

## ON THE FATE OF PVC IN MSW COMBUSTION.

**Jacqueline Kanters and Robert Louw.**

Center of Chemistry and the Environment, Leiden Institute of Chemistry,  
Gorlaeus Laboratories, Leiden University, P.O.Box 9502, 2300 RA Leiden,  
The Netherlands.

### Abstract

Regular and modified samples of real MSW have been combusted in a mini-model reactor mimicking practical MSW Incineration. Emitted (poly)chloro-phenols (CP) have been taken as an indicator for PCDD/F. Given the chlorine load mainly due to kitchen salt, that of PVC hardly leads to "extra" CPs, even if the PVC load is increased to 8-fold the usual level. Also, when replacing the combustibles and chlorine carriers, including PVC, by cellulose and NaCl, the level of CP emission does not change.

### Introduction

Combustion of Municipal Solid Waste (MSW) in Municipal Waste Incinerators (MWIs) yields "Products of Incomplete Combustion" (PICs) such as PolyChlorinated Dibenzo-p-Dioxins (PCDDs) and PolyChlorinated DibenzoFurans (PCDFs). Since 1977, when these compounds were first analysed in flyash samples of a MWI <sup>1</sup>, it became clear that MW Incineration was one of the main sources of PCDD/PCDF. Recent research in our laboratory has shown that, at least in the formation of PCDDs via fly-ash catalysed reactions at temperatures at 300-400°C, (poly)chlorophenols (CPs) are key intermediates <sup>2</sup>. CPs can be formed from various organic materials in the MSW, whereas NaCl - in the compostable fraction of the MSW - and PVC are about equal contributors to the chlorine load. PVC, stemming from packaging, electrical wire insulation, electrical and drainage piping etc., amounts to ca. 0.6% wt of Dutch MSW. Heating PVC smoothly gives HCl, and when PVC is combusted, yields of HCl are high. The major part of the chloride salt initially present in MSW is also converted into HCl. With the usual excess of O<sub>2</sub>, an atmosphere conducive for oxychlorination is present throughout the MWI process. In this study we concentrated on the formation of CPs, also as an indicator for 'dioxin' production. A central question was: What is the role of PVC in the formation of CPs?

# FORM

## Experimental

For our laboratory-scale investigation representative Dutch MSW was available separated into 14 different fractions, allowing for wide variation in composition. It was therefore possible to make MSW-samples with extra PVC, without PVC and even with a very low NaCl content. Furthermore, the effect of other additives can easily be investigated.

In a mini-model combustion reactor, a reconstructed Euroglas AOX-apparatus, portions of MSW have been combusted usually at 850°C.

In each experiment about 1 gram of wet MSW was, in a batchwise manner, slowly brought into the furnace with a boat control. In about 60 minutes the boat arrived in the middle of the furnace with an additional combustion time of 9 minutes. If this protocol is followed, the process is optimal and mimicks real MSW combustion; the level of CO is low, and the amount of emitted Polycyclic Aromatic Hydrocarbons (PAHs) is quite acceptable (Table). With the right flow of air the rest oxygen is about 10% for a few minutes. The carrier gas could be dry, or humidified, by passing it through water. HCl could also be added, if this water was replaced by aq. hydrochloric acid of desired strength. For analysis of organics and HCl the emitted gases passed a cooling section and were then collected in cold traps.

## Results and Discussion

A regular run with standard MSW and wet air produces chlorophenols, totalling 70 µg Cl/ kg wet MSW, and a congener distribution as shown in the Table.

To find out if there is a correlation between the amount of PVC in the MSW and the chlorophenol emission, a series of samples with up to 4.5 %wt of added (virgin) PVC were combusted under the same standard conditions. Addition of PVC led to accordingly higher HCl emissions, but had little, if any effect on CP production.

In a second series the MSW standard composition was maintained but HCl was added to the - wet - carrier air and varied <sup>3</sup>. Already some 0.1 g HCl/Nm<sup>3</sup> - a value greatly below 'real' HCl concentrations in MWIs, 0.5-1.5 g/Nm<sup>3</sup> - led to a doubling of the CP formation. This is likely to be the consequence of the presence of HCl in every stage of the combustion process, which is the case in real MWIs <sup>3</sup>. A further increase of [HCl] had hardly any effect (Figure).

Next we have composed a 'MSW' sample which contained only traces of chlorine, by leaving out the PVC, bread, vegetable and paper fractions. To compensate for the loss of caloric value an appropriate amount of pure cellulose was added. Logically, when using wet, HCl free air only minute amounts of (chloro)phenols were recorded. Restoration of the regular chlorine content by adding aq. NaCl to the above-mentioned cellulose containing feed restored the CP emission to the usual value for runs with standard MSW with wet (HCl free) air.

We wish to point out further that - other things being equal - a change of the temperature of the reactor exit part also changes the level of CP production as in real MWIs <sup>4</sup>. Our ongoing study therefore comprises not only variation in composition of the feed - with special attention for the behaviour of the 'rest fraction', lacking compostable matter - and other

process variables. The fate of markers - e.g. a labeled CP - added to the various stages of the process, substituting PVC with other halogenated materials, and in general where and how (oxy)chlorination to give the observed CPs takes place, are also under investigation.

## Summarizing Conclusions

- \* Enlarging the PVC content to even eightfold the normal value does not give higher CP production;
- \* Replacing actual chlorine containing fractions - those with chloride salt and PVC - by dummy NaCl + cellulose leads to comparable levels of CP;
- \* The kitchen salt - in Dutch MSW - engenders CP emission; the PVC in the MSW creates more HCl but no 'extra' CPs;
- \* Accepting CPs as surrogate for PCDD/F, the same can be said about dioxin production/emission.

## References/notes

1. Olie K., Vermeulen P. L. and Hutzinger O., Chemosphere, 1977;6:455-59.
2. J. G. P. Born, Thesis: "On the formation of Dibenzofurans and dibenzodioxins", Leiden 1992.
3. With added HCl, conditions are in better agreement with those in a real MWI; in our semi-batch wise operation, HCl formation (and hence concentration) will vary with time and without adding HCl, in some stages of the combustion process HCl may even be absent.
4. Fängmark I., Marklund S., Rappe C., Strömberg B. and Berge N., Chemosphere, 1991;23:1233-43.

# FORM

Table: Standard run with MSW  
airflow with 2 mol% water.

Conditions:	
intake	600 mg dry MSW + 400 mg H <sub>2</sub> O
airflow	460 mmol/h (dry)
Temperature in oven	850 °C
Residence time in oven*	ca. 10 s
Temperature in exit part	300 °C
Residence time in exit*	ca. 1 s
Products:	
HCl	3.1 mg Cl/g wet MSW
PAHs**	16 µg/g wet MSW
CPs total	140 ng/g wet MSW
	or 2 µmol org. Cl/kg wet MSW
monoCP:triCP:pentaCP	10:100:30

\* of gaseous components.

\*\* sum of indene, naphthalene, acenaphthylene and phenanthrene.

## Total organic Chlorine vs. [HCl]

