PRODUCTION OF PCDD/Fs BY THE PVC INDUSTRY

Stringer, R.L. * , Johnston, P.A. * & Costner, P. **

* Greenpeace Research Laboratories, Earth Resources Centre, University of Exeter, North Park Road, Exeter EX4 4QE, UK.
** Greenpeace International, P.O. Box 548, Eureka Springs, Arkansas 72632, USA.

The incineration sector is widely regarded as the largest source of atmospheric emissions (Johnson 1994, DoE 1995). However, source reconciliation studies based on atmospheric release estimates can only account for approximately 10% of environmental loadings of PCDD/Fs (Harrad & Jones 1992). 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.

It has been established since the late 1980s that the manufacture of PVC results in the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans. However, there is still very little information on the quantities generated in processing and emitted to the environment. 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 (EPA 1994).

This paper will present some recent information on the PVC/PCDD/F connection and suggest some areas for future action.

Experimental

Samples of chlorinated wastes were obtained from a number of PVC and VCM manufacturing facilities in the USA. Sediment was also obtained from the watercourse receiving effluents from one facility in Venice, Italy. PCDD/F analyses were conducted as previously described (Ambidge 1989). Data quality assurance was the same as for UK government laboratories (Ambidge et al. 1990).

3. Results

Analytical data are presented in table 1 below.

PCDD/F concentrations were elevated in all samples. Concentrations in sample PU4017, EDC reboiler residues (EDC tars) were particularly high at 6.37ppm of dioxin toxicity equivalents (ITEQ). To the Authors' knowledge, levels this high have not previously been reported in the open literature. The sediment sample from another Porto Marghera, Venice contained 753ppt ITEQ. Concentrations of this magnitude have only been observed in highly polluted industrial areas.

Dioxins are ubiquitous contaminants. The normal "background" dioxin contamination is characterised by a large proportion of octachlorinated dioxin. The samples presented here show a preponderance of polychlorinated dibenzofurans (PCDFs), particularly the higher chlorinated congeners. This is typical of manufacture of short chain aliphatic compounds such as EDC (Evers et al. 1993). The profile of sample PU4016 is similar to that adjacent to a VCM factory in Rotterdam Harbour, Netherlands (Wenning et al. 1992).

Unusually high proportions of higher chlorinated furans were found in the sediment sample from Porto Marghera and also in a sediment sample from the same area reported by Benfenati et al. (1993). The presence of unusually high proportions of higher chlorinated furans in the sediment points to the source of the dioxins as being from the nearby VCM manufacture.

4. Discussion

It is well established that the oxychlorination process widely used in vinyl chloride manufacture gives rise to PCDD/Fs (Evers 1989). The PVC product subsequently contains dioxins in the ppt TEQ range (Hagstrom 1995). The concentrations reported here in the process wastes are far greater.

Disposal routes for dioxin-contaminated wastes relating to vinyl chloride manufacture are varied. Documented routes include incineration, landfill, deep well injection and direct discharge to waterways. Whether as a result of ineffective disposal procedures or fugitive emissions, significant contamination of the sites of PVC manufacturing facilities has been documented and in some cases, rank amongst the highest environmental concentrations of these chemicals reported. The exposure status of workers is currently unknown.

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. The facility from which sample PU4016 was collected reported generating 210 tonnes of this F024 waste in 1991. At a concentration of 19.978 f g/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 (Louisiana Department of Environmental Quality 1993). No such figures were available for the other two wastes sampled, but given the high PCDD/F concentrations recorded it is apparent that significant quantities of dioxins could be generated in these waste streams.

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. Publicly available data indicate that generation from this process can be as much as 3-6g ITEQ/kT of production capacity.

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. 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. 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 (Evers 1995). Benfenati et al. (1993) demonstrated that Porto Marghera had higher concentrations of PCDD/Fs than other sites in Venice. The concentration of PCDD/F reported here is over twice that. The most likely input route would be via aqueous effluent and indicates the importance of this source as the primary contributor to the dioxin burden in Venice lagoon. 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.

Fugitive emissions are rarely considered, but severe contamination adjacent to manufacturing facilities has been recorded and much of this must be attributable to fugitive emissions. Nevertheless, generation and emissions would appear to be higher than previously assumed.

4. Conclusions

Analyses of PCDD/Fs from Europe and the USA have indicated that there is a wide variation in the concentration of PCDD/Fs in wastes from the PVC industry. Some samples are in the parts per trillion range for ITEQ but others are in the parts per billion or even parts per million range. The more highly contaminated wastes must be regarded as extremely hazardous to handle with the potential for substantial fugitive emissions to the environment.

This problem cannot be addressed simply by introducing end-of-pipe solutions such as effluent filtration or incineration of organic wastes. It is becoming clear that PVC industry process streams and wastes contain high concentrations of dioxins. Bearing in mind the huge volume of the global PVC industry, 4.5 million metric tonnes of PVC/annum in the USA (EPA 1994) and 17.5 million tonnes of EDC/annum globally CEC 1990), the total amount of dioxin generated by this manufacturing process will be considerable. Further work should be initiated to investigate the size of emissions and ways of preventing them.

5. References

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

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

Benfenati, E., Fattore, E., Mariani, G. & Fanelli, R. (1993) PCDD and PCDF in the lagoon of Venice. Poster Presentation at the Workshop On The Determination of PCDD and PCDF, Como, Italy, 17-22 April 1993.

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

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

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

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

Evers, E. (1995) Personal Communication.

Evers, E.H.G., Klamer, H.J.C., Lane, R.W.P.M. & Govers, H.A.J. (1993) Polychlorinated dibenzo- p -dioxin and dibenzofuran residues in estuarine and coastal North Sea sediments: Sources and distribution. Environ. Toxicol. Chem. 12: 1583-1598

Hagstrom, P. (1995) Personal Communication.

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

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

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

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

Sample	PU4016	PU4017	PU404	MI5021
Conc. units	µg/kg	µg/kg	µg/kg	µg/kg
Sample type	Organic waste	Organic waste	Organic waste	Lagoon sediment
EPA category	F024	K019	K020	n/a
Location	USA	USA	USA	Italy
2378-TCDD	0.37	260	0.06	0.0061
Total TCDD	3.100	1230	1.90	0.77
12378-PnCDD	0.14	890	0.05	0.0011
Total PnCDD	3.60	3540	1.70	0.90
123478-HxCDD	0.30	260	0.078	0.450
123678-HxCDD	0.14	330	0.064	0.059
123789-HxCDD	0.11	620	0.071	0.130
Total HxCDD	1.30	3950	0.077	1.600
1234678-HpCDD	4.20	920	0.890	10.0
Total HpCDD	5.00	1270	1.70	13.0
OCDD	15.00	1060	3.00	12.0
2378-TCDF	0.91	680	0.44	0.049
Total TCDF	15.00	20600	6.00	2.40
12378-PnCDF	9.50	975	1.80	0.29
23478-PnCDF	1.60	1050	0.58	0.36
Total PnCDF	65.00	45300	11.00	2.00
123478-HxCDF	110.00	10100	11.00	1.50
123678-HxCDF	24.00	9760	2.40	0.30
123789-HxCDF	9.50	21800	1.30	0.73
234678-HxCDF	3.10	930	0.89	0.24
Total HxCDF	300.00	63700	27.00	5.30
1234678-HpCDF	250.00	13400	38.00	1.10
1234789-HpCDF	51.00	1340	6.00	2.80
Total HpCDF	450.00	16600	58.00	10.00
OCDF	390.00	43500	650.00 3	6.50
ITEQ	19.978	6370	3.912	0.753

TABLE 1: Analyses of PVC-related samples from the USA and Italy.