Spatial and temporal trends of toxaphenes in eggs of common terns *(Sterna hirundo)* breeding at the North Sea coast of Germany

Jürgen Witte, A. Büthe and W. Ternes

ZA für Chemische Analytik und Endokrinologie, Tierärztliche Hochschule Hannover,
Bischofsholer Damm 15, 30173 Hannover, Germany; E-mail: jwitte@chemie.tiho-hannover.de

Introduction

Toxaphenes are complex mixtures of polychlorinated bornanes, bornenes, bornadienes and camphenes (1) and still in use as an insecticide. Until 1993 the estimated output of toxaphenes in the world was 1.3 million tons, 46.000 tons were produced in the former GDR from 1955 - 1991. Besides the exportation the GDR used toxaphenes for e.g. rape cultivation under the trade name "Melipax" until 1991 (2, 3, 4). An investigation of its environmental relevance according to ecotoxicological criteria led to a first ban of toxaphene in the Federal Republic of Germany in 1980 (5) and residue limits (LMBG) were fixed by the official food control for fish and fish products in 1997.

Toxaphenes are atmospherically transported and they enter oceans, lakes and rivers by wet and dry deposition and gas exchange across water surfaces (6). The determination in fish and marine mammals from the North Eastern Atlantic and the North Sea showed an aerial transport of toxaphene from the American continent, resulting in higher concentrations at the west coast of Ireland and lower levels in the North Sea depending on the drift (7).

Materials and Methods

Table 1: Collected and analyzed eggs

species	*place*	*year*	*n.*	*remarks*
Common tern	Hullen, Elbe estuary	1989	10	
(Sterna hirundo)	Trischen	1989	10	Monitoring
	Norderoog	1989	10	program,
	Hullen, Elbe estuary	1997	10	Germany
	Trischen	1997	10	
	Norderoog	1997	10	

All samples were homogenized and stored at –21 °C.

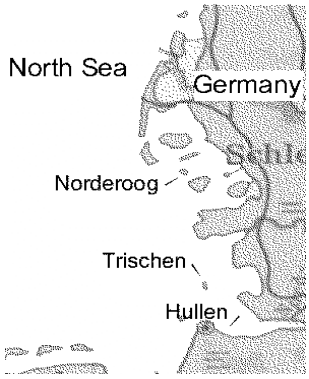

Figure 1: German Bight

About four [g] of each material was cleaned up nearly identically to the method described by Xu (8). Soxhlet extraction was followed by clean up with concentrated sulfuric acid and further separation with defined silica gel. 1,2,3,4-tetrabromobenzene (internal standard 1, IS 1) and 1,4-exo,7,8,9,10,10-heptachloro-5-methoxytricyclo[5,2,1,$0^{2,6}$]dec-3,8-diene (IS 2) were added at the beginning of the clean-up procedure. The resulting two fractions (I, II) were evaporated nearly to dryness and resolved with 50 □L toluene. The GC/MS conditions were described before (9). After GC-separation with a 50 m HT-8 column the MS-analysis was running in NCI-/ SIM-mode with

detection of the isotope cluster of $[M]^-$, $[M-Cl]^-$, $[M-HCl]^-$ and $[M-2Cl]^-$. This wide range of masses is essential for the determination of toxaphenes in unknown samples.

Results and Discussion

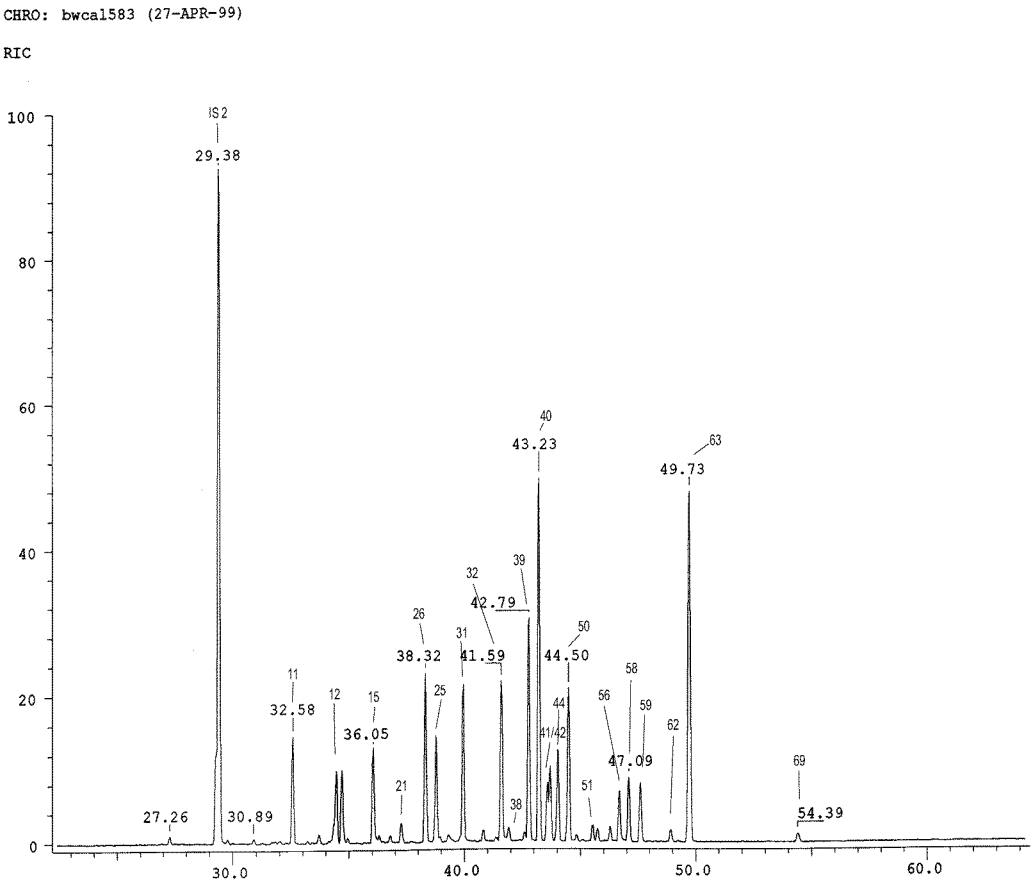

Figure 2: Chromatogram of the Parlar 22 standard and the IS 2 on the HT-8 column

In the second fraction we attached ten toxaphenes to their Parlar number. The toxaphenes with the Parlar No. 26, 32, 40, 41, 44, 50, 51, 58 and 63 were detected in all samples. Parlar 11 was found in two samples of the year 1989. TOX 7 (10) is probably fixed by its relative retention time in all samples. Alltogether we assigned 62 peaks to well-known and unknown chlorobornanes and -bornenes with a degree of chlorination from six to nine in the second fraction. In fraction I penta-hexachlorobornanes and -bornenes and two heptachlorobornenes were detected. Noteworthy heptachlorobornanes and -bornenes settle the main part in the second fraction of all samples followed by the octa- and nonachlorobornanes and -bornenes.

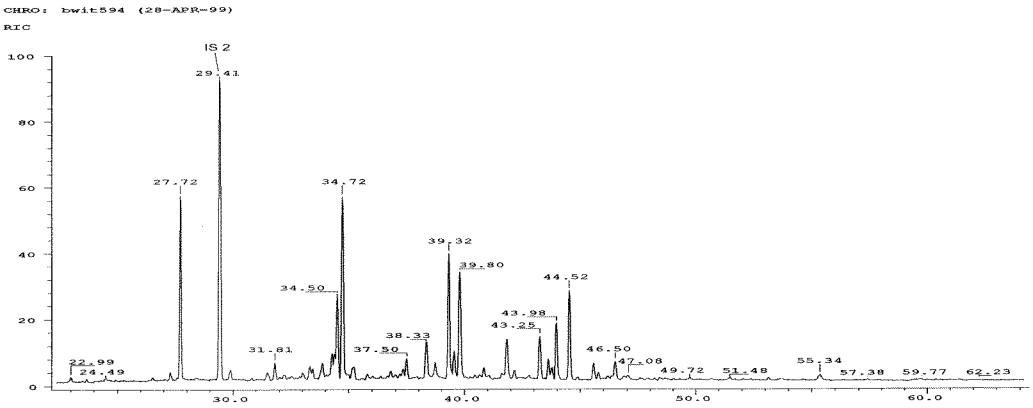

Figure 3: Chromatogram of a typical common tern (Norderoog 1997) [min]

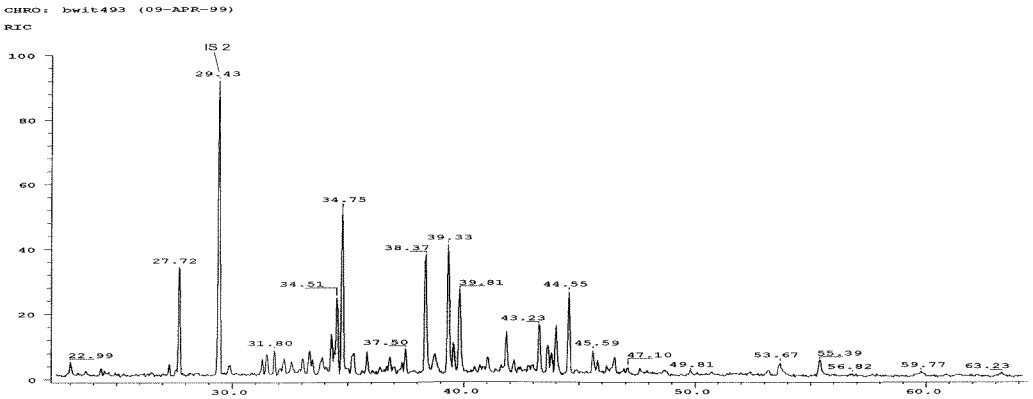

Figure 4: Chromatogram of a typical common tern (Trischen 1997) [min]

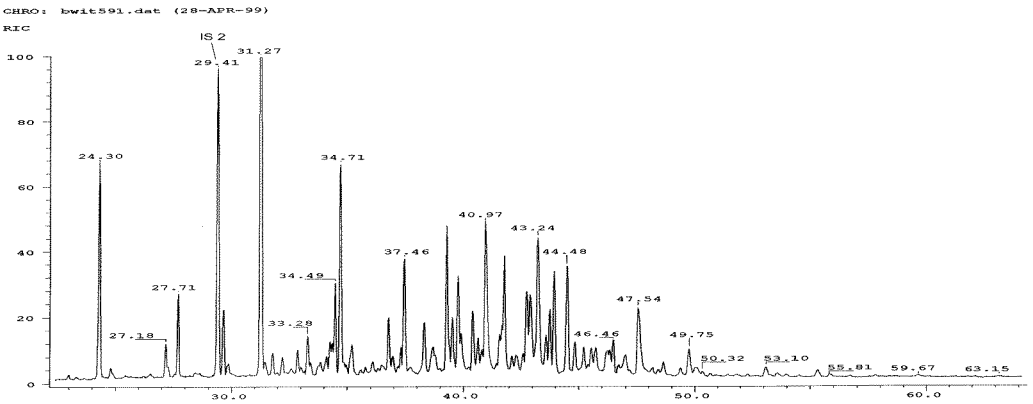

Figure 5: Chromatogram of a typical common tern (Hullen 1997) [min]

The intensities of all peaks in the chromatograms (fig. 2-6) are brought into relation with the IS 2 (29.41 min) to 95%.

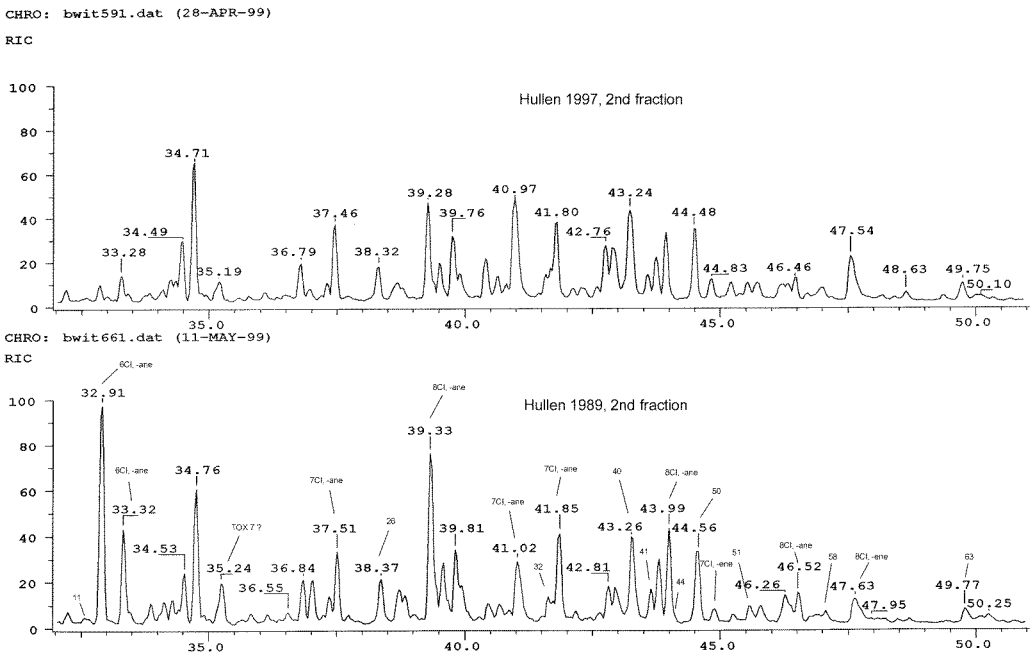

Figure 6: Essential parts of typical chromatograms of common terns (Hullen 1997 and 1989) min]

The toxaphene levels in the eggs of the common terns are increasing from the northern breeding places Norderoog (fig. 3) and Trischen (fig. 4) to the southern places at the Elbe estuary (Hullen, fig. 5). There might be still an input by the river Elbe depending on the prior use and production in the former GDR. The comparison of the chromatogram of the same breeding places (fig. 6) is showing a decrease of some toxaphenes in 1997 with no change in the total pattern and no remarkable variations of well-known toxaphenes in their relative amounts. But in 1997, a few peaks of unknown toxaphenes with a higher degree of chlorine were significantly higher in their relative amounts than in 1989. The toxaphene contamination in eggs of seabirds in Germany is mainly influenced by the global use and production.

References

1. Saleh M A; *J.Agric.Food.Chem*. **1983**, p. 748-751.
2. Heinisch E, A. Kettrup, A. Jumar, S. Klein, J. Stechert, P. Hartmann and P. Schaffer; *Zu einigenFolgen der Anwendung von Toxaphen im chemischen Pflanzenschutz der ehemaligen DDR*, **1993**.
3. Beitz H and W. Hamann; *Nachrichten-Blatt Pflanzenschutz*, **1990**, 44, 242.
4. Hollstein A; *Die Nahrung*, **1991**, 35 (10), p. 1029-1040.
5. Saleh M A; *Rev. Environ. Contam. Toxicol*., **1990**, 118, p. 1-85.
6. Cotham W E and T. F. Bidleman; *Chemosphere*, **1991**, 22, p. 165-188.
7. Boer J. de and P. Wester; *Chemosphere*, **1993**, 27, p. 1879-1890.
8. Xu L, *(Thesis)* Fachbereich Biologie/Chemie, Gesamthochschule Kassel, Germany, **1994**.
9. Witte J, A. Büthe and W. Ternes; *Organohalogen Compounds*, **1998**, Vol. 35, p. 251-254.
10. Vetter W, B. Krock, B. Luckas and G. Scherer; *Chemosphere*, **1996**, 33, p. 1005-1019.