DIOXINS SOURCES TO THE AQUATIC ENVIRONMENT: RE-ASSESSING DIOXINS IN INDUSTRIAL PROCESSES AND THEIR INFLUENCE ON WATER QUALITY

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Introduction

We previously established that dioxins were released to the aquatic environment from newly-recognized industrial sources such as the production of caprolactam by cyclohexane photonitrosation, and calcium carbide-based acetylene manufacture[1]. Acetylene is a highly reactive, commercially important gas used throughout the world in the synthesis of organic raw materials. While the calcium carbide process has been replaced in the United States by alternate methods of acetylene manufacture, it remains an important source of acetylene in countries such as China, India, and Japan with ready access to inexpensive coal- the source of coke for calcium carbide. While Japan has now established dioxin water quality standards for the acetylene and caprolactam industries, the importance of calcium carbide-based acetylene manufacture[2,3] and the large-scale production of caprolactam[4] in Asian-Pacific countries prompted us to re-examine the chemistry of dioxin formation in acetylene and caprolactam manufacture to highlight the potential for these waste streams to release dioxins to the aquatic environment.

This paper also examines triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether, CAS No.3380-34-5), as an important source of dioxins to aquatic systems. This broad-spectrum antibacterial agent is manufactured and used throughout the world, and has become a ubiquitous contaminant of surface waters[5,6]. Triclosan manufactured outside of the United States and Europe may be contaminated with dioxins as synthesis impurities [7,8]. Triclosan also undergoes chlorination in wastewater treatment systems and photodegradation to form multiple dioxin species[9-11].

Materials and methods

In 2001, the Japanese Ministry of the Environment (JMOE) conducted an in-depth survey of acetylene manufacturing, collecting and analyzing samples for dioxins from ten different acetylene manufacturers. The manufacturers produced acetylene by either the Dry or Wet calcium carbide process, and purified the acetylene by reacting it with hypochlorite or sodium hypochlorite (HClO or NaClO); chlorine water (Cl_2); ferric chloride and copper chloride ($FeCl_3$ and $CuCl_2$); or by an unspecified bleaching powder. The JMOE collected samples from the source of industrial water used by each facility, and from each waste stream in the purification processes. Acetylene purification waste samples were analyzed for 9 dioxin congeners (polychlorinated dibenzodioxins, PCDD) and 11 furan congeners (polychlorinated dibenzofurans, PCDFs). For each of three caprolactam manufacturers, the JMOE collected five samples including industrial water, wastewater from the dehydration process, wastewater from the neutralization process, wastewater from the exhaust gas cleaning process, and combined wastewater (see Ref. 1 for a process flow diagram). Caprolactam waste samples were analyzed for dissolved and suspended PCDD/PCDFs. PCDD/Fs in both acetylene and caprolactam wastes were analyzed by the methods of the Japanese Industrial Standards Committee[12].

Peer-reviewed scientific literature provided the information on Triclosan.

Results and discussion

Dioxin formation in calcium-carbide acetylene manufacturing

Calcium carbide (CaC_2) is produced from the high-temperature reaction of calcium oxide (CaO) and coke (C) in an electric arc furnace. The calcium carbide is subsequently reacted with water to form acetylene (C_2H_2), yielding calcium hydroxide ($Ca(OH)_2$) as a waste product. Acetylene's major impurities are phosphine (PH_3) and hydrogen sulfide (H_2S); these are removed in various oxidative purification processes that introduce chlorine. PCDD/Fs have been detected in acetylene waste streams in Japan[1], Taiwan[13], Brazil[14], and Korea[15]. While the

PCDD/F formation mechanism is not known, it is likely that dioxin and furan precursors form from acetylene during its synthesis, and are chlorinated during purification.
We evaluated the PCDD/F content of acetylene purification wastes from ten different Japanese acetylene manufacturing facilities (JMOE as cited in Ref.1). The dioxin content varied substantially between facilities, from a low of 3.6 pg-TEQ/L to 36,470 pg-TEQ/L (Table 1).

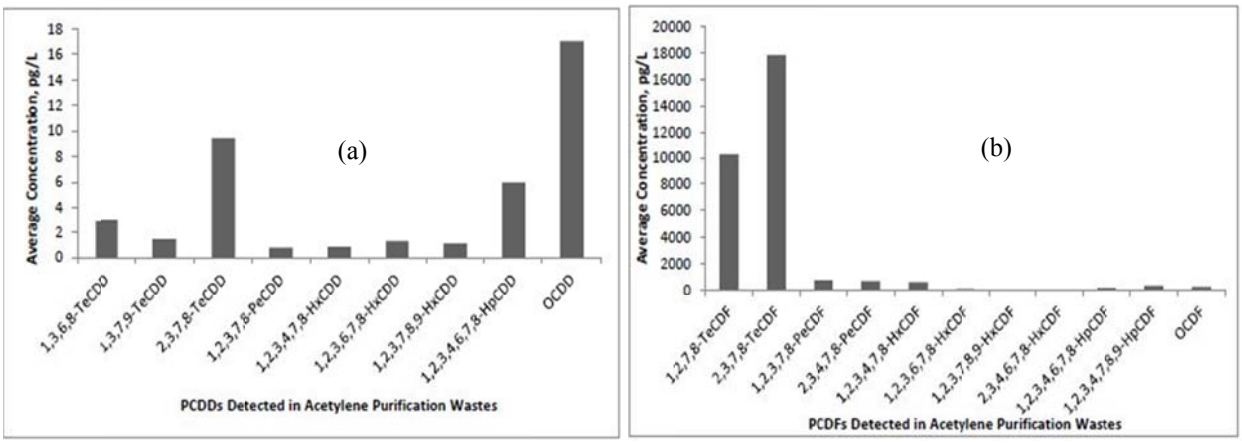
These differences could not be explained by the purification method or waste stream type, and the basis for the variability in dioxin production remains unknown.

Table 1.PCDD/Fs formed in Calcium Carbide-based Acetylene Manufacture (pg-TEQ/L)

Type of Purification	Background Water	Waste Stream 1	Waste Stream 2	Waste Stream 3	Waste Stream 4	Total
HClO	0.19 Industrial water	13,000-21,000 HClO purification tower	13,000-15,000 NaOH washing tower	240-470 Water washing tower	0.38-0.70 Overall discharge	26,240-36,470
NaClO	0.1 Well water	0.0035-0.16 Dust removal	130-240 HClO purification	0.58-11 Water discharge	1.0-1.3 Overall discharge	131.1-252.5
$FeCl_3$, $CuCl_2$	0.1 Industrial water	0.013-2.5 $FeCl_3$ purification sink	3.6 NaOH washing tower	N/A	N/A	3.6-6.1
$Ca(ClO)_2$	0.13 Industrial water	26,000-58,000 Bleaching tower	210 Water washing tower	26-56 Activated carbon sink	5.1 Overall discharge	26,241-58,271
HClO	0.1 Well water	2.3 HClO purification tower	8.4-15 Acid washing tower	4.5 NaOH washing tower	N/A	15.2-21.8
Cl_2	0.14 Industrial water	1,800 Cl_2 water sink	0.082 H_2SO_4 tower	530-2,200 Cl_2 water tower	130 NaOH washing tower	2,460-4,130
Cl_2	0.084-0.11 Industrial water	700 Cl_2 water sink	0.18 H_2SO_4 tower	240-320 Cl_2 water tower	7.9 NaOH washing tower	948-1028
$FeCl_3$, $CuCl_2$	0.13 Well water	5.7-31 $FeCl_3$ purification tower	0.0013 NaOH washing tower	N/A	N/A	5.7-31
$FeCl_3$, $CuCl_2$	0.098 Industrial water	1.7-2.7 $FeCl_3$ purification tower	2.3 NaOH washing tower	N/A	N/A	4-5
$Ca(ClO)_2$	0.11 Industrial water	0.099-3.4 Cooling tower	150-270 Bleaching tower	210 NaOH washing tower	N/A	360-483

Source: Report on the emission sources of unregulated dioxins (FY 2002) by the Ministry of Environment, Government of Japan
This report, written in Japanese, was edited by the Japan Environmental Sanitation Center in March 2003.
The PCDD/F sources to the aquatic environment identified in this report were regulated by the Government of Japan as a result of this investigation.
N/A indicates not applicable or not available
pg-TEQ/L indicates picograms (pg) dioxin toxic equivalents (TEQ)

The PCDD congener distribution from acetylene manufacturing facilities is shown in Figure 1a; Figure 1b provides the PCDF congener distribution (JMOE as cited in Ref.1).
These figures indicate that the tetrachlorinated furans, 1,2,7,8-tetrachlorodibenzofuran, and 2,3,7,8-tetrachlorodibenzofuran are the dominant isomers produced in acetylene purification wastes based on the average concentrations from ten facilities. PCDFs were produced in much greater amounts than PCDDs in all

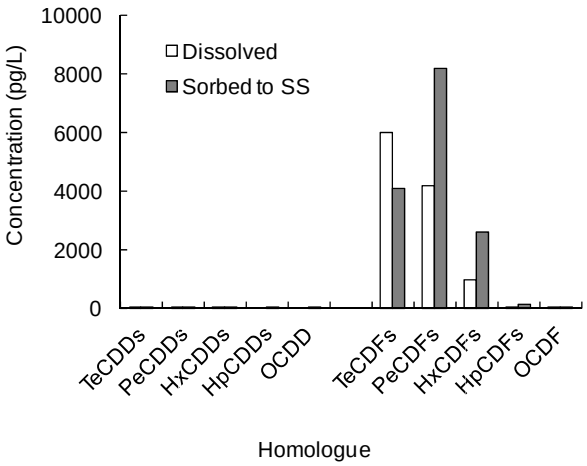


but four of the 32 waste streams measured. 2,3,7,8-Tetrachlorodibenzodioxin was produced inconsistently (seven of ten facilities) and at generally low concentrations (non-detect to 129 pg/L).

Dioxin formation in caprolactam manufacturing process

Kawamoto[1] reported that dioxins form in the caprolactam manufacturing process and are discharged to wastewater. JMOE measured PCDD/Fs in wastewater samples from the different process units of caprolactam manufacturing[1]. Wastewater from the dehydration process and wastewater from the neutralization process within the oxime synthesis process had 565 – 683 pg-TEQ/L and 90 – 248 pg-TEQ/L, respectively. The typical isomer distribution pattern from these samples is shown in Figure 2, in which both the PCDD/F concentration in the dissolved component and sorbed to suspended solids are shown.

This figure demonstrates that PCDFs, especially from tetra-CDFs to hexa-CDFs, are the dominant PCDD/F congeners in wastewaters produced during the manufacture of caprolactam. We believe that the dioxins are formed in the nitrosyl chloride production process and are carried forward to the final synthesis process together with nitrosyl chloride gas. Although we do not have a comprehensive understanding of the mechanisms of dioxin formation in caprolactam manufacturing, practical techniques now control the PCDD/Fs in effluent to below the PCDD/F standard (10 pg-TEQ/L). In 2011, the total emission of dioxins from caprolactam manufacturing in Japan was 0.010 mg-TEQ/year, which represents approximately 0.07 % of the PCDD/Fs discharged to Japanese water bodies.



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Dioxin formation in triclosan

Triclosan has become ubiquitous in consumer products: annual usage estimates range from ~ 350 tons in Europe[16] to ~20 tons in Australia [17]. Buth et al.[18] estimated that in the US, more than 24 tons of triclosan are released to US surface waters each year.

Triclosan manufactured in the US must meet purity standards for select dioxins (e.g., 2,3,7,8 TCDD content of < 1pg/g)[19]. However, Ni et al.[8] and Menoutis and Parisi[7] have demonstrated that triclosan manufactured in China and India are contaminated with PCDD/Fs as synthesis impurities. Because it is not clear whether countries that

import triclosan effectively regulate PCDD/F levels, the PCDD/F content of manufactured triclosan represents a potentially important source of dioxins to the aquatic environment.
In the US, the majority of triclosan is released from household water systems to wastewater treatment facilities[20]. Once released to the aquatic environment, triclosan can undergo photodegradation to form 2,8-dichlorodibenzodioxin[9]. Triclosan can also react with chlorine in treated water to form derivatives that may subsequently undergo UV-mediated conversion to 2,3,7-trichlorodibenzodioxin, 1,2,8-trichlorodibenzodioxin, and 1,2,3,8-tetrachlorodibenzodioxin[18]. It has been estimated that the PCDD load from triclosan and its degradation products may be 46 to 92 g-TEQ/year, or approximately 1.8 to 3.7% of air emissions[18]. These estimates do not account for the potential presence of synthesis impurities, and thus the true loading of PCDD/Fs from triclosan to the aquatic environment is unknown.

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