Characterization of Emissions of Dioxins and Furans from Ethylene Dichloride (EDC), Vinyl Chloride Monomer (VCM) and Polyvinylchloride (PVC) Facilities in the United States. II. Wastewater Treatment Solids and Aqueous Hydrochloric Acid

W. F. Carroll, Jr., F. E. Borrelli, R. A. Jacobs, J. W. Lewis, R. L. McCreedy, D. R. Tuhovak, and A. F. Weston
The Vinyl Institute, 65 Madison Avenue, Morristown, NJ 07960 USA

ABSTRACT

This is the second interim report of results from the Dioxin Characterization Program of the Vinyl Institute (VI)[1,2], comprising analyses of polychlorodibenzodioxins and polychlorodibenzofurans (PCDD/F) in wastewater treatment solids (solids) from EDC, VCM and PVC resin manufacturing facilities and aqueous hydrochloric acid (HCl_{aq}) product. PCDD/F concentration in solids ranged from 0.0028 to 5.9 ng/g TEQ on a dry-weight basis (Non-detect assumed to be half the limit of quantitation, i.e., ND=DL/2) Solids obtained from EDC/VCM plants had higher PCDD/F concentrations than those from PVC plants. Samples of commercial HCl_{aq} product taken from the two U.S. producers were 21 and 28 pg/L TEQ (ND=DL/2). Samples of solids were taken from facilities comprising approximately 56% of industry production capacity for EDC/VCM, 33% of PVC production capacity and 100% of industry production capacity for HCl_{aq} produced for sale as a byproduct of EDC manufacturing capacity.

INTRODUCTION

EDC is manufactured at 15 sites in the U.S. by 11 companies; however only two of these sites manufacture HCl_{aq} for sale. Production of EDC in the U.S. was approximately 11,115,000 metric tons in 1995, and 18,000 metric tons of HCl_{aq} were produced as a byproduct of EDC manufacturing for sale in the U.S. annually.

Seven of the 15 EDC sites, accounting for approximately 56 percent of industry capacity, submitted samples of solids. Of these, three manufacture EDC and VCM and four manufacture EDC, VCM and PVC. Combined (i.e., EDC/VCM/PVC) sites account for 29 percent of U.S. PVC capacity; two standalone PVC manufacturing sites were sampled as well, comprising about an additional 4 percent of the industry. Both EDC sites in the U.S. manufacturing HCl_{aq} for sale submitted samples.

EXPERIMENTAL

The VI Program utilized standard sampling procedures to ensure that the samples collected from each of the participating member facilities were representative of that particular matrix. For solids, 24-hour composite samples were collected, or if solids were stored in "roll-off" containers prior to

disposal, a representative (*e.g.* five-point) composite was collected. Samples were cooled to 4°C(+/-2°C), and sent to Wright State University where they were analyzed in Dr. Thomas O. Tiernan's laboratory using EPA Method 1613A[3]. Representative samples of HCl_{aq} product were collected, cooled to 4°C(+/-2°C), and analyzed at Alta Analytical Laboratory using Method 1613A. Standard Chain of Custody protocols were used in all cases.

RESULTS

EDC/VCM site samples were taken from facilities representing the wide variety of manufacturing processes and wastewater treatment technologies in use in the U.S. today: direct and oxychlorination processes; fixed and fluidized reactor beds; low and high temperature direct chlorination; and air, oxygen and mixed air/oxygen feeds. Table 1 summarizes the PCDD/F results for the solids samples obtained. They range from 0.0028 to 5.9 ng/g. Table 2 contains results obtained sampling sales-grade HCl_{aq}. Summary data on sites, wastewater sources, disposal methods and estimated PCDD/F emissions are contained in Table 3.

DISCUSSION

PCDD/F concentrations in solids are low, but somewhat variable. Studies are underway to determine whether this variability is due to process or temporal factors. For EDC/VCM and EDC/VCM/PVC manufacturing sites, calculations based on the measured dioxin concentrations for sampled facilities, and an extrapolation using the largest and the smallest emission factors for the unsampled facilities, suggests that annually between 1.3 and 40 grams TEQ is sent to landfill in solids from EDC/VCM production. The maximum likelihood estimate is 2.7 to 11 grams TEQ. PVC production, albeit on limited data from standalone facilities, seems to account for less than one gram TEQ. HCl_{aq} produced for sale as a byproduct of EDC manufacturing appears to be a very minor source of PCDD/F amounting to less than one milligram TEQ in the 18,000 metric tons per year production.

WORK IN PROGRESS

Peer review of data on combustor stack emissions is incomplete at the time of writing this paper.

ACKNOWLEDGEMENT

The authors would like to thank the VI and all participating member companies of the VI Dioxin Characterization Program for their input and permission to publish their analytical results.

REFERENCES

[1]The Vinyl Institute is a division of The Society of the Plastics Industry, Inc.
[2]W. F. Carroll, Jr., F. E. Borrelli, P. J. Garrity, R. A. Jacobs, J. W. Lewis, R. L. McCreedy and A. F. Weston, *Organohalogen Compounds* 27, 62 (1996)
[3]Method 1613A; "Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS; U.S. EPA April 1990.

Table 1. Results of analyses of wastewater treatment solids, ng/g.

Congener	105	124	128A	132-1	132-2	156A	156B	159-1	174A	174B	180-1	180-2	201
2,3,7,8-TCDD	0.014	ND 0.0010	ND 0.0049	ND 0.0027	ND 0.0048	0.010	0.011	ND 0.0068	ND 0.0011	0.0020	0.028	0.19	0.015
1,2,3,7,8-PeCDD	0.046	ND 0.0013	ND 0.014	ND 0.011	ND 0.016	ND 0.018	ND 0.010	0.013	ND 0.0018	ND 0.0017	0.081	0.56	ND 0.010
1,2,3,4,7,8-HxCDD	0.064	ND 0.0018	ND 0.039	0.034	ND 0.0085	ND 0.025	ND 0.025	0.024	ND 0.0029	0.0032	0.12	0.79	ND 0.024
1,2,3,6,7,8-HxCDD	0.16	ND 0.017	0.030	0.031	ND 0.0080	0.030	0.030	0.027	ND 0.0027	0.0023	0.14	0.90	0.041
1,2,3,7,8,9-HxCDD	0.12	ND 0.0018	0.028	0.049	ND 0.027	0.037	0.038	ND 0.022	ND 0.0032	0.0024	0.19	1.1	0.035
1,2,3,4,6,7,8-HpCDD	0.38	0.032	0.42	0.77	0.074	0.25	0.24	0.13	0.028	0.035	0.96	5.5	0.48
OCDD	0.39	0.64	2.6	8.2	0.55	0.64	0.72	0.56	0.18	0.22	2.0	11	9.7
2,3,7,8-TDCF	0.46	ND 0.0005	0.15	0.029	0.11	0.023	0.022	0.018	ND 0.0011	ND 0.0010	0.10	0.62	0.15
1,2,3,7,8-PeCDF	0.078	ND 0.0006	0.070	0.036	0.082	0.13	0.12	0.037	ND 0.0011	ND 0.0008	0.40	2.6	0.56
2,3,4,7,8-PeCDF	0.082	ND 0.0008	0.090	0.046	0.11	0.089	0.078	0.050	ND 0.0014	ND 0.0022	0.50	3.0	0.15
1,2,3,4,7,8-HxCDF	0.18	ND 0.0012	0.67	0.49	0.82	0.79	0.70	0.22	0.0033	0.0040	2.1	13	4.5
1,2,3,6,7,8-HxCDF	0.15	ND 0.0011	0.29	0.46	0.15	0.48	0.44	0.074	ND 0.0021	0.0024	1.1	6.2	1.2
1,2,3,7,8,9-HxCDF	0.018	ND 0.0015	0.033	0.067	ND 0.0067	0.044	0.042	0.0098	ND 0.0017	ND 0.0014	0.14	0.71	0.28
2,3,4,6,7,8-HxCDF	0.080	ND 0.0026	0.17	0.34	0.18	0.30	0.28	0.078	0.0038	ND 0.0040	0.90	4.7	0.35
1,2,3,4,6,7,8-HpCDF	1.1	0.0097	3.1	5.3	1.0	5.4	6.5	0.57	0.012	ND 0.012	3.2	38	11
1,2,3,4,7,8,9-HpCDF	0.32	0.0020	0.94	1.5	0.30	0.94	0.91	ND 0.12	ND 0.0043	ND 0.0021	1.9	11	12
OCDF	2.6	0.043	8.9	38	2.5	24	21	1.8	0.037	0.042	75	410	4200
Total TEQ ND=0	0.23	0.0011	0.24	0.30	0.20	0.32	0.31	0.088	0.0013	0.0040	0.96	5.9	5.2
Total TEQ ND=DL/2	0.23	0.0028	0.25	0.30	0.21	0.33	0.31	0.093	0.0034	0.0054	0.96	5.9	5.2

1. Samples 132-1 and -2 were collected from separate streams and were treated as separate samples.
2. Samples 156A and B; 180-1 and -2; and 174A and B were replicates, averaged and treated as one sample

Table 2. Results of analyses of sales-grade aqueous HCl, pg/L.

Congener		105		124
2,3,7,8-D4	ND	1.5	ND	4.1
1,2,3,7,8-D5		5.5	ND	5.0
1,2,3,4,7,8-D6		7.5	ND	3.4
1,2,3,6,7,8-D6		24		4.2
1,2,3,7,8,9-D6		13	ND	2.5
1,2,3,4,6,7,8-D7		68		53
D8		71		380
2,3,7,8-F4		1.6		5.4
1,2,3,7,8-F5		5.3		7.6
2,3,4,7,8-F5		5.8		7.5
1,2,3,4,7,8-F6		27		42
1,2,3,6,7,8-F6		16		28
1,2,3,7,8,9-F6		14		23
2,3,4,6,7,8-F6		5.8		7.8
1,2,3,4,6,7,8-F7		150		510
1,2,3,4,7,8,9-F7		44		88
F8		570		240
				0
Total ND=0		20.		24.
Total ND=DL/2		21.		28.

Table 3. Summary of statistics, EDC,VCM and PVC facilities. ND=DL/2.

Site	Site Type	Wastewater from non EDC/VCM/PVC Sources, percent	Solids Disposal Method: RCRA Landfill	Solids Disposal Method: Secure Landfill	Solids Disposal Method: Land Farm	Concentration PCDD/F, Dry solids, ng/g TEQ	Emission Factor, mg/KMT EDC or PVC
105	EDC/VCM	64-69	x			0.23	0.084
128A	EDC/VCM/PVC	66		x		0.25	0.74
132-1 (1)	EDC/VCM	20		x		0.30	0.14
132-2	EDC/VCM	0		x		0.21	0.029
156A (2)	EDC/VCM/PVC	48		x		0.33	0.28
156B (2)	EDC/VCM/PVC	48		x		0.31	0.26
159-1	EDC/VCM/PVC	80			x	0.093	0.054
180-1 (2)	EDC/VCM/PVC	70		x		0.96	1.1
180-2 (2)	EDC/VCM/PVC	70		x		5.9	6.9
201	EDC/VCM	0		x		5.2	2.4
124	PVC			x		0.0028	0.0043
174A	PVC			x		0.0034	0.060
174B	PVC			x		0.0054	0.095

1. Samples 132-1 and -2 were collected from separate streams and were treated as separate samples.
2. Samples 180-1/180-2 and 156A/156B were replicates and were averaged.