The PVC and the Dioxin Issue

Christoffer Rappe
Institute of Environmental Chemistry, Umea University, Umea, Sweden

The polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are two groups of pollutants very intensely discussed during the last three decades. They are lipophilic compounds and they are stable under normal conditions, consequently they have a pronounced tendency to bioaccumulate in the environment, especially the aquatic environment. The PCDDs and PCDFs are highly toxic, especially the 2,3,7,8-substituted tetra-, penta- and hexachlorinated congeners.

The PCDDs and PCDFs have been identified in biologic samples throughout the environment, especially in the Northern Hemisphere. They are also ubiquitous in sediment, sewage sludge, soil and air samples, especially in the urban area. Background levels of PCDDs and PCDFs have also been identified in human samples, although the levels vary between different parts of the world. The highest levels have been found in Europe and in the USA and Canada.

A series of laboratory experiments has shown that PVC can be converted into PCDDs and PCDFs and it is also clear that the reclamation of PVC coated wire also leads to the emission of PCDDs and PCDFs. However, it is unclear to what extent these experiments are relevant to MSW incineration.

Marklund et al. (1) have reported on a fire in the early part of 1987 in a plastic carpet company in Sweden. A wooden warehouse containing 200 tonnes of pure PVC plastic and 500 tonnes of plastic carpets was completely burned out. A series of snow samples was collected and analyzed. During the fire the ambient temperature was low - 30°C, and thus resulted in the formation of an inversion layer. It was estimated that the total deposition of PCDDs and PCDFs outside the plant, within a radius of 1500 meters, was less than 3 mg, calculated as dioxin equivalents (I-TEQ).

A series of studies can be found in the literature where an additional amount of PVC has been burned together with the normal MSW at existing MSW incinerators (2-9). The emission levels of PCDDs and PCDFs from these incinerators have been measured, and the results are contradictory and controversial. Some of the studies indicating a correlation could have been biased by carry-over of minute amounts of PCDDs and PCDFs on soot particles from earlier activities. It is practically impossible to clean a full-scale MSW incinerator completely between the different test burns. In addition these studies have other major drawbacks. They are often poorly designed especially from a statistical point of view, the sampling and trace analysis of PCDDs and PCDFs are performed using non-validated methods, the emission levels for the incinerators are usually quite high, and in some cases conclusions are drawn after substantial data reduction.

A recent study in Denmark has been reported to show a correlation between the amount of PVC and the emission levels of PCDDs and PCDFs. It is stated that doubling the amount of PVC increased the emissions of PCDDs and PCDFs by 37% (2). However, this conclusion is based on very few data points (including only two experiments, with a high addition of PVC), strategic data reduction, and the use of a non-validated analytical method. The four highest levels of PCDDs and PCDFs were found in experiments with no addition of PVC or a minor addition of PVC. These experiments were considered as outliers and were then not included in the statistical analysis or included with an arbitrary correction.

Studies performed at Hamburg, FRG and Milan, Italy; as well as Pittsfield, MA, USA are reported not to show any correlation between emission of PCDDs and PCDFs and additional amounts of PVC (7,8,9). However, the study in Hamburg was poorly designed. All emission levels were unusually high both in the experiments with and without additional PVC. In only one experiment additional PVC was added to the fuel, but in this case the basic fuel was paper and not MSW, not allowing any direct comparison (8).

In the Italian study, normal MSW was burned together with up to 10% of PVC by weight. All the results for PCDDs and PCDFs were below the detection level. However, the analytical technique is not further discussed (9).

In the Pittsfield study, performed in 1985-86, in total 8 experiments were performed with four different types of waste (7).

Normal MSW
Normal MSW + PVC
PVC-Free MSW
PVC-Free MSW + PVC

In all experiments the emission levels were higher than in modern incinerators today. In other experiments at the same incinerator it has been found that there is a direct correlation between incineration temperature and emission levels. In the experiments with and without PVC the temperature was found to vary between 940°C and 1030°C. The specific incineration experiments, which should be compared, were not performed at the same temperature, consequently a direct comparison or correlation is difficult to perform. It is reported that additional PVC did not significantly affect the emission levels of PCDDs and PCDFs.

The Vehlow Study, 1994-1997 (10)

Experiments performed by Vehlow in 1994 on the Karlsruhe TAMARA incinerator in Germany for MSW did not support the theory that there is a correlation between the PVC concentrations in the waste feed with the dioxin concentrations in the flue gas. In these experiments up to 15% of mixed plastics from the packaging sector were added to a reference waste feed. The PVC inventory of the plastics increased the concentration of chlorine in the fuel by a factor of approximately 5. As Figure 1 points out (data reported in 1997) the absolute concentration of PCDDs and PCDFs in the raw gas fell into a band of variation between 100 mg/cm and 350 mg/cm. This band showed no correlation with the chlorine concentrations in the input.

The Rigo and Chandler Study, 1995 + 1998 (11, 12)

The study by Rigo and Chandler (11, 12) reports that there is no significant relationship between the PCDDs and PCDFs on one side and the input chlorine data. In their study they are using data already published in the literature. While PCDDs and PCDFs cannot be made without chlorine, the amount of chlorine already present in commercial combustion systems is great enough that other effects like combustion and stable temperature predominates. Even very large changes between 2 and 10 in the amount of chlorine present could not be seen in this study.

It has been found that good combustion virtually eliminates furnace carry-over and flame formation PCDDs and PCDFs. It has also been shown that reducing the gas temperature entering the particulate control device minimized the formation of PCDDs and PCDFs because the flue gases are cooled down between the 250-400°C, the "dioxin formation window". Activated carbon can be used to trim the small amounts of PCDDs and PCDFs that still remain in the gas flow. Little benefit is likely to result from even draconian attempts to reduce the chlorine content in the feed stocks.

The Wickstrom et al. Study (13)

A laboratory scale vacuum cleaned fluidized bed reactor was used in order to achieve reproducible and well-controlled combustion experiments. The fluidized bed free board reactor was insulated with ceramic fiber covered by aluminum foil to achieve a homogeneous temperature profile inside the reactor. In addition, the reactor was preheated to the desired temperature by combustion of propane. This process gave low CO values. The reactor was operated with a cyclone directly after the combustion unit.

Each of seven different fuels (Table 1) was combusted three times in a random order to minimize the effect of systematic errors. Each experiment performed in duplicate was normalized to 1 atmosphere and 10% CO_2. CO and O_2 were detected by electrochemical sensors. The temperature in the bed, freeboard and in the cooling section were measured. Principal component analyses (PCA) was used for the flue gas samplers. The analyses of PCDDs and PCDFs as well as Σ PCBz (polychlorobenzenes) were all performed by standardized analytical methods.

Table 2 presents the levels of PCDDs and PCDFs counted as I-TEQ in the different experiments with each fuel and also the Σ PCBz. The reproducibility within each fuel mixture was good. Figure 2 shows the average, minimum and maximum values of the I-TEQ and Σ PCBz in each of the flue gases from the experiments. The Σ PCBz is almost 1,000 times higher than the values for the I-TEQ.

The concentrations of I-TEQ in the flue gas increased by a factor of more than 10 between the fuel with 0.12% Cl and 1.7% Cl. The experiments with 0.12% Cl, 0.20% Cl, 0.46% Cl, 0.63% Cl and 0.56% Cl gave all about the same number of I-TEQ; 0.11 to 0.23 mg/N cm (Table 2 and Figure 2). The three fuels (P4, P5 and P6, see Table 2 and Figure 2) with a concentration of chlorine around 0.5% but with different forms gave all the same value of I-TEQ. Thus fuel P4 has only $CaCl_2$ as the chlorine source and P6 has only PVC, while fuel P5 contains them both in a ratio of 1:1. The indication of this shows that the emission of I-TEQ is not influenced by the form of the chlorine in the fuel, either organic or inorganic.

The amount of chlorine is the same in P2 and P3. This indicates that chlorine content up to 0.63% does not affect the amount of I-TEQ. The amount of PVC corresponding to this value is more than 1% PVC in the total waste stream.

The Costner Studies, 1997, 1998 (14, 15)

In a recent study Costner discusses findings that chlorine has an influence on the emissions of the PCDDs and PCDFs in the waste stream. Costner conducted a review of the Rigo and Chandler (1995) report and disagreed with the conclusions of that report. The Costner review was essentially a critique of the statistical treatment applied by Rigo and Chandler. A detailed review of the methodology applied by Costner is beyond the scope of this Report. However, in general, Rigo and Chandler's findings are reflective of the majority of the literature on this subject, and Costner's critique lacks a scientific peer review to support its stated conclusion (14).

Costner also reports data from a study where various amounts of chlorinated compounds have been added to a contaminated soil. She gives a complete description of the flow rate and the waste characteristic but the most interesting parameter, the temperature of the oven, is completely neglected. Conclusions drawn from this type of experiment have to be neglected (15).

Conclusion

The most rigorous scientific examination of the influence of the level and form of chlorine on the formation of dioxins and furans under controlled combustion conditions could not support the opinion that an elimination of PVC in MSW would contribute to a reduction of PCDD/PCDF emissions. Wikstrom, et. al. (13) gives a clear indication, under almost ideal combustion conditions, that MSW with a chlorine content of up to 0.63% has no positive correlation between chlorine in MSW and PCDDs and PCDFs in the emissions. MSW in the U.S. is estimated to contain about 0.3% Cl. This is well under the highest point at which no relationship has been established. Another observation is that in this range of Cl content in MSW, it is evident that the nature of the effects of additional chlorine is independent of whether the addition is organic or inorganic chlorine. So, efforts to remove chlorine, whether it is PVC or common table salt, would have no measurable effect on PCDD/PCDF emissions.

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Table 1: Chlorine Variation in Fuel Pellets

Fuel	Inorganic Cl (%)	Organic Cl (%)	Total Cl (%)
P2	0.04	0.08	0.12
P3	0.15	0.05	0.20
P4	0.33	0.13	0.46
P5	0.37	0.26	0.63
P6	0.03	0.53	0.56
P7	0.29	0.55	0.84
P8	0.41	1.31	1.72

Source: Wikstrom et al., (1996)

Table 2: I-TEQ (in ng/Nm^3) and Σ3-6 PCBz (in μg/Nm^3) Flue Gas for All Samples from Each Fuel

		Experiment 1		**Experiment 2**		**Experiment 3**		
Fuel	**Organic Compound**	**I**	**II**	**I**	**II**	**I**	**II**	**Avg**
P2	I-TEQ	0.15	*A*	0.30	0.22	0.08	0.05	0.16
	Σ3-6Cl-PCBz	0.15	*A*	0.05	0.06	0.10	0.10	0.09
P3	I-TEQ	0.06	0.08	0.18	0.15	0.10	0.10	0.11
	Σ3-6Cl-PCBz	0.06	0.05	0.10	0.10	0.16	0.07	0.09
P4	I-TEQ	0.21	0.20	0.21	0.29	0.24	0.23	0.23
	Σ3-6Cl-PCBz	0.22	0.14	0.15	0.07	0.11	0.07	0.13
P5	I-TEQ	0.17	0.16	0.17	0.14	0.28	0.15	0.15
	Σ3-6Cl-PCBz	0.19	0.17	0.11	0.10	0.27	0.21	0.17
P6	I-TEQ	0.08	0.07	0.12	0.26	0.24	0.20	0.15
	Σ3-6Cl-PCBz	0.09	0.12	0.05	0.11	0.20	0.15	0.12
P7	I-TEQ	0.21	0.30	0.64	0.67	*A*	*A*	0.46
	Σ3-6Cl-PCBz	0.29	0.41	0.33	0.43	*A*	*A*	0.36
P8	I-TEQ	1.23	1.55	1.28	1.32	1.47	0.72	1.26
	Σ3-6Cl-PCBz	1.47	1.51	0.74	0.88	0.96	0.86	1.07

A- Problems during the combustion period

Source: Wikstrom, E., et al. (1996)

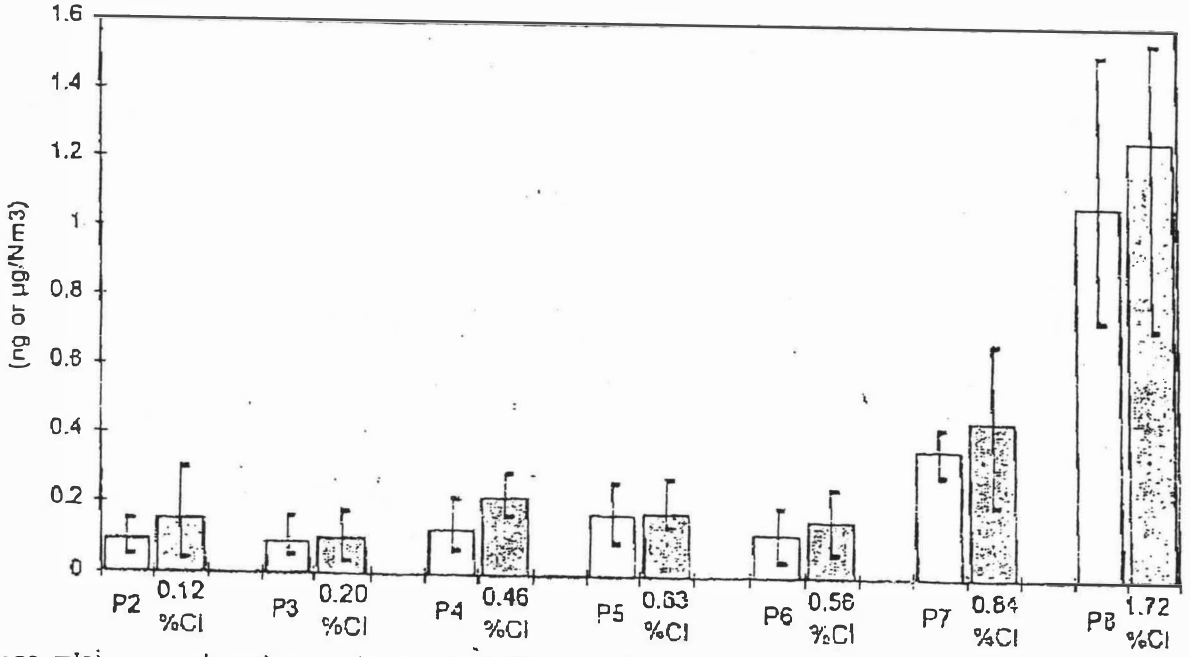

FIGURE 2: Average, minimum, and maximum values of the I-TEQ ng/Nm^3 (shaded bars) and $\sum$3–6 PCBz µg/Nm3 (open bars) as a function of chlorine content in the fuels.

Source: Vehlow 1997