PVC Manufacture as a Source of PCDD/Fs

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1. Introduction

In the last few years the knowledge base on the human health effects of the PCDD/Fs has grown very rapidly. As scientists and regulators have realised the serious potential impact of current levels, attempts to identify and curb emissions have intensified. The US and UK governments have recently proposed further measures to lessen releases from the incineration sector which is widely regarded as the largest source of atmospheric emissions[1,2]. However, source reconciliation studies based on atmospheric release estimates can only account for approximately 10% of environmental loadings of PCDD/Fs[3]. Other PCDD/F generating processes and non-atmospheric release routes therefore need to be identified and quantified if real reductions in the environmental burdens and concomitant risks are to be achieved. Little information on dioxin generation within the PVC manufacturing sector is available. Despite its comprehensive nature in many respects, the recent USEPA draft reassessment concluded that no estimate of PCDD/F generation associated with this industry could be made[4]. As no data were found for the US, samples of wastes were collected to provide preliminary information on the dioxin generation in the PVC industry in that country.

2. Experimental

Samples of chlorinated wastes were obtained from a number of PVC and VCM manufacturing facilities in the United States (Table 1).

Sample PU4016 was identified as a F024-containing waste. F024 are defined by EPA as: Process wastes, including, but not limited to, distillation residues, heavy ends, tars, and reactor clean-out wastes, from the production of certain chlorinated aliphatic hydrocarbons by free radical catalysed processes. These chlorinated aliphatic wastes are those having carbon chain lengths ranging from one to and including five, with varying amounts and positions of chlorine substitution.

Sample PU4017: This is a category K019 waste. K019 wastes are defined by EPA as: Heavy ends from the distillation of ethylene in ethylene dichloride production.

Sample PU4043: This is probably a category K020 waste. EPA defines K020 as: heavy ends from the distillation of vinyl chloride in vinyl chloride monomer

production.

PCDD/F analyses were conducted as previously described[5]. Data quality assurance is the same as for UK government laboratories[6].

3. Results

Analytical data are presented in table 1.

PCDD/F concentrations were elevated in all samples. Concentrations in sample PU4017, EDC reboiler residues (EDC tars) were particularly high at 6.37ppm ITEQ. To the Authors' knowledge, levels this high have not previously been reported in the open literature.

The samples show a preponderance of PCDFs, particularly the higher chlorinated congeners. This is typical of manufacture of short chain aliphatic compounds such as EDC[7]. The profile of sample PU4016 is similar to that adjacent to a VCM factory in Rotterdam Harbour, Netherlands[8]. Sample PU4043 was described as a probable K020 waste under the USEPA classification, ie heavy ends from the vinyl chloride in vinyl chloride monomer production. The profile with its heavy predominance of OCDF is extremely similar to the profile from vinyl chloride distillation residues at the Imperial Chemical Industry (ICI) plant in Runcorn, UK[9].

4. Discussion

It is well established that the oxychlorination process widely used in vinyl chloride manufacture gives rise to PCDD/Fs[9,10]. The PVC product subsequently contains dioxins in the ppt TEQ range[11].

The Georgia Gulf facility reported generating 210 tonnes of F024 waste in 1991. At a concentration of 19978 ng/kg ITEQ, this would equate to slightly over 4g ITEQ. Most of this waste is incinerated but some 37.5 tonnes were deep-well injected[12]. No such figures were available for the other two wastes sampled.

Concentrations in the vinyl chloride distillation residues (PU4043) were consistent with those reported in the UK; 3191.2 ng/kg ITEQ in PU4043 and between 3102 and 7561 ng/kg ITEQ (mean 5602ng/kg) for three samples analysed by ICI[9]. ICI estimated that this would result in the manufacture of 12 to 30g of dioxin per annum at 200kT VCM/yr facility in this waste stream alone.

Wastewaters sampled at a VCM manufacturer in Jemeppe, Belgium in 1993 and analysed by the Vakgroep Milieu- en Toxicologische Chemie at the University of Amsterdam contained 15.7 pg/l ITEQ. Those from VCM manufacture in the UK[9] were considerably higher (1740 and 3722pg/l) with annual emission rates calculated to be 0.54 and 10g ITEQ based on these results. The higher result in the latter case was due to both a higher suspended solids level and greater contamination of those solids. The receiving settling lagoon was highly contaminated as a result. Similarly, aqueous discharges from the plant in the Netherlands were formerly associated with high levels of contamination in Chemieharbor, Rotterdam, but subsequent installation of filtration devices have

lowered solids levels and associated PCDD/F emissions[13]. Consequently it is not possible to make predictions about the magnitude of the aqueous emissions from any particular plant from the available data but this must remain an area of concern.

Assessment of the total dioxin generation from PVC manufacture is complicated by the use of different production technologies and the co-production of chlorinated solvents via oxychlorination of vinyl chloride distillation residues. This process in the UK was found to generate in the region of 350 to 625 g ITEQ/annum for 110 kT/annum of product[9]. Actual emissions are also hard to quantify since aqueous discharges vary widely and much of the organic waste is incinerated at on-site facilities for which feed rates and emission data are hard to come by. Fugitive emissions are rarely considered, but severe contamination adjacent to manufacturing facilities has been recorded in a number of cases. Nevertheless, generation and emissions would appear to be higher than previously assumed. Bearing in mind the huge volume of the global PVC industry, 4.5 million metric tonnes of PVC/annum in the USA[4] and 17.5 million tonnes of EDC/annum globally[14], further work should be initiated to investigate the size of emissions and ways of preventing them.

5. Acknowledgements

Analyses were carried out by Drs P.F. Ambidge and A. Fernandes of the AEA Technologies Laboratory at Harwell, U.K.

Sample	PU4016	PU4017	PU4043
Sample type	Organic waste	Organic waste	Organic waste
EPA category	F024	K019	K020
Location	Georgia Gulf, La.	Vulcan Chem. La	Formosa Chem. Tx
2378-TCDD	0.37	260	0.06
Total TCDD	3.100	1230	1.90
12378-PnCDD	0.14	890	0.05
Total PnCDD	3.60	3540	1.70
123478-HxCDD	0.30	260	0.078
123678-HxCDD	0.14	330	0.064
123789-HxCDD	0.11	620	0.071
Total HxCDD	1.30	3950	0.077
1234678-HpCDD	4.20	920	0.890
Total HpCDD	5.00	1270	1.70
OCDD	15.00	1060	3.00
2378-TCDF	0.91	680	0.44
Total TCDF	15.00	20600	6.00
12378-PnCDF	9.50	975	1.80
23478-PnCDF	1.60	1050	0.58
Total PnCDF	65.00	45300	11.00
123478-HxCDF	110.00	10100	11.00
123678-HxCDF	24.00	9760	2.40
123789-HxCDF	9.50	21800	1.30
234678-HxCDF	3.10	930	0.89
Total HxCDF	300.00	63700	27.00
1234678-HpCDF	250.00	13400	38.00
1234789-HpCDF	51.00	1340	6.00
Total HpCDF	450.00	16600	58.00
OCDF	390.00	43500	650.00
ITEQ	19.978	6370	3.912
Conc. units	µg/kg	µg/kg	µg/kg

TABLE 1: Analyses of wastes from the U.S. PVC industry

5. References

1) Johnson, J. (1994) Incinerators targeted by EPA. Environ. Sci. Technol. 29(1): 33A-35A

2) DoE (1995) United Kingdom comment on the United States Environmental Protection Agency's External Review Draft reassessment of dioxins. Publ. Department of the Environment Toxics Substances Division, 60pp

3) Harrad, SD. & Jones, K. (1992) A source inventory and budget for chlorinated dioxins and furans for in the United Kingdom environment. Sci. Tot. Environ. 126: 89-107

4) EPA (1994) Estimating Exposure to Dioxin-Like Compounds. Volume II: Properties, sources, Occurrence and Background Exposures. EPA/600/6-88/005Cb pp3-33 - 3-35

5) Ambidge, P., (1989) Determination of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in environmental samples. Chromatography and Analysis Aug. 1989: 5

6) Ambidge, P., Cox, E.A., Creaser, C.S., Greenberg, M., de M. Gem, M.G., Gilbert, J., Jones, P.W., Kibblewhite, M.G., Levey, J., Lisseter, S.G., Meredith, T.J., Smith, L., Smith, P., Startin, J.R., Stenhouse, I. & Whitworth, M. (1990) Acceptance criteria for analytical data on polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Chemosphere 21(8): 999-1006

7) Evers, H.G., Klamer, H.J.C., Lane, R.W.P.M. & Govers, H.A.J. (1993)

Polychlorinated dibenzo-*p*-dioxin and dibenzofuran residues in estaurine and coastal North Sea sediments: Sources and distribution. Environ. Toxicol. Chem. 12: 1583-1598

8) Wenning, R.J., Harris, M.A., Ungs, M.J., Paustenbach, D.J. & Bedbury, H. (1992) Chemometric comparisons of polychlorinated dibenzo-p-dioxin and dibenzofuran residues in surficial sediments from Newark Bay, New Jersey and other industrialised waterways. Arch Environ. Contam. Toxicol. 22:397-413

9) ICI (1994) Report to the Chief Inspector HMIP authorisation AK6039 Improvement Condition part 8, table 8.1, item 2: Formation of dioxins in oxychlorination, significance for human health and monitoring proposals. ICI Chemicals & Polymers Ltd report NWJP/BMTD, 27th April 1994, 16pp

10) Evers, E. (1989) De vorming van PCDFs, PCDDs en gerelateerde verbindingen bij de oxychlorering van etheen. Vakgroup Milieu en Toxicologische Chemie report MTC89EE, University of Amsterdam, 62pp

11) Hagström, P. (1995) Personal Communication.

12) Louisiana Department of Environmental Quality (1993) Biennial reporting system. Hazardous Waste report. GM report. Program ID: BRRPDOGM

13) Evers, E. (1995) Personal Communication.

14) CEC (1990) Organo-chlorine solvents. Commission of the European Communities/Royal Society of Chemistry, London