# OCCUPATIONAL CONTAMINATION WITH PCDD/F's DURING RECYCLING OF NON-GAMMA HCH IN A CHINESE CHEMICAL FACTORY. PART IV COMPARISON OF SAMPLES IN AND OUTSIDE THE FACTORY WITH ISOMER AND CONGENER PATTERNS

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## Introduction

Several years ago we reported on the occurrence of chloracne in workers in a Chinese factory (1,2). The reason for the contamination was discussed during the dioxin2000 meeting in Monterey (3). Contamination by the factory was also found outside the factory (4,5,6). It was not known whether the recycling of the non-gamma isomers of HCH is the only source. In this paper the results of the comparison of samples from outside the factory and inside the factory are given. Samples are taken outside the factory at places where the effluents from the factory flow through. Inside the factory samples are taken from the outside of the reactor that converts HCH to trichlorobenzene. The isomer patterns and the congener patterns of the PCDD/F's found in the samples from the factory and outside the factory are compared.

## Sampling Locations And Sample Description

The pesticide plant is located on an industrial/residential area of Dagu outside the city of Tianjin. The wastewater from smaller ditches flows through a large canal that empties into the Pacific Ocean at the Bohai Bay, approximately 10 kilometers from the plant. Just before entering the bay, the canal flows through the evaporation ponds of a salt production facility. The samples inside the factory are taken from the outside of the metal reactor.

## Analytical Method

Standard analytical procedures are used and after the cleanup HRGLC/HRMS or HRGLC/LRMS are used. The high resolution GLC is performed with a 50m Supelco 2331 column. The isomeric distribution is determined as good as possible. A list of the isomers together with the numbering as used in this paper is available on request from the first author.

## Results

In figure 1 the relative amounts of the Pentachlorodibenzofurans are given. The correlation with the scrap samples from the reactor is rather good considering the fact that the scrap samples are taken from the outside from the reactor and are influenced by several potential catalysts when the hot HCH reacts with the air and the hot surface of the reactor.

Peak nr 64 is the 1,2,3,7,8 $P_5$CDF and peak nr 74 is the 2,3,4,7,8 P5CDF.

The relatively high amount of the latter compound in blood reflects the longer half-life of this compound compared to the other isomers.

From figure 2 it is obvious that the relative amount of the lower chlorinated PCDD/F's is lower for the samples outside the factory.

The samples from the outside of the reactor do contain large amounts of unreacted HCH. (Unpublished results).

The blood samples of the workers who work with the reactor show relatively large amounts of higher chlorinated compounds. These workers not only inhale the fumes of the evaporating compounds from the reactor but also when they open the reactor to fill it with HCH they inhale the hot HCH fumes which escape from the reactor. With this they also inhale the PCDD/F's from the original HCH.

From fig 3 that shows ratios of the hepta and hexa isomers it is clear that the first eluting heptachlorinated dioxin (nr 97: 1,2,3,4,6,7,9) is considerable less abundant than the second one (nr 98: 1,2,3,4,6,7,8) this reflects the HCH pattern.

In incineration samples these two compounds are always found in nearly equal amounts.

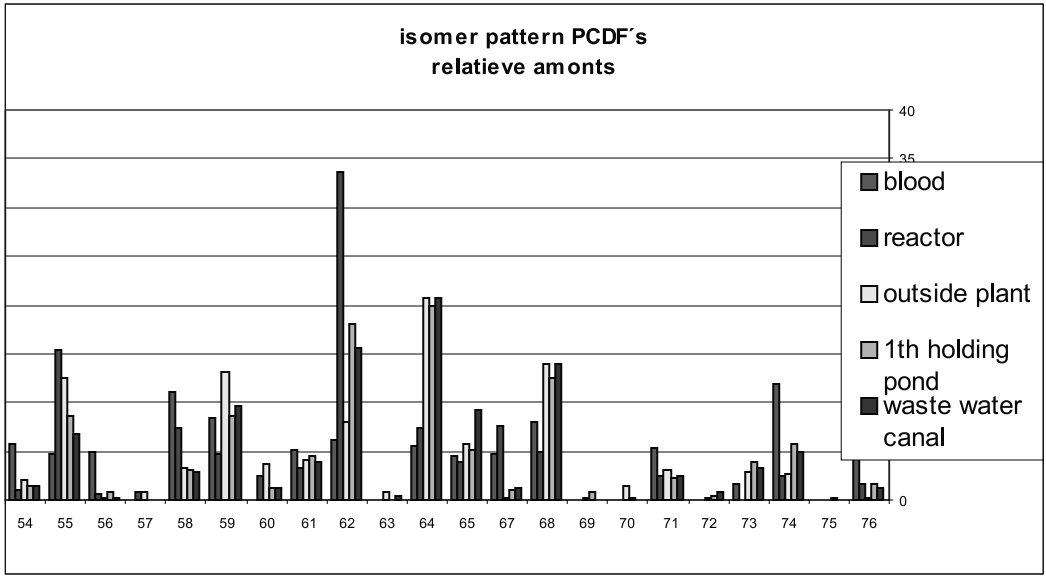


**Figure 1.**

**Discussion**

From figure 1 it is clear that the ratios of the isomers found in and outside the factory are not identical although the differences are not dramatically. The results from this figure indicate that the reactor is not the only source for the contamination. When we consider the process that takes place close to the reactor. It is found that relative high amounts of the lower chlorinated compounds are formed. This can be seen from figure2. The HCH, which is used in the reactor, does mainly contain higher chlorinated compounds. And also the PCP, which is produced, is relatively clean in lower chlorinated compounds as expected.

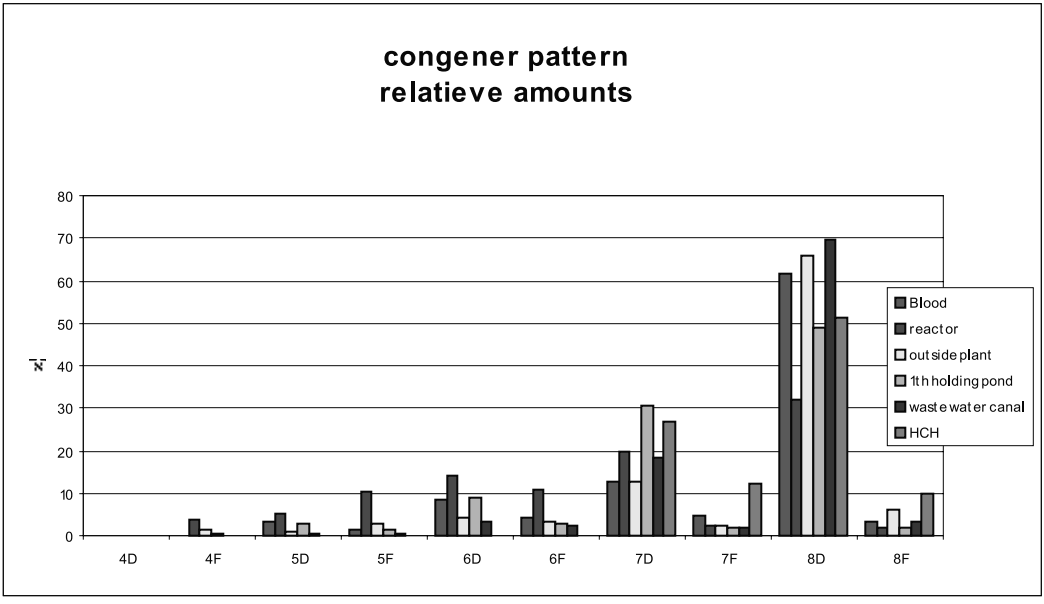


**Figure 2.**

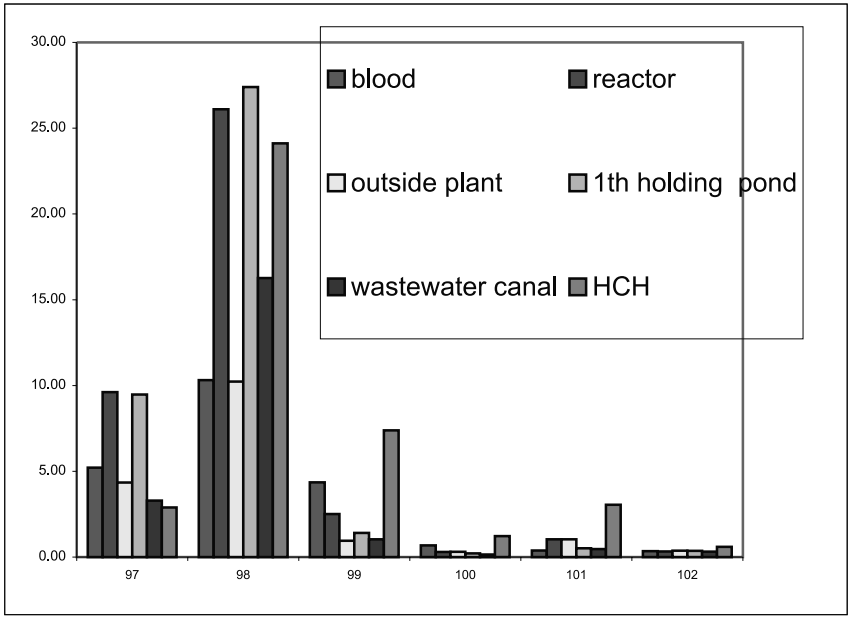


**Figure 3.**

There seems to be productions in the plant, which are not correlated with the HCH transformation to PCP.

The higher chlorinated PCDD/F's are partly due to the original HCH and partly due to the transformations that take place in the reactor. It is not possible to separate on a quantitative basis these two waste streams.

The fact that the Octa and Hepta PCDD/F's are relatively higher outside the factory than at the reactor gives support to the hypothesis that HCH Is produced also at that plant

Finally it can be concluded that information from the non-2378substituted PCDD/F's gives valuable information about sources.

So determination of the non-2378 substituter PCDD/F's together with the 2378 substituted PCDD/F's is improving the possibilities of the analitical results.

**References**

1. Coenraads,P.J.; Brouwer, A.; Olie,K.; Tang,N. *Dermatologic Clinics* 1994 12,3 569-576.
2. Olie, K.; Coenraads, P.J.; Slot, P.; Wever,H. and Tang,N. *Organohalogen Compounds* 1997 33, 386-389.
3. Olie,K.; Coenraads,P.J.; Scholten, O.; Wever,H. and Tang,N. *Organohalogen Compounds* 2000 46, 55-57.
4. Luksemburg,W.J.; Mitzel,R.S.; Zhou, H.; Hedin,J.M.; Silverbush,B.B. and Wong,A.S. *Organohalogen Compounds* 1996 28, 262-266.
5. Luksemburg,W.J.; Mitzel,R.S.; Hedin,J.M.; Silverbush,B.B. and Wong,A.S. *Organohalogen Compounds* 1997 32, 38-40.
6. Luksemburg,W.J.; Wong, A.S.; Maier, M.M., and Spas, R.A.Alta and Zhou, H, . *Organohalogen Compounds* 2001 51, 223-225.