in alumina fiber manufacturing	In the fiber material manufacturing, aluminum oxychloride or basic aluminum chloride is mixed with silica sol and organic thickener, then the liquid is fired. Dioxins were detected in the wet scrubbing water from the flue gas cleaning equipment.	Wastewater from the flue gas cleaning equipment: 7.63–11,400 (Five data; 7.63, 62, 557, 2500 and 11,400)	Produced unintentionally through dehydrochlorination in the burning process (approx. 1000 °C) and through the breakdown and elimination of organic compounds used as thickener.
Purification in exhaust gas cleaning and wet scrubbing facilities for zinc recovery in steel making electric furnace	Wet refinery process of crude oxidized zinc, Wet dust collection process for flue gas from chlorination-volatilization furnace	Effluent water from wet refinery process: 4.9–230 Effluent water from flue gas rinsing process: 520–10,000 Effluent water from wet dust collection process: 140–4800	Dioxins adsorbed on the crude oxidized zinc can enter into process effluent waters from flue gas rinsing and wet dust collection processes. Also, they can enter into process effluent waters in wet refinery process.

- 1) A variety of industrial facilities and processes are point sources of PCDD/PCDF releases to the aquatic environment: manufacturing processes that use chlorine, hypochlorite or other chlorinating agents, and thermal processes that use water scrubbing systems for stack gases. In Japan, total annual PCDD/PCDF release to the aquatic environment is, however, quite small compared to the releases to air and solid residues from thermal processes. Stringent limits on releases are important in encouraging adoption of best available techniques for reducing the formation and release of the PCDD/PCDFs.
- 2) In the case of releases from acetylene manufacturing, oxidative purification process using chlorine or hypochlorite to remove impurities was the source of PCDD/PCDF formation (and likely other unintentional POPs that were not monitored). PCDFs were produced in much greater amounts than PCDDs with the particular chlorine pattern. This also indicates that attention is needed to residues from acetylene manufacturing and other processes demonstrated in this study to release PCDD/PCDFs. The large difference in PCDD/PCDF levels in the wastewaters of different acetylene processes using the same technology could not be clarified in this study.
- 3) In the case of caprolactam manufacturing, a series of production process beginning with nitrosyl chloride synthesis can form PCDD/PCDFs. Through this investigation, the formation and release of PCDD/PCDFs in caprolactam manufacture was revealed and confirmed and the process of photonitrosation of cyclohexane was identified as the source of PCDD/PCDF formation.
- 4) Overall the formation processes of PCDD/PCDF can be classified in two categories A) chemical synthesis processes involving

- chlorine or a chlorinating agent and B) flue gas treatment in high temperature processes with waste water generating processes.
- 5) Other unintentional POPs should be included in such assessments in future for an overall picture of the release and for the further elucidation of formation processes.
- 6) Also chlorine-containing chemicals such as HCl, bleach, and metal chlorides that are used in manufacturing processes should be assessed for their PCDD/PCDF and other UPOPs content similar to screenings of PCDD/PCDFs in organochlorine pesticides [48,49]. This was not assessed in the current study but is meanwhile known from other studies where, for example, HCl was contaminated with PCDD/PCDFs and its use further contaminated other products including food [26,50,51]. The UNEP Toolkit recommends such an assessment of PCDD/PCDFs and other UPOPs in chemicals from the chlorine and organochlorine industries [26b].

The investigation demonstrates that PCDD/PCDFs are formed in different industrial processes in the presence of chlorine, hypochlorite and other chlorinating agents. Processes using these chlorinating agents should be assessed for their potential for PCDD/PCDF formation and release as part of the Stockholm Convention implementation in a country. The initial screening of processes can be carried out by assessing the use of chlorine and other chlorinating agents as suggested by the UNEP Toolkit in Annex 2 (UNEP 2013) as well as by monitoring chemicals from the chlorine and organochlorine industries.

The survey in Japan showed that the final effluent water can meet the stringent emission criteria (10 pg TEQ for effluent and environmental criteria of 1 pg TEQ/L in surface water) by applying advanced treatment such as the activated carbon adsorption

process and accelerated oxidation process using O<sub>3</sub> etc. to minimize the release of PCDD/PCDF from these industries.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgement

The authors thank Dr. Takumi Takasuga (Shimadzu Techno Research, INC) for providing information and knowledge regarding details of the PCDD/PCDF analysis and Pat Costner for the native corrections of the bit challenging Japanese-German English.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.emcon.2021.01.002>.

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