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Tetrachlorobenzyltoluenes in Eel from the Netherlands

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For a few years tetrachlorobenzyltoluenes (TCBTs) have now been used as hydraulic fluids to replace polychlorobiphenyls (PCBs) in underground mining in the Federal Republic of Germany. This substitution has been carried out because of the supposed superior environmental properties of the TCBTs. The use of PCBs as hydraulic fluids leads to extensive environmental contamination, due to their small degradability and high bioaccumulation factors.

TCBTs are commercially available under the trade names Ugilec, BP-Olex and others. Like the PCBs, TCBTs consist of a complex mixture of isomers. Due to the production process used (figure 1), isomers are formed in which both rings carry two chlorine atoms (Mathais et al. 1980; Pontoglio 1984). Theoretically 96 isomers of this type are possible.

The estimated quantity of Ugilec used in Western Germany is about 700,000 kg/year (Klingenberg 1988). Areas with extensive underground mining are situated around the rivers Lippe and Rur. TCBTs were reported before in fish from these rivers (Fürst et al. 1987; Rönnefahrt 1987). The river Lippe flows into the river Rhine, which enters the Netherlands at Lobith. Likewise, the Rur enters the Netherlands at Vlodrop (and its name changes in Roer) and flows into the river Meuse. In this way TCBTs can be transported into the Netherlands.

MATERIALS AND METHODS

In May 1987 and 1988 yellow eel (Anguilla anguilla) samples were caught in several rivers in the Netherlands. Samples sites are indicated in figure 2. Each sample consists of a number of eels ($10<n<25$) and equal quantities of the single fillets were pooled and homogenized with a Waring Blendor. After grinding with Na_2SO_4, the samples were soxhlet extracted for six hours with n-pentane/dichloromethane (1/1 v/v). Fat was removed by a 15 g Al_2O_3.6%H_2O column and the concentrated samples were further cleaned up by means of a 1.8 g SiO_2. $1\frac{1}{2}$% H_2O column.

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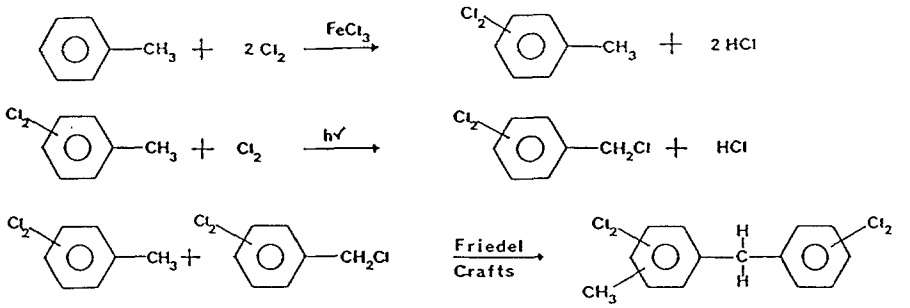

Figure 1. Production process for TCBTs.

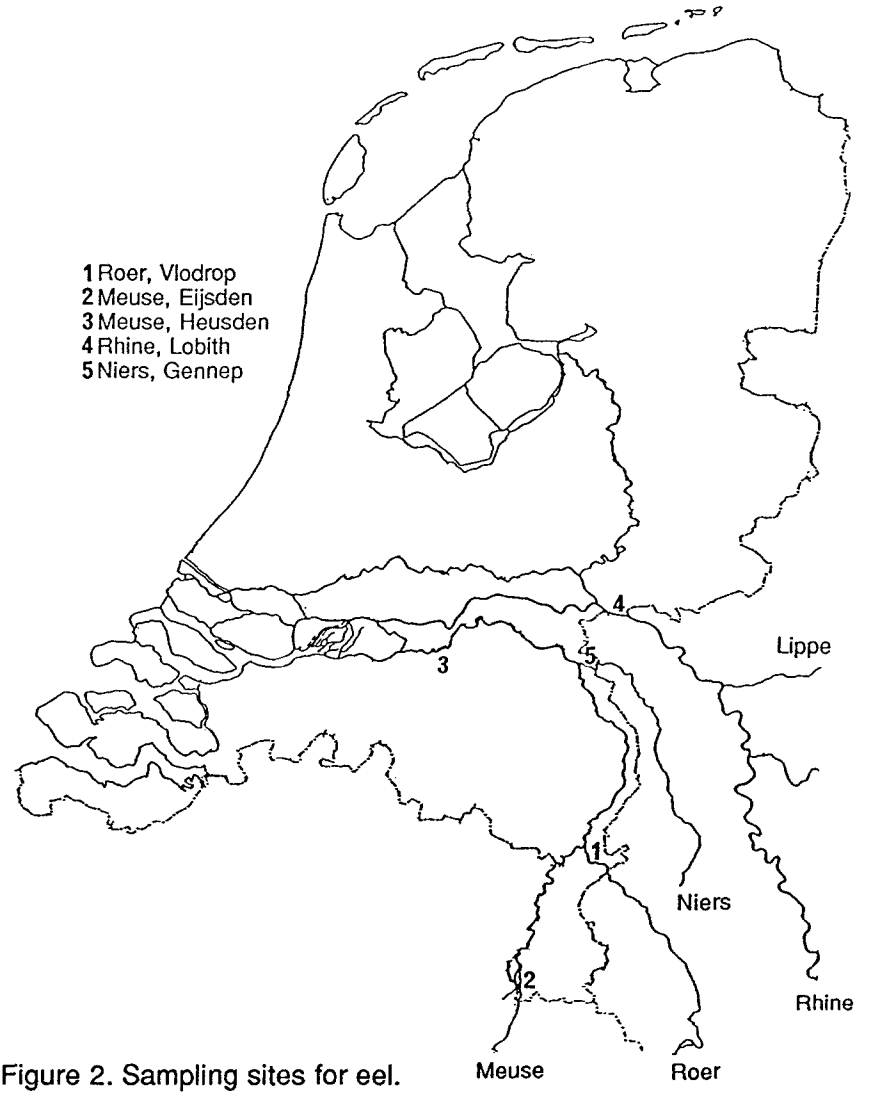

Figure 2. Sampling sites for eel.

Blanks and standards were included in the series. Tetrachloronaphtalene (0.1 µg/mL) was used as internal standard. Details of the clean-up procedure are given elsewhere (de Boer 1988).

TCBTs were determined with a Hewlett-Packard 5993C GC/MS apparatus, using electron impact ionization and selected ion monitoring. A 23 m x 0.24 mm i.d. CP Sil 8CB column (film thickness 0.44 µm; Chrompack) was used with helium as carrier gas. Samples (2 µL) were injected in the split/splitless mode at 260°C. For the GC oven the following temperature program was used: an initial temperature of 90°C, held for three minutes; subsequently heated to 200°C at a rate of 20°C/min and held for 1 minute; finally heated to 250°C at a rate of 5°C/min and held for 25 minutes.

The ions monitored for TCN were m/z = 193.9, 263.9, 265.9 and 267.9 and for TCBT m/z = 213.0, 283.0, 285.0 and 320.0. For the TCBTs, the sum of the intensities of the four ions was used, so that a better signal to noise ratio was obtained than in the case of one single ion. Concentrations were calculated by comparing the total area under all peaks within the TCBT retention time window to that of an Ugilec 141 standard (Promochem). Care was taken not to include p,p'-DDE, which exhibits signals at the same ions. In this way a detection limit of *circa* 15 µg/kg was found. Results were corrected for recovery, which was around 95%. Since the isomer patterns of the TCBTs in the technical mixture and in eel differ somewhat (figure 3), the obtained concentrations are approximate. The method of calculations implies that the response factors for all isomers are assumed to be equal. The use of individual isomers as standards would make a more accurate quantification possible.

RESULTS AND DISCUSSION

Table 1 shows the TCBT levels found in eel samples. The blanks showed no detectable TCBT levels. Clearly, the contamination in the Roer has already mounted to a disquieting level, comparable to that of PCBs. The established rapid increase is particularly alarming. In the same time, we have observed a corresponding decrease in PCB levels in eel from the Roer (table 2).

Table 1. TCBT levels in yellow eel (mg/kg fillet).

Location	1987	1988
Roer, Vlodrop	1.1	4.8
Meuse, Eijsden	not measured	<0.015
Meuse, Heusden	0.2	0.1
Rhine, Lobith	0.1	0.1
Niers, Gennep	not measured	0.07

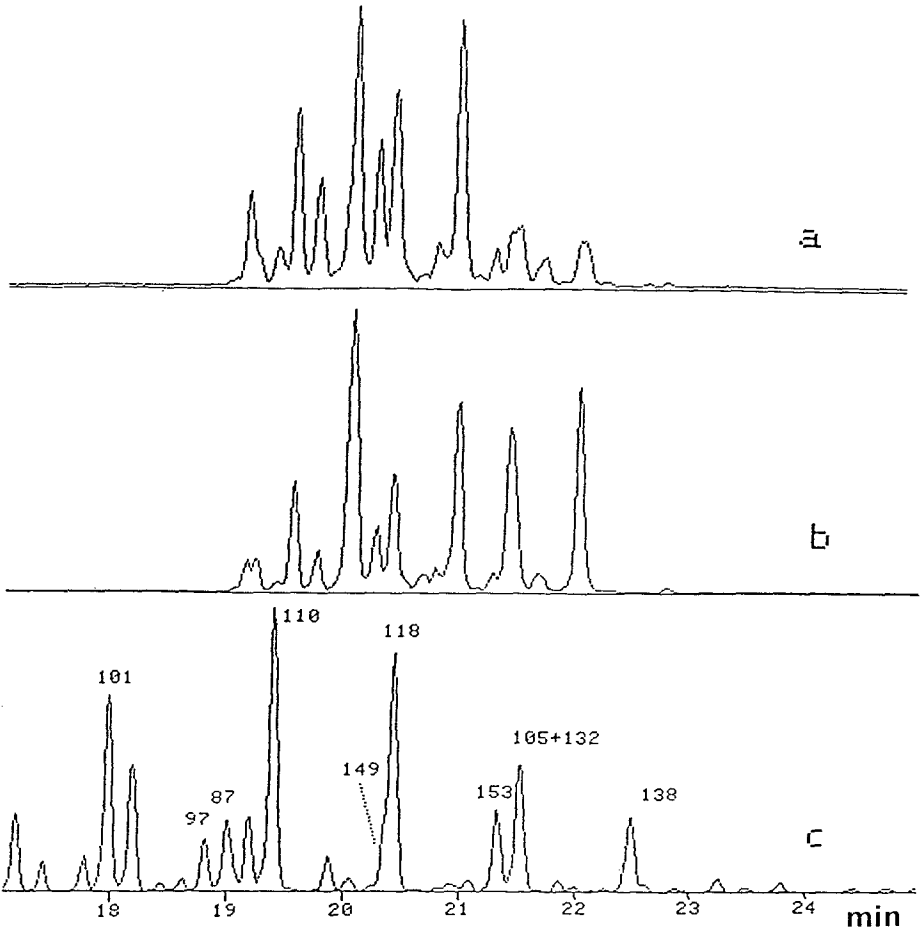

Figure 3. Selected ion chromatograms of a. Ugilec 141 (2 µg/mL) (ions 213.0+283.0+285.0); b. eel from the Roer (same ions); c. eel from the Roer (ions 324.0+326.0+358.0+360.0; $[M]^+$ and $[M+2]^+$ of penta- and hexachlorobiphenyl).

Since TCBTs and PCBs behave similarly in common clean-up procedures and because their gas chromatographic patterns overlap (figure 3), the co-occurrence of these compounds poses a serious problem to an accurate determination of either class, particularly if ECD detection would be used.

Close to the mining areas Fürst et al. (1987) determined TCBT levels in fish up to 25 mg/kg in the German part of the Roer. They did not yet find these compounds in larger rivers like the Rhine. However, considerable levels were found in fish from the Rhine's tributary, the Lippe (Fürst et al. 1987; Rönnefahrt 1987). Apparently, the dispersion of these compounds in the environment proceeds rapidly, so that eel from large rivers like the Rhine and the Meuse already exhibit measurable levels. In the Meuse

Table 2. PCB levels in yellow eel from the Roer (mg/kg fillet).

year	CB-28	CB-52	CB-101	CB-118	CB-153	CB-138	CB-180
1986	0.12	3.0	1.3	0.98	0.44	0.58	0.14
1987	0.11	3.1	1.3	1.2	0.59	0.60	0.15
1988	0.046	1.1	0.62	0.59	0.39	0.46	0.10

the difference between the locations upstream and downstream of the outlet of the Roer is striking. The thus far observed environmental behaviour of these compounds poses a serious challenge to the suggestion of environmental safety, which was made in several patents (Casale et al. 1982; Dobratz and Flucke 1985; Mathais et al. 1980).

In this context it is understandable that the Dutch government has banned TCBTs under the Act on Substances Hazardous to the Environment (Staatscourant 1988). International adoption of this ban would be highly recommendable.

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