Releases of PCDD/F from U.S. Chemical Production Facilities

Patrick Dyke[1], Gary Amendola[2], Todd Abel[3]

[1]PD Consulting, Brobury
[2]Amendola Engineering, Westlake, Ohio
[3]CCC, Arlington, Virginia

Introduction

There is continuing concern over the exposure of humans and ecosystems to trace levels of highly toxic organic compounds, in particular chlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD and PCDF). The U.S. Environmental Protection Agency (EPA) is developing inventories of releases of PCDD/F. As a contribution to this effort the Chlorine Chemistry Council (CCC is a business council of the American Chemistry Council) worked with EPA to develop estimates of releases of PCDD/F to the environment and off-site transfers from selected chemical production facilities in the U.S. that produce or use large quantities of chlorine.

Methods

CCC engaged independent consultants to carry out an audit of PCDD/F release estimates at 22 plants operated by four member-companies and two non-member companies that agreed to participate. The principal objective was to produce site-specific estimates for releases of PCDD/F for the year 2000 to be compatible with the EPA inventory.

In recognition of the fact that releases are affected by technology changes as well as changes in production and the treatment of waste and effluent streams, an assessment of year 2002 releases was given (where there was a significant change from year 2000) and indications of whether estimates could be used to represent future year releases.
The protocol for developing release estimates was developed with EPA and required:

- The best estimate of releases to air, water, land or transfers (e.g. in waste for further treatment) but not transfers in saleable products, expressed on a congener specific basis (17 congeners assigned TEF values);
- Site-wide release data in terms of an “activity statistic” and “emission factor”;
- Non-detected congeners be set to zero;
- Narrative on how the estimates were derived and an assessment of the quality of the estimate for each release addressing: the identification of possible release points; data used

to estimate releases (activity and data on concentrations of PCDD/F); sampling and analytical protocols; handling of data and calculations of releases.

In order to make the best possible estimates data from different years (other than 2000) could be used, provided that the processes had not altered in a way that would make this unrepresentative.

Visits were made to companies in order to understand each site's operation, identify release points and to examine the analytical and process data available. Estimates were developed with the company experts for each release point and aggregated to give site-wide releases. Data were reviewed for accuracy, completeness and representativeness. Analytical reports were selected for further review to ensure that recognised procedures had been followed and that the data provided were of suitable quality for the purposes of making release estimates suitable for use in the EPA inventory of sources of PCDD/F.

The approach adopted goes beyond the requirements of the US Toxic Release Inventory (TRI) and typical inventory compilation techniques using mainly site-specific, validated data and using a site-by-site approach rather than industry or sector estimates. Releases to the environment and transfers in residues were the focus; no releases as trace contaminants in products were included.

Results and Discussion

In total, six companies participated in the project with a total of 22 individual production sites considered and for which estimates of releases were developed and assessed.

The majority of sites consisted of several production processes co-located and with significant commonality in environmental control systems, in particular liquid effluent treatment or waste treatment such as incinerator units. This practice of routing effluents or wastes from several processes to single units for treatment means that it is generally not possible to allocate calculated releases to one or other particular process on the site.

In addition it became clear during the project that the differences in plant design, layout and operation and differences in the precise types of environmental pollution controls that were applied mean that seeking to transfer estimates of releases or "emission factors" (release of PCDD/F per unit of activity, production, volume of waste, etc.) is not straightforward and in most cases cannot be supported.

Results are tabulated below. The quality ratings for each release estimate indicate the quality of the emission factor and activity statistic used to derive each estimate. In general, a high rating (H) for the emission factor indicates that one or more sets of site-specific analytical data were available. A high rating for activity indicates that measured and recorded data were available. The great majority of the estimates were based on site-specific analytical data. In all cases considered the analytical data that underpin the estimates were judged to be of sufficient quality to be suitable for making inventory estimates. The methods used in general followed EPA standards, although in one case a company had developed in-house methods for sampling and analysis that significantly increased the throughput of samples and provided robust data on their processes.

The quantity of data available varied considerably from site to site and between streams. More effort had been directed at characterizing releases to air and water in general compared to releases in wastes and residues.

In some cases data had to be transferred from one plant to another in order to make estimates of releases. In such cases each data transfer was assessed by considering the similarities of the processes and environmental controls, as well as the way the data were applied. For some streams there were few data available within the universe of sites examined, such as some of the solid waste streams that arise periodically and are believed to be relatively insignificant (e.g. refractory bricks, scrap process piping).

Significant changes were identified at some plants that would impact on releases in future years (post 2000). The biggest changes were where incinerators had been upgraded to meet the requirements of the Clean Air Act. Changes for hazardous waste incinerators ensured substantial reductions in releases of PCDD/F to air.

Table 1 summarizes results, expressed as g of I-TEQ released or transferred by each route on a plant-wide basis, for each plant. For each release estimate the quality rating is also given for the activity statistic and the emission factors that have been used to derive the overall release estimate. The quality ratings were designed to be comparable to those used for overall source assessment in the EPA inventory development effort.

Overall the project has developed release estimates for 22 chemical production facilities in the U.S. (19 reported here), using the best available data and auditing for quality of the estimates to ensure that the data can be used in the EPA inventory. Any release points that were identified but not quantified are noted. No large releases of PCDD/F are believed to have been neglected.

Acknowledgements

The authors would like to acknowledge the valuable help and assistance from: the staff from the participating companies; David Wood of SAL and Dale Rushneck of Interface Inc for review of the analytical reports; staff at Amendola Engineering (Matt Oxsalida, Mark and Susan Amendola) for audits, reporting, and assessment. Also, thanks to Dwain Winters of EPA Office of Prevention, Pesticides and Toxic Substances for his invaluable input and cooperation.

Table 1. Annual release estimates of PCDD/F to air, land and water

Plant / Process(es) / Year	ON-SITE RELEASES (g I-TEQ)										OFF-SITE TRANSFERS (g I-TEQ)					
	Air Releases		Water Releases Gross		Water Releases Net		Secure Landfill		Land Farm		Secure Landfill		Incineration		Deep Well Injection	
	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002
Dow Chemical - Midland, TX *Integrated ag chem., polymers, others*	0.046 H/H	NC	0.037 H/H	NC			12.6 H/H	16.3 H/H								
Dow Chemical - Plaquemine, LA *Integrated,, Cl_2, EDC, others*	0.092 H/H	NC	7.71 H/H	2.74 H/H	7.03 H/H	2.48	12.8 H/H	1.03 H/H								
Dow Chemical - Freeport, TX *Integrated, Cl_2, EDC, VCM,, solvents, others*	3.08 H/H	2.03 H/H	6.91 H/H	3.76 H/H	6.48 H/H	3.28 H/H	89.3 H/H	81.7 H/H								
Company A, plant A1 *Cl_2, EDC, VCM, others*	0.068 H/H	0.068 H/H	0.023 H/H	0.024 H/H					1.45 H/H	NC	1.5 H/H	1.74 H/H	2.18 H/H	0.237 H/H		
Occidental – Convent, LA *Cl_2,, NaOH, EDC*	0.022 R/H	NC	0.002 LR/H	NC							0.081 H/H	NC	12.1 R/H	NC		
Occidental - Deer Park, TX *VCM*	0.581 H/H	0.585 H/H	0.031 H/H	NC							0.474 H/H	NC	22.2 H/H	NC		
Occidental – Ingleside, TX	1.61	0.53	0.011	0.011							1.47	1.09				

Plant		ON-SITE RELEASES (g I-TEQ)										OFF-SITE TRANSFERS (g I-TEQ)					
		Air Releases		Water Releases				Secure Landfill		Land Farm		Secure Landfill		Incineration		Deep Well Injection	
				Gross		Net											
Process(es)	*Year*	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002
Cl_2 (diaphragm cell), NaOH, EDC, VCM		RH/H		H/H	H/H							H/H	H/H				
Occidental - LaPorte, TX[1]		0.039	NC	0.0064	NC							5.1	NC	44.4	NC		
VCM		H/H		H/H								H/H		H/H			
Occidental - Mobile, AL		NE		$3.6x10^{-5}$	NC							0.83	NC				
Cl_2 (membrane cell), caustic potash, sodium silicate		H		LR/H								LR/H					
Occidental – Battleground, TX		NE		$4.8x10^{-4}$	NC								$6.6x10^{-2}$				
Cl_2 (diaphragm cell), NaOH		H		R/H									R/H (no brine)				
Occidental - Deer Park, TX (CA)		NE		0.54	NC	0.5	NC					0.38					
Cl_2 (mercury/diaphragm cell), NaOH				H/H		H/H						R/H					
Occidental – Delaware City, DE		NE		$1.3x10^{-4}$	NC							0.81	NC	$3.5x10^{-6}$	NC		
Cl_2 (mercury cell), NaOH, caustic potash, sodium silicate		H		R/H								H/H		H/H			

Plant		ON-SITE RELEASES (g I-TEQ)										OFF-SITE TRANSFERS (g I-TEQ)					
		Air Releases		Water Releases				Secure Landfill		Land Farm		Secure Landfill		Incineration		Deep Well Injection	
				Gross		Net											
Process(es)	*Year*	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002
Occidental – Hahnville (Taft), LA		NE		1.08	NC							0.2	NC	9.6×10^{-9}	NC	0.04	NC
Cl_2 (mercury/diaphragm cell), NaOH, sulfur monochloride		H		H/H								R/H		R/H		R/H	
Occidental - Muscle Shoals, AL		NE		8.7×10^{-8}	NC							0.38	NC				
Cl_2 (mercury cell) and caustic potash		H		R/H								H/H					
Occidental – Niagara Falls[2]		3.8×10^{-3}	1.4×10^{-3}	1.4×10^{-3}	1.3×10^{-3}							0.028	0.023	210	0.023		
Cl_2, NaOH, organic chemicals		H/H	H/H	H/H	H/H							R/H	R/H	R/H	R/H		
PPG Industries – Lake Charles, LA		0.02	0.02	8.98	0.653							0.303	0.365	8.66	5.32		
Cl_2 (mercury/diaphragm cell), hydrogen, NaOH, EDC, and VCM		H/H	H/H	H/H	H/H							H/H	H/H	H/H	H/H		
PPG Industries - Natrium, WV		0.034	0.036	0.193	NC	0.19	NC					0.085	NC				
Cl_2 (mercury/diaphragm cell), NaOH		R/H	R/H	R/R		R/R						H/H*					
Company B, plant B1[3]		0.037	NC	1.07	0.879							NC	NC	0.208	NC		

	ON-SITE RELEASES (g I-TEQ)										OFF-SITE TRANSFERS (g I-TEQ)					
	Air		Water Releases				Secure		Land		Secure		Incineration		Deep Well	
Plant	Releases		Gross		Net		Landfill		Farm		Landfill				Injection	
Process(es) *Year*	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002	2000	2002
Cl_2, solvents, other chlorinated organics	R/H	R/H	*	*							*	*	*	*		
Company B, plant B2	$8.38x10^{-3}$	$8.83x10^{-3}$	0.372	0.46							NC	NC	NC	NC		
Cl_2, EDC, solvents	R/H	R/H	R/H	R/H												

Letters indicate quality rating for emission factor and activity statistic, L – low, R – reasonable, H – high (rating of overall estimate is lower of the two)

[1]Off-site transfers to incineration for the Occidental LaPorte facility includes transfers to incineration and to another chemical manufacturing facility as feedstock. [2] for Niagara Falls also 0.29 (2000) and 1.04 g to activated carbon regeneration and $5.2x10^{-5}$ g I-TEQ off-site transfer of waste water. [3] – plant B1 estimates for water are partial and for deep well injection, incineration partial. Some data for Company B were in total homologue so I-TEQ could not be calculated, some streams could not be assessed

NC: Estimated PCDD/F releases to air, water and off site transfers were not calculated for 2002 because of lack of data to characterize year 2002 releases and off site transfers independent of year 2000 releases. In these cases, estimated 2000 releases are considered reasonably representative of year 2002 releases. NE – no estimate made (ie any release judged trivial)