

## ANNEX 7: CONCENTRATIONS OF *TRIS* (4-CHLOROPHENYL) METHANOL AND *TRIS* (4-CHLOROPHENYL) METHANE IN FISH

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### Abstract

*Tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) were determined in fish samples from Europe and Eastern Canada. TCPM and TCPMe were found in most of the samples analysed. Levels of TCPM were generally higher than those of TCPMe, resulting in average TCPM/Me ratios > 1. Differences in TCPM/Me ratios could be due to differences in the proximity of the various sources, in the trophic levels of the fish and to the presence of interferences in analytical methods. We suggest that an interlaboratory validation study be conducted to improve our ability to compare results from different laboratories and geographic regions.

### Introduction

*Tris*(4-chlorophenyl)methanol(TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) are among the newest persistent organic pollutants (POPs) reported in environmental samples. TCPM was first found in marine mammals in the late 1980s (Walker *et al.*, 1989). Soon after, the presence of TCPM was reported, along with the qualitative presence of its presumed precursor, TCPMe, in both marine mammals and birds (Zook *et al.*, 1992; Jarman *et al.*, 1992). These two compounds were then quantified in sediments, fish, marine mammals and human milk (Rahman *et al.*, 1993, de Boer *et al.*, 1996; de Boer, 1997). Recent studies have confirmed that these compounds are ubiquitous in the marine environment and that they are bioaccumulated, since organisms at the top of the aquatic food chain, such as birds and mammals, have the highest reported levels (de Boer *et al.*, 1996; Muir *et al.*, 1996a, 1996b; Lebeuf *et al.*, 1998; Falandysz *et al.*, 1999; Minh *et al.*, 1999; Watanabe *et al.*, 1999; Lebeuf *et al.*, 2000).

Few data are available on the toxicity of these compounds. In rats, Poon *et al.* (1997) reported that short-term exposure to TCPM led to the induction of liver enzymes and resulted in higher spleen weights and elevated white blood cell and lymphocyte counts. Recently, Foster *et al.* (1999) demonstrated that TCPM modifies reproductive physiology in the male rat. There is clearly a need for more information on the toxicity of these compounds.

The principal source of TCPM and TCPMe to the marine environment is unknown. These compounds may originate from a variety of sources including the production of synthetic high polymers and of light-fast dyes for acrylic fibres, and the manufacture of anthelmintic drugs (Jarman *et al.* 1992). Other potential sources include agrochemicals such as formulations of Dicofol and technical DDT, both of which contain structurally related compounds (Jarman *et al.*, 1992). Walker *et al.* (1989) did not detect TCPM in technical formulations of DDT at a level above 0.1 %. More recently, Buser (1995) showed that, under conditions used in the synthesis of technical DDT, 10 TCPMe isomers were formed in small amounts. However, the link between  $\Sigma$ -TCP (TCPM and TCPMe) and technical DDT in environmental samples has not been clearly established.

During the last few years, several members of the MCWG expressed an interest in studying these compounds. Following the initiative of the DLO-Netherlands Institute for Fisheries to distribute TCPM and TCPMe standards, several laboratories volunteered to set up an analytical method for these compounds and to collect data in various environmental samples. The present paper summarises the results obtained in fish samples specifically, and provides an overview of data reported in the scientific literature. The main objective of this paper is to compare the levels and ratios of TCPM/Me in various fish species from different areas in Europe and Canada. In addition, the relationship between  $\Sigma$ -TCP and  $\Sigma$ -DDT levels is assessed to verify the hypothesis that technical DDT is the main source of TCPMe in the marine environment.

### Methods

Most laboratories applied very similar methods of extraction, clean-up and fractionation, yet different techniques were used to quantify the compounds. Although all laboratories used capillary columns (HRGC) to isolate the compounds of interest, the selectivity of the different detection methods varied. For instance, the Canadian laboratory used LRMS/MS;

the studies conducted by Rahman *et al.* (1993), Falandysz *et al.* (1999), and by the Netherlands laboratory were done with LRMS, while the German and Belgian laboratories used ECD.

## Results

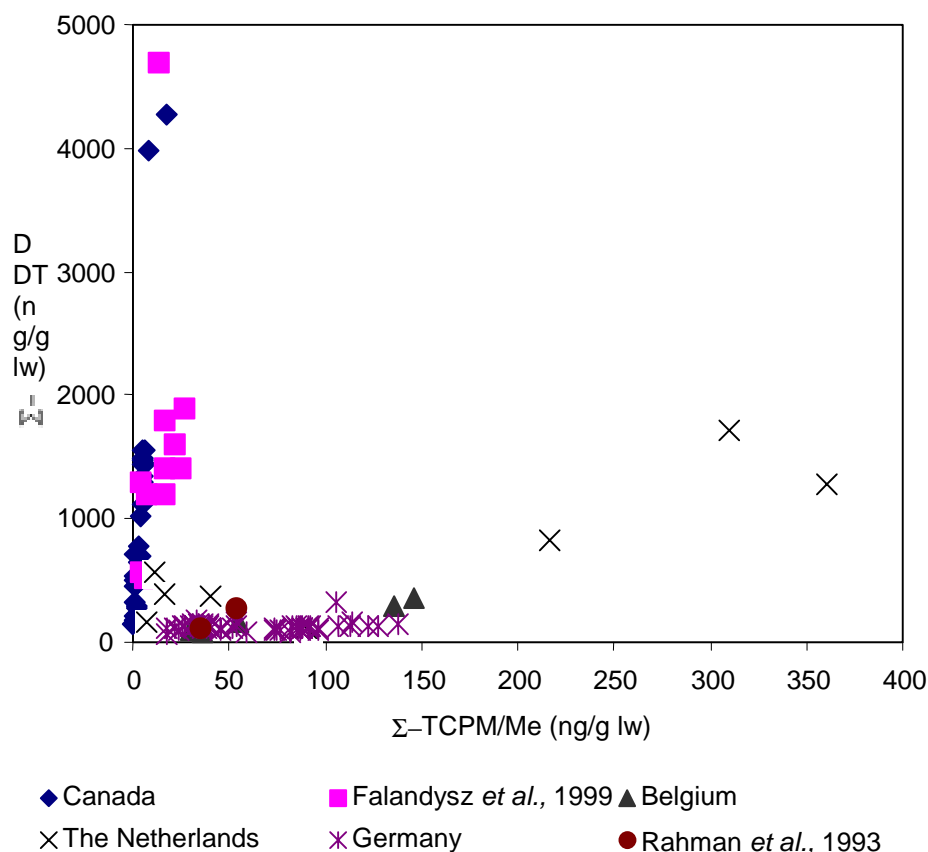
TCPM and TCPMe were detected in most of the fish samples (Table A7.1). Samples of yellow eel from the Netherlands, and of dab from the Belgium coast, contained the highest concentrations of TCPM and of TCPMe, respectively. In comparison to samples from Europe, levels of both TCPM and TCPMe in Canadian fish samples were relatively low. In particular, concentrations of these compounds in lake trout from Lake Ontario were also low. In general, TCPM levels in most of the fish species examined were higher than those of TCPMe. However, this is not the case for some fish samples from the Belgian coast and the Baltic south coast. These samples show an opposite tendency, with higher concentrations of TCPMe compared to TCPM.

## Discussion

The data on TCPM and TCPMe in fish samples do not allow us to draw a clear conclusion regarding the relative degree of contamination of the examined areas. There are too many variables involved, which complicate the comparison of TCPM and TCPMe levels between these areas. In addition to the different analytical methods used by the laboratories involved, the analyses were conducted on several different tissues, from several different species of fish. The dissimilar TCPM/Me ratios could also be related to differences in the proximity of sources and to differences in the trophic levels and habitats of the fish species sampled. Nevertheless, one can appreciate that these compounds are universally distributed in the marine environment.

To determine if technical DDT is the main source of TCPMe in the marine environment, the levels of  $\Sigma$ -DDT (DDT and its metabolites) are plotted against the tissue concentrations of  $\Sigma$ -TCPM/Me (Figure A7.1). There is clearly no significant correlation between  $\Sigma$ -DDT and  $\Sigma$ -TCPM/Me in fish tissues, which does not support the hypothesis that technical DDT is the main source of environmental TCPM and TCPMe. It is noteworthy that, in Canadian fish samples, the  $\Sigma$ -DDT:  $\Sigma$ -TCPM/Me ratio is approximately 10 times higher than that in most of the European fish samples. In contrast, the levels of TCPM and TCPMe in some European fish, as reported by Falandysz *et al.* (1999), are more similar to those in Canadian fish samples and the  $\Sigma$ -DDT:  $\Sigma$ -TCPM/Me ratios in these samples also resemble Canadian values.

**Figure A7.1.** The relationship between  $\Sigma$ -DDT and  $\Sigma$ -TCPM/TCPMe in fish.



## Conclusion

There is a need for additional studies to assess the levels of TCPM and TCPMe in fish samples. However, the fish species selected must be comparable in terms of their trophic level and habitat and the analyses should be conducted on a standard tissue or tissues. An interlaboratory calibration study is needed if we are to improve our ability to compare analytical results from different geographic areas. There is also a need for more information on the toxicity of TCPM and TCPMe.

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