

# FORMATION AND SOURCES II –POSTER

## PCDD/F GAS/PARTICLE PARTITIONING AND ITS RELEVANCE IN GAS CLEANING PROCESSES AND IN MECHANISTIC STUDIES (II)

Alfons Buekens<sup>1</sup>, Kathleen Schroyens<sup>1</sup>, Nadezhda Zyaykina<sup>1</sup>, Pierre Jacobs<sup>2</sup>

<sup>1</sup>Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium, E-mail: [abuekens@vub.ac.be](mailto:abuekens@vub.ac.be)

<sup>2</sup>Center for Surface Chemistry & Catalysis, K.U.Leuven, Leuven, Belgium

### Introduction

Gas/particle partitioning of PCDD/F was studied from de novo test data (part I); in part II actual plant data are described by a partition parameter  $\alpha$ , determined as the dimensionless ratio of the gas phase to the particle associated concentration (both in ng/Nm<sup>3</sup>) of each studied compound. The following equations, both based on a Langmuir adsorption equilibrium, were methodically tested to describe gas/particle partitioning of PCDD/F, their homolog groups, and congeners:

$$K_p = \frac{C_p/TSP}{C_G} = 1/\alpha \cdot TSP \quad [A] \quad TSP \cdot \alpha = 1/K + C \quad [B]$$

### Materials and Methods: Experimental

Industrial plant PCDD/F-data are obtained with a separate preparation and analysis of filter and cartridge PCDD/F. For a discussion of the possible artefacts of the method, such as volatilisation losses and adsorption gains, it is referred to<sup>2,3</sup>.

### Materials and Methods: Experimental

Industrial plant PCDD/F-concentration data were obtained for raw and clean gas, with a separate preparation and analysis of filter and cartridge PCDD/F. The possible artefacts of the method, such as volatilisation losses and adsorption gains, are discussed in the relevant literature<sup>2,3</sup>.

### Results

The gas to particle phase PCDD/F-partition was studied using  $\alpha$  and TSP.  $\alpha$  for a representative number of incineration and metallurgical plants (some examples of data shown in Table 1). Incineration samples show a much higher adsorption than those for dust from metallurgical units, the latter were studied with respect to the spread, to be expected for data obtained on consecutive days or during more distant campaigns. Spread between different data is much higher, than warranted by analytical error. A vast difference was found (Table 2) between the adsorption qualities of process particle (pp) proper, pp + hydrated lime (hl), pp + molecular sieves (ms), and of hl + lignite coke (hok) or activated carbon (ac). Note: sorbalit = hl + ac or hok.

Plant A is a metal casting plant treating virgin metal together with a limited amount of a relatively clean scrap. Nevertheless it generated fairly substantial emissions, of the order of 10 ng TE/Nm<sup>3</sup>. After the problem was identified a series of measures were taken, and the emission levels decreased by almost 3 orders of magnitude. Quenching the off-gas reduces residence time in the de novo formation temperature range. Moreover carbon and later sorbalit adsorbent were injected. The raw gas has a moderate and fairly constant dust load. By far the largest part of the PCDD/F load is in the gas phase, with  $\alpha$ -values ranging from 11 to 240 in the raw gas, in the clean gas reduced to between 0.23 and 1.6, due to the effect of adsorption onto the (sorbalit) carbon injected.

### ORGANOHALOGEN COMPOUNDS

## FORMATION AND SOURCES II - POSTER

The  $K_p$ -values rise from 0.1 to 0.8 to 240 – 720  $m^3/g$ . The PCDD/F-load of the dust is well defined, with values between 1 and 7.2 ng TE/g in the raw gas, 3.2 to 6.7 ng TE/g in the clean gas, and filter dust values of 1.45 and 1.65 ng TE/g. The clean gas is lean in dust although there is some increase with filter sleeve age. In 7 out of 9 cases the particle PCDD/F-load, computed from dust PCDD/F and dust load, is higher in the clean gas after the filter, which may be linked to various factors: (a) the particles permeating through the filter sleeves are smaller and therefore higher in load than those retained, due to a larger external surface, (b) these particles have had a longer dwelling time, and thus became more loaded (in another plant 8.6 ng TE/g was found on the dirty side and 102 ng TE/g on the clean side of the filter, reflecting the effect of a very long dwelling time), or (c) the escaping particles are more enriched in carbon adsorbent (the particle size distribution is not supporting this assumption since process dust and lime are even finer).

Plant B is fairly similar to the first, a major difference being that there is a heat exchanger and hence a slower cooling of the gas, leaving more room for de novo formation. The raw gas is also more heavily particle laden, and in one campaign the particle load (for reasons unknown) was a factor of 10 to 20 higher than usual. This high dust load prompted a deep redistribution of PCDD/F towards the solids phase and the extra particles even exhibited stronger adsorption than average, the  $\alpha$ -value dropping from 850 to 4 (at the high particle load). Later data were taken with sorbalit in the raw gas, leading to  $\alpha$ -values of 0.004 to 0.045, after all memory effects had vanished. The clean gas has a dust loading of 2.1 to 8.9  $mg/Nm^3$ , with  $\alpha$ -values related to the type of adsorbent used: zeolites only achieved an  $\alpha$  of 180 to 1000, whereas sorbalit reduced these to 0.9 – 5 upon the change in adsorbent and eventually to 0.14 – 0.8. Table 2 shows the PCDD/F-load of dust samples from plant A and B. The dust phase PCDD/F-load, even on consecutive days, varies over a factor of 5 to 20 under comparable operating conditions, including similar dust load. Sometimes outliers occur, however, without affecting the reproducibility of the other data. Table 1 shows that the particles seeping through a filter sleeve have a higher load than those in the raw gas, especially after application of sorbalit (7 % activated carbon), than with process dust, lime or zeolite.

**Gas/Solids partition for congeners and homologs.** Figure 1 exemplifies data for the relationship of  $\alpha$  vs. vapour pressure. The following data were considered: OCDD, OCDF, TCDD, TCDF, as well as some of the 2,3,7,8-substituted congeners. In most cases studied quite 'sensible' relationships were found. The selectivity of adsorption on the dust increased with decreasing volatility. The linear relationships [A] or [B], within experimental error, were hardly ever observed. There is both a great variability in the adsorptivity and selectivity of dust samples, even in samples obtained on the same day (see the vastly different two samples in Figure 1).

### Conclusions

The partition was studied of PCDD/F between gas and particle phase, both in actual raw and clean gases, and in a de novo laboratory test (part I). A parameter  $\alpha$ , the ratio between the respective gas and dust PCDD/F-concentrations, is useful as a quick guide to a particular system or situation.  $K$  adds the dust concentration to this ratio, since more PCDD/F are expected to report to particles with a rising concentration of the latter, a fact supported by numerous plant data. Applying the Langmuir adsorption equilibrium, as in [B], generally fails to provide a linear relationship for the numerous sets of available data and also shows a lack of internal coherence between data. These findings are in line with those obtained by de novo tests (part I). The PCDD/F load of clean gas dust was slightly (plant A) or markedly higher (plant B) than that in the raw gas. The particulate seeping through the sleeves is much more PCDD/F-laden after carbon injection.

# FORMATION AND SOURCES II -POSTER

## Acknowledgements

We would like to thank the European Union Programme 'Environment & Climate' for financial support of the project "Minimization of Dioxins in Thermal Industrial Processes: Mechanisms, Monitoring and Abatement (MINIDIP). The various participants to the Karasek meeting in Belgium (April 2001) are thanked for the numerous stimulating discussions.

## References

1. R. Lohmann, K.C. Jones, The Science of the Total Environment 219(1998) 53-81.
2. Pankow JF, Atmos Environ 28(1994) 185-188.
3. Smolka A., Schmidt KG, Chemosphere Vol. 34, Nos 5-7, pp. 1075-1082, 1997.

Plant	Raw Gas Data		Clean Gas Data	
	Values	Max/Min	Values	Max/Min
<i>Plant A</i>				
Dust concentration, mg/Nm <sup>3</sup>	27 - 48*	1.8	< 1 - 6.9**	< 6.9
Particle Load, ng TE/g dust	1.0 - 7.2	7.2	3.2 - 6.7	2.1
PCDD/F in both phases, ng TE/Nm <sup>3</sup>	2.0 - 33	10.4	0.019 - 0.047	2.4
Gas/solids partition parameter $\alpha$ , -	11 - 240	22	0.23 - 1.6*	7
Solids/gas parameter K, m <sup>3</sup> /g	0.1 - 0.8	8	240 - 720	3
<i>Plant B</i>				
Dust concentration, mg/Nm <sup>3</sup>	71 - 2000	28	2.1 - 8.9**	4.2
Particle Load, ng TE/g dust				
- process dust	0.016 - 0.93*	60	1.43 - 3	2
- sorbalit in the crude gas	1.9 - 46.1	24	25 - 91	3
PCDD/F in both phases, ng TE/Nm <sup>3</sup>	2.4 - 43	18	0.14 - 980	7000
Gas/solids partition parameter $\alpha$ , -	4 - 850	200	180 - 1000	6
- sorbalit in the crude gas	0.004 - 0.05*	12	0.14 - 5	40
Solids/gas parameter K, m <sup>3</sup> /g	0.016 - 0.3		0.2 - 1.7	8
- sorbalit in the crude gas, m <sup>3</sup> /g	6.6 - 120		75 - 3000	40
<i>Plant D</i> (mechanical grate incinerator)				
Dust concentration, mg/Nm <sup>3</sup>			2 - 4	2***
Particle Load, ng TE/g dust			30 - 50	3
PCDD/F in both phases, ng TE/Nm <sup>3</sup>			0.25 - 0.35	1.4
Gas/solids partition parameter $\alpha$ , -			1 - 3.1	3.1
Solids/gas parameter K, m <sup>3</sup> /g			ca. 250 - 750	3

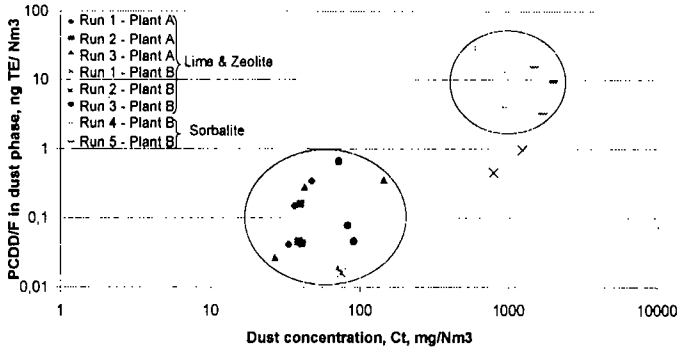
\* disregarding one or two outlier(s), \*\* rising trend with time, \*\*\* dust mainly occurs as a base load, assorted with brief pulses

**Table 1: Dust/gas partitioning data in two metallurgical plants and one incinerator plant.**

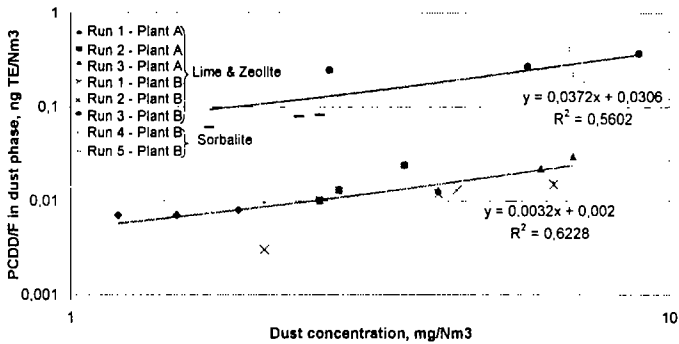
Plant & Operating Conditions	Raw Gas	Average <sup>*</sup>	Clean Gas	Average <sup>*</sup>	Ratio <sup>**</sup>
Plant A, all conditions confounded	1 - 7.2	3.2 +/- 2.4 (2.43)	3.2 - 6.7	4.6 +/- 1.1 (4.45)	1.4 (1.83)
Plant B:					
Very high dust load, raw gas	0.58 - 0.78	0.68 +/- 0.1 (0.67)	1.4 - 3	2.2 +/- 0.8 (2.05)	3.2 (3.06)
Standard dust load	0.21 - 0.27	0.48 +/- 0.24 (0.4)	2.3 - 2.9	2.6 +/- 0.3 (2.6)	5.4 (6.5)
With sorbalit	1.9 - 46	13.5 +/- 11 (7.95)	42 - 91	44.7 +/- 15 (41.3)	3.3 (5.2)

# FORMATION AND SOURCES II -POSTER

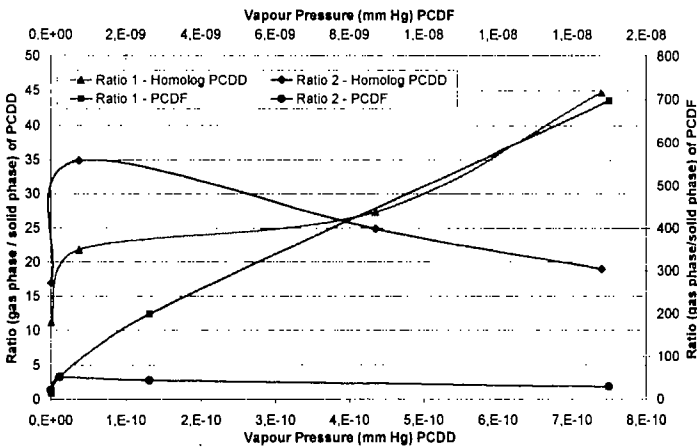
**Table 2: Particle Load, ng TE/g. \* Arithmetic Average (Geometric), \*\* Ratio Clean/Raw Gas**



**Figure 1: Raw Gas**



**Figure 2: Clean Gas**



**Figure 3:  $\alpha$  as a function of vapour pressure**