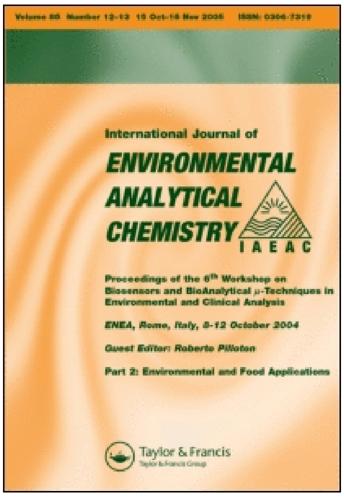


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of Toxaphene

Harun Parlar[a]
[a] Gesellschaft für Strahlen- und Umweltforschung mbH München, Institut für Ökologische Chemie, Freising, Attaching, F.R.G.

To cite this Article Parlar, Harun(1985) 'Analysis of Toxaphene', International Journal of Environmental Analytical Chemistry, 20: 1, 141 — 158

To link to this Article: DOI: 10.1080/03067318508077052

URL: http://dx.doi.org/10.1080/03067318508077052

Intern. J. Environ. Anal. Chem., 1985, Vol. 20, pp. 141–158
0306-7319/85/2002-0141 $18.50/0

Printed in Great Britain

Analysis of Toxaphene

HARUN PARLAR†

Gesellschaft für Strahlen- und Umweltforschung mbH München, Institut für Ökologische Chemie D-8050 Freising-Attaching, F.R.G.

(*Received November 25, 1984*)

Toxaphene, a widely and chlorinated hydrocarbon insecticide produced by chlorination of camphene, consists of a poorly defined mixture of at least 180–190 substances. Most of these conform the formulars $C_{10}H_{18-n}Cl_n$ and $C_{10}H_{16-n}Cl_n$, where n is 6–10. Although the chromatographic behaviour of the toxaphene components is extremely similar, seven components have been isolated up to now, six of which are hepta- to decachlor derivatives of bornane. In the following work, isolation and identification of these compounds with the help of spectroscopical methods are described and their behaviour under biotic and abiotic conditions are studied. The experiments shown, that toxaphene is slowly to rapidly degraded in various environmental systems.

KEY WORDS: Toxaphene, spectroscopical characterization, residue analysis.

INTRODUCTION

The development of new plant protection agents during the past decade had among others the essential aim to produce new substances for the replacement of banned compounds or compounds suffering from severely curtailed manufacture. These include, e.g., DDT and cyclodiene insecticides. On the other hand, there are preparations which have been known as insecticides for a long time and whose fields of application, especially after the ban on DDT, were expanded strongly. One preparation in this group is toxaphene.

---

†Presented at the 14th Annual Symposium on the Analytical Chemistry of Pollutants, Barcelona. November 21–23, 1984.

Toxaphene was developed in 1945 by Hercules Inc., U.S.A., and has been one of the most widely used insecticides in the United States since that time. It has played an increasing role in pest control in agriculture and forestry during recent years because of the limitations put on other chlorinated hydrocarbons such as DDT, aldrin, chlordane, dieldrin, etc. Its economic importance can be appreciated by the fact that since its introduction in 1946 cumulative world use until 1974 has been 450000 tons. The range of applications of this pesticide covers practically all areas of agriculture. Concentrations ranging from 0.5 to 10 kg per ha are recommended and tolerated depending on the type of plant. It can be applied either upon seeding or repeatedly for specific intervals. Its effect is immediate and preventative against many types of pests. Toxaphene is, therefore, a broad spectrum insecticide with a wide application range and with a certain, although not a well defined effective life span.

Toxaphene appears to be widely disseminated in the environment. This paper presents after a description of its chemistry, use and toxicity a survey of its occurrence as well as conversion and degradation in the environment.

COMPOSITION OF TOXAPHENE

Toxaphene represents chlorinated camphenes in technical purity grades. It is produced by passing chlorine gas through a solution of camphene in carbon tetrachloride upon UV-irradiation. The product obtained is marketed without further purification. It contains 67–69% chlorine, corresponding the empirical formula $C_{10}H_{10}Cl_8$. The term for the purity grade "technical" refers to the quality of the final product, meaning that no attempt is made to fractionate or characterize the mixture with respect to a definite chemical composition after chlorination of camphene. Also an important point is that the camphene (1) used for the production is of technical quality only. Due to the lack of selectivity on chlorination, the number of isomers increases with a non-uniform degree of substitution. An example is the addition of chlorine to the double bond of camphene, which follows an unspecific pathway. This reaction was the topic of many investigations.[1–3] Despite contradictory evidence, it has long been

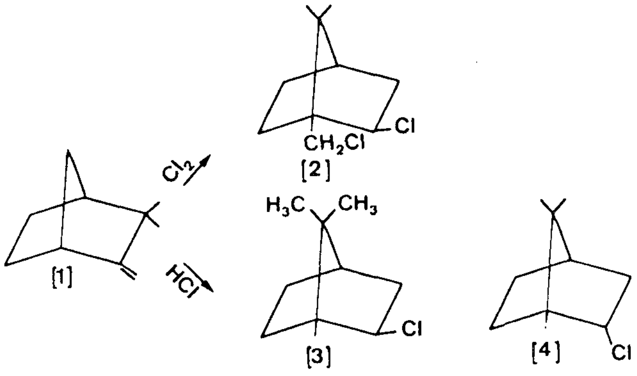


FIGURE 1 Reactions of camphene (1) with chlorine and hydrochloricacid.

accepted that the addition of chlorine to the double bond leads to a conformation resulting in 2-exo, 10-dichlorobornane (2) (Figure 1). From this reaction, it is assumed that toxaphene consists of higher substituted chlorobornanes. This assumption is further substantiated by the fact that an equivalent amount of HCl is evolved during the preparation. In this case 2-exo as well as 2-endo-chlorobornane (3, 4) are formed in a Wagner–Meerwein rearrangement.

Attempts to separate all the constituents in the commercial product by using the known separation procedures (column and thin-layer procedures, high pressure liquid chromatography and preparative gas chromatography) have led to unsatisfactory results so far.

Four groups took part in the isolation and identification of the toxaphene components (Figure 2). The compounds 6, 7, and 8 (compound I, II, and III) were identified by a German group in 1974[4], while compounds 5 (Toxicant B) and 9, 10 (Toxicant A) were isolated by another group.[5] Toxicant A is identified by ^{1}H-NMR studies as a mixture of 2, 2, 5-endo, 6-exo, 8, 8, 9, 10-octachlorobornane and 2, 2, 5-endo, 6-exo, 8, 9, 9, 10-octachlorobornane. These components have many structural features in common with the previously identified compounds (5–8).[6] A third research group isolated the compounds 9 and 10 also during this time.[7] Finally, a fourth research group identified a compound (11), which does not have the bornane skeleton, and they also identified again compound (8).[8] The

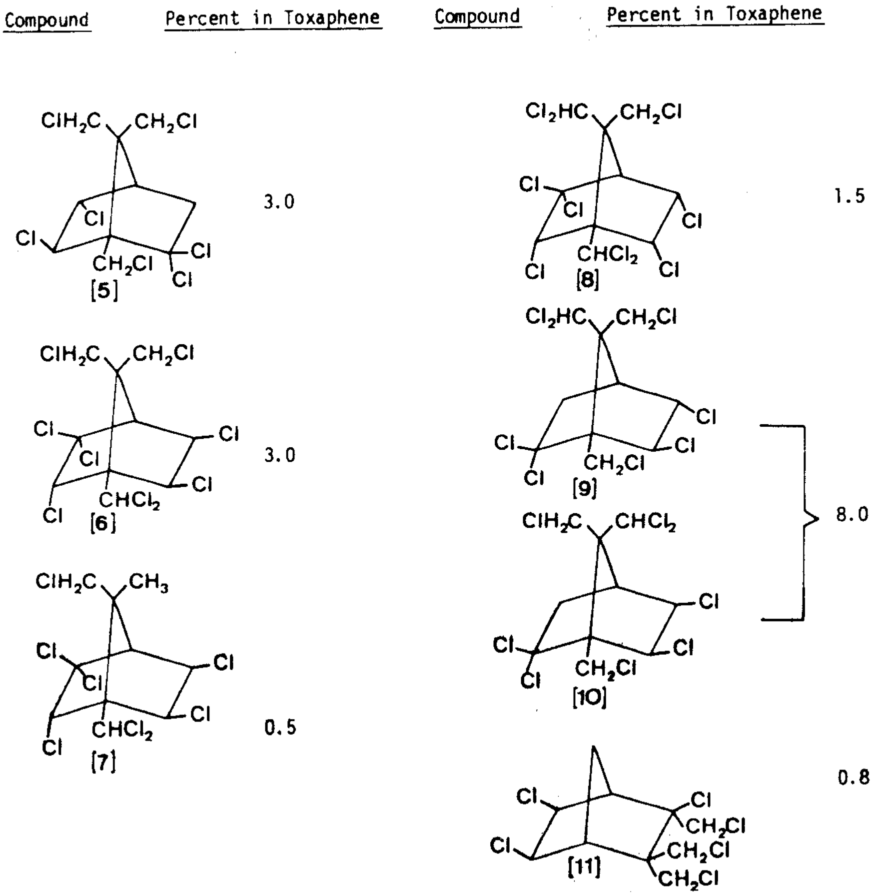


FIGURE 2 Identified toxaphene components from the technical mixture.

non-bornanoid structure of compound (11) was confirmed by X-ray structural analysis.[8] From the combined application of gas chromatography and mass spectroscopy, it was determined that the toxaphene is composed of at least 177 polychlorinated compounds of the formula $C_{10}H_{18-n}Cl_n$; 26 of these compounds occur in concentrations higher than 1%.[9] Attempts to dechlorinate the product resulted in a hydrocarbon $C_{10}H_{18}$ with a 20% yield (bornane) and several mono-, di-, tri- and tetra-chlorinated C_{10} compounds.

Attempts at isolating the components of the commercial product have in general failed to yield reproducible results. There are several reasons for this: the ivestigated products originated from different batches and producers and, due to the complexity of the reactions taking place during the commercial productions, there is no guarantee that the product should have a quantitatively identical composition. It should also be mentioned that the starting material used for the separations was not always the usual commercial available product. The material obtained underwent one or more recrystallization steps before the actual separation procedure was undertaken. The recrystallized complex mixture is by no means constant with respect to composition.

The results of previous investigations on commercial toxaphene and from primary reactions of camphene chlorination (1) have shown that the product obtained consists of a mixture of polychlorinated bornanes. The question on whether the product contains further non-bornanoid polychlorinated compounds was confirmed through the isolation and characterization of compound (11). This substance probably results from camphene (1); in this case the primary conformation of mono- and dichlorobornanes (2, 3, 4) does not take place. Dehydroderivatives with the empirical formula $C_{10}H_{16-n}Cl_n$ with $n=6$–9 have also been reported.[9] These compounds were detected by the use of the gas chromatography/mass spectroscopy combination, although it is uncertain whether these compounds are also present in the mixture. Their formation is more likely due to the employed analytical method: the required temperature for gas chromatography is above the decomposition temperature of the recrystallized toxaphenes (approx. 160°C). By comparing the stabilities of various synthetically prepared low chlorinated bornane derivatives, it is to be expected that the dehydrochlorination of toxaphene components would result in the formation of polychlorinated bornylene or camphene (the formation of 8-chlorocamphene form the dehydrochlorination of 2-exo, 10-dichlorobornane has actually been demonstrated).[10] However, it should not be assumed that toxaphene components are limited to compounds with the structures of bornane or dihydro-camphene or tricyclene, since all these structures are formed from pure camphene (1).

The term "technical" does not refer to the final products, since the camphene (1) used is in turn obtained from terpene oil, and practically all terpene hydrocarbons are found in terpene oil. The β-pinene fraction is obtained from terpene oil by distillation. β-pinene is catalytically converted to the α-isomer. The technical procedure for the purification of pinene is a difficult operation, due to the similar physical properties of the terpene hydrocarbons.

We do not know for certain whether the α-pinene is further purified prior to its final conversion into camphene (1). In any case, the catalytically induced rearrangement is by no means uniform. The monocyclic olefins and dienes and bicyclic compounds of the menthene and carene types are formed. Camphene (1) is obtained in a technical quality (75%). The impurities can be separated by distillation. Even if the impurities in the basic material camphene (1) would not be considered, it is likely that further C_{10} chlorinated hydrocarbons are present in toxaphene. Since the components isolated up to now constitute only a small part of the toxaphene mixture, it can be expected that in the future other substances will be isolated in similar amounts as the compounds known today. Technical mixtures originating from various producers were analysed by capillary gas chromatography. This provides a better characterization of technical toxaphene and gives important information concerning the gas chromatography behaviour of the mixture.[11] Probably, combined capillary column GC with MS will be the most feasible tool to characterize chemically a larger portion of the toxaphene constituents.

PREPARATION OF INDIVIDUAL CONSTITUENTS

Low chlorinated bornane derivatives with known structures provide necessary information for the structural analysis of toxaphene and can also be employed as model substances to elucidate at least in part the potential environmental impact of toxaphene.

Besides the already-mentioned 2-endo, 6-endo-dichlorobornane (12), 2-exo, 10-dichlorobornane (2) and 2-exo, 10, 10-trichlorobornane (13), also 2-exo, 8, 10-trichlorobornane (14A) or 2-exo, 9, 10-trichlorobornane (14B), 2-exo, 3-endo, 10-trichlorobornane (15), 2-exo, 6-endo, 10-trichlorobornane (16) and 2-endo, 3-exo, 5-exo, 6-endo-tetrachlorobornane (17) were prepared (Figure 3).[12]

Toxicant B (Compound 5), a major toxaphene component (~3%)

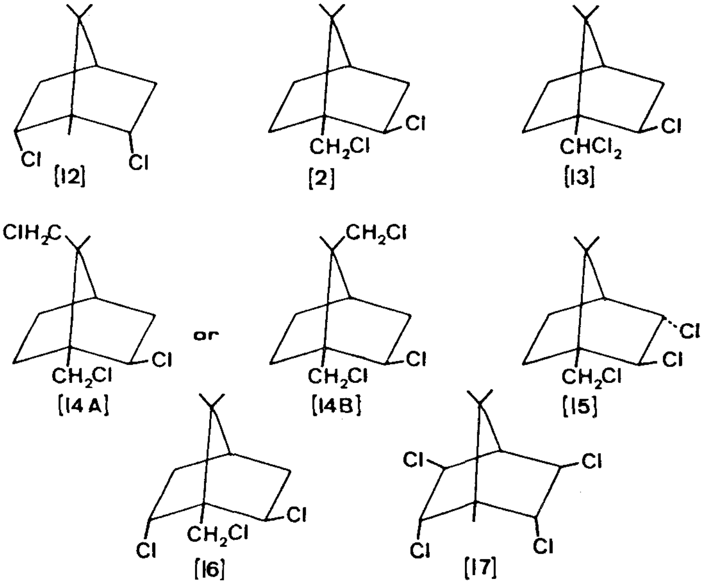


FIGURE 3 Prepared low chlorinated bornane derivatives.

is conveniently prepared in gram quantities of exo-2, 10-dichlorobornane (2), chromatography of the reaction mixture on a silicic acid column with hexane, and crystallization.[6] Chlorination of 5 yields compounds Toxicant A (9 and 10) and 18 and 19 which are likely to be toxaphene components (Figure 4).

Nelson and Matsumura have also examined the products of chlorination reactions of purified exo-2, 10-dichlorobornane (2) and determined the toxicities of these chlorinated products (four frac-

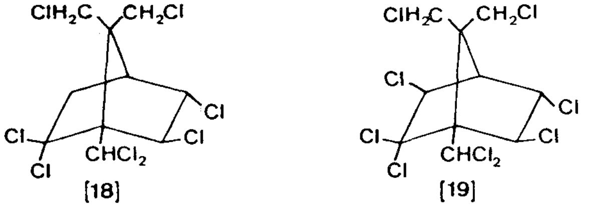
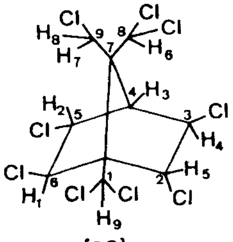


FIGURE 4 Structure of the components 18 and 19 from the chlorination of the component 5.



[20]

FIGURE 5 Structure of the 2-endo, 3-exo, 5-endo, 6-exo, 8, 8, 9, 10, 10-nonachlorobornane (20).

tions). With the help of chromatographic methods a major peak with a retention time equal to a toxic component of toxaphene could be isolated (compound 5).[13,4]

Chandurkar *et al.* have recently reported that there is a persistent contaminant in the preparations of Toxicant A (9 and 10).[15] They have isolated this compound and identified 2-endo, 3-exo, 5-endo, 6-exo, 8, 8, 9, 10, 10-nonachlorobornane (20) (Toxicant Ac) (Figure 5).

SPECTROSCOPIC ELUCIDATION

Low chlorinated bornane derivatives were analysed by ^{1}H- and ^{13}C-NMR, MS and IR spectroscopy and the data obtained were compared with those of (6).[16]

Mass spectroscopy studies on low chlorinated bornane derivatives

The relative intensities of selected fragments of low chlorinated bornane derivatives as well as of compound (6) are compiled in the following table (I).

The intensity of $(M\text{–}HCl)^+$ was used as reference fragment ion with an intensity of 100. The mass number 35 was used for the chlorine atoms contained in the molecules and fragment ions. A suggested pathway for the fragmentation of the chlorinated bornane derivatives is given in the following figure (Figure 6).

TABLE I

Mass spectroscopic data of low chlorinated bornane derivatives

Compound	M^+	rel. intensity	no. of Cl atoms	$(M–CH_3)$	rel. intensity	no. of Cl atoms
13	240	1.6	3	225	25.2	3
14A or 14B	206	4.8	2	191	33.3	2
15	240	8.0	3	225	2.0	3
16	240	0.2	3	225	11.1	3
12	240	20.5	3	225	7.8	3
17	206	10.2	2	191	5.2	2
6	274	8.0	4	395 (CH_2Cl)	30.0	8

Compound	$(M–Cl)$	rel. intensity	no. of Cl atoms	$(M–HCl)$	rel. intensity	no. of Cl atoms
13	205	74.8	2	204	100.0	2
14A or 14B	171	92.7	1	170	100.0	1
15	205	92.4	2	204	100.0	2
16	205	82.3	2	204	100.0	2
12	205	47.1	2	204	100.0	2
17	171	66.7	1	170	100.0	1
6	239	19.6	3	238	100.0	3
	409	250.0	8	408	100.0	8

Compound	$(M–Cl–HCl)$	rel. intensity	no. of Cl atoms
13	169	135.0	1
14A or 14B	135	3400.0	0
15	169	130.0	1
16	169	231.0	1
12	169	133.0	1
17	135	165.0	0
6	203	926.0	2
	373	250.0	7

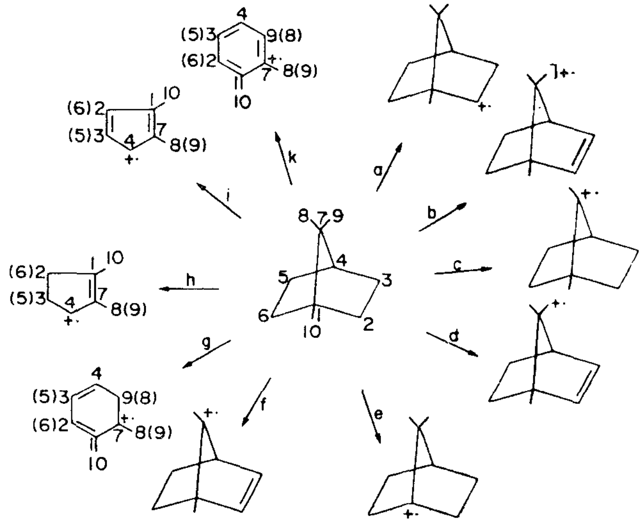


FIGURE 6 Fragmentation pathway of the chlorinated bornane derivatives.

The fragmentation is characterized by elimination of small groups like Cl (path a), HCl (path b), CH_3, CH_2Cl and $CHCl_2$ (path c or e). The compounds 14A or 14B contain a CH_2Cl group as can be seen from the mass spectra. The fragmentation $(M–CH_2Cl)^+$ is observed with two chlorine atoms at m/e 191. This fragmentation is not only missing with compounds 12 and 17 which do not possess a CH_2Cl group, but notably also with compounds 2 and 15. Compounds 13 and 6 possess a $CHCl_2$ group at the C-1 position. The fragment ion $(CHCl_2)^+$ is recorded at m/e 83. The same elimination was found in the spectra of Toxicants A (9 and 10) and B (5). Important clues to structures in this class of compounds are obtained from characteristic fragmentation, e.g., the ions of m/e 161 with two chlorine atoms of compound 13 (path i); m/e 127 with one chlorine atom of compound 2 (path i); m/e 129 with one chlorine atom (path h) and m/e 139 with one chlorine atom (path k) of compound 14A or 14B; m/e 161 with two chlorine atoms (path i) of compound 15; m/e 127 with one chlorine atom (path i) of compound 16; m/e 129 with one chlorine atom (path h) and m/e 127 with one chlorine atom (path i) of compounds 12 and 17. The ions m/e 277 with five chlorine atoms (path g), m/e 243 with four chlorine atoms (path g), m/e 265 with five chlorine atoms (path h), m/e 263 with five chlorine atoms (path i), and m/e 207 with three chlorine atoms (path k) were formed by the fragmentation of compound 6.

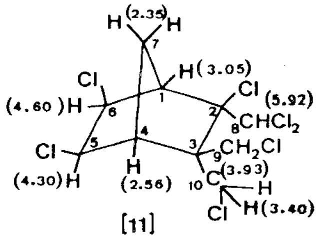
IR, ^{1}H- and ^{13}C-NMR spectroscopic studies of low chlorinated bornane derivatives

It is possible to characterize the chlorosubstitution at the methyl groups of the bornane derivatives from IR spectra alone. From the ^{1}H-NMR coupling constants of chlorinated bornane derivatives it is possible to determine the position of individual protons on the bornane skeleton. From the given spectroscopic data of the low chlorinated bornane derivatives and of the toxaphene fraction the composition of technical toxaphene can be better resolved. The data can also be of use in the interpretation of compounds isolated from toxaphene and of possible chemical, photopchemical, and biological conversion products resulting from the toxaphene mixture.[17]

X-ray analysis

The first toxaphene component known to retain the ring structure of camphene 2, 5, 6-exo, 8, 8, 9, 10-heptachlorodihydrocamphene (11) was determined by single crystal X-ray diffraction method and ^{1}H-NMR spectroscopy.[8]

The crystals of $C_{10}H_{11}Cl_7$ have the space group Pl with a = 8.75, b = 11.16, c = 7.94 and $\alpha = 99.83$, $\beta = 114.65$, $\gamma = 85.16°$ (reduced cell and Z = 2. Intensity data (2863 reflections in one hemisphere) were collected at about 85 K, with an automatic four circle diffractometer,



[11]

FIGURE 7 X-ray data of the 2, 5, 6,-exo, 8, 8, 9, 10-heptachlorodihydro-camphene (11).

using Mo Kα radiation and the θ–2θ scan method, to 2θ max of 55°. The structure was solved by direct methods using 2576 reflections with intensities $>3\sigma$ and refined to a reliability index of 0.022.

OCCURRENCE IN THE ENVIRONMENT

a) Plants

Numerous residue data on toxaphene-treated plants have shown that toxaphene may persist on plants. Half-life on leafy crops is reported to be between 5 and 13 days, depending on weathering conditions, plant type, growth rate, and formulation.[18] After application at recommended rates, residues of about 2 ppm may be expected after 30 days.[19] The mechanism of residue disappearance was investigated by Carlin *et al.*[20] and by Nash *et al.*[21]

Carlin *et al.* did residue decline studies on alfalfa, range grass, and winter wheat treated with toxaphene emulsion sprays.[20] Toxaphene residues were measures by electron capture gas chromatography (ECGC) after partial dehydrochlorination (de-HX) in potassium hydroxide-ethanol solution and were confirmed by total organic chloride (TOCl) determination after reduction by sodium-liquid ammonia. All residues were identified as toxaphene by ECGC. ^{36}Cl-Toxaphene was applied to living cotton plants, and the treated plants were maintained in a closed all-glass system for 7 days. Samples from various sites throughout the system were analyzed by de-HX/ECGC and by liquid scintillation counting (LSC) procedures. ^{36}Cl-Toxaphene components were distributed throughout the apparatus, but the majority of the residue was detected on the cotton plants. The residue on the plants was identified by ECGC as toxaphene. No evidence of metabolism was detected. The mechanism of loss was suggested to be by volatilization.

In order to get further information on the volatilization of toxaphene from treated plants into the atmosphere, Nash *et al.* applied toxaphene to cotton plants at weekly intervals for six weeks in an enclosed chamber (agro-ecosystem), and the volatilization was monitored for 90 days.[21] The volatilization seemed to follow log concentration with log time the first week and then log concentration with linear time thereafter. Calculated first-order equation half-life for volatilization of toxaphene was 15.1 days.

Bioaccumulation of toxaphene by plants (lake vegetation) was found to be about 3.000 times.[22]

b) Soil

Residues of toxaphene in soil may persist for years; also in this case, volatilization is suggested as a major loss mechanism.[23] In cropland under regular use, the recovery rate, 1–3 years after the last application, is in the order of 10–30%.[24] The evaporation from the surface of soil is rapid providing the surface is not dry. The process of volatilization is nearly stopped if the soil is cultivated or the toxaphene is mixed with the soil.[24]

c) Air

The occurrence of volatilized residues in the atmosphere was demonstrated at various locations in the United States.[25] The correlation to agricultural sprayings was studied by Arthur *et al.*[26] Over the most intensive cotton growing area of Mississippi, the residue levels of toxaphene were highest in August for three consecutive years (1972–1974), indicating the spray activities in the area. The levels of toxaphene found were in the same order as those of methylparathion. However, toxaphene is not found exclusively in the air over application sites, but may be transported over long distances. Bidleman and Olney reported a long-range transport of toxaphene through the atmosphere, at least 1.200 km from the application sites out to sea: during 1973–1974, toxaphene was detected in air samples collected over the western North Atlantic.[27] The mean concentration of 56 samples was 0.63 ng/m^3, as against 0.024 for *p,p'*-DDT; the ratio of these concentrations is close to the ratio of the outdoor evaporation rates of the two pesticides.

d) Water

Besides transport by air, movement from soil to water may be regarded as another source of toxaphene dispersion. The primary route of entry of toxaphene into water is through surface runoff. Sediment carriers nearly all the toxaphene in the surface runoff. It is possible to measure toxaphene yields of runoff in sediment and to get the rough estimates of time that it takes for toxaphene concentrations to be reduced to biologically inactive levels once sediment contaminated with toxaphene is introduced into the water. For the most part, these time periods are relatively short varying from a few days to a few months depending on the size of the surface area of the body of water, the organic matter in the water, the sediment load, and the toxaphene concentration in the sediment.[24]

Movement of toxaphene through the soild to ground water was studied.[25] According to this study, toxaphene loss from top soil treated with 100 kg/ha seems to occur in two stages. The second (major) stage is about linear on a log residue vs. log time plot. Half-residues time in the top soil is about 100 days. Toxaphene was found in underlying ground water within two months after application to the top soil and persisted in ground water during one year of monitoring. However, it should be emphasized that this extremely high level is very unlikely to occur under normal environmental conditions, except accidents or areas near manufacturing plants.

In surface waters of streams in Western U.S.A., toxaphene was not found within two years (1966–1968) among the samples collected in 20 stations.[26]

Bioaccumulation ration in lake sediments was measured to be about 700.[22] However, when the Mississippi river sediment was analyzed,[27] toxaphene was not detected, notably in the delta area where the greatest concentration of other pesticides was reported by another author.[28] There were two samples where indeed point source contaminations resulting from manufacturing and formulating activities on toxaphene have been found to occur. It seems that such point source contaminations do not spread noticeably, as attested to by the absence of contamination in the downstream localities and by other studies on toxaphene-contaminated factory outlets.[29]

Disappearance from water is mostly due to volatilization, like for plant and soil residues. The rate at which it moves to the surface layer of water is controlled by several factors including rates of diffusion and rate of desorption. However, it was observed that a very small amount stayed in a lake for a fairly long period of time.[24]

In spite of volatilization and other residue disappearance mechanism, toxaphene may find its way into the drinking water: 27 of 680 samples throughout the U.S.A. were positive, 2 had residues above

0.05 ppm.[30] In more than 500 samples along the Mississippi and Missouri rivers, however, toxaphene was not detected.[31]

e) Wildlife

In wildlife, toxaphene occurs very infrequently. However, the frequency of finding toxaphene in fish and mollusks was about 16 out of 1000 and residue levels ranged from 0.01 to 1.25 ppm in fish and 11 to 54 ppm in molluks. There is evidence to indicate that toxaphene has not caused severe population reductions or affected the survivability of land-living animal species. The role which toxaphene plays in the different fish kill episodes, in comparison to other pesticides, is not fully clarified.[24]

f) Humans

Contrary to DDT, hexachlorobenzene and some cyclodiens, toxaphene has not been detected in *human tissues.*[24] This fact may be due partly to quick elimination, partly to the relatively rare occurrence of toxaphene residues in *human food.* Market-basket surveys in the U.S.A. between 1965 and 1969 revealed an incidence rate of less than 2% and an average concentration of less than 0.2 ppm for most food groups. However, oils and oily crops showed a higher incidence of toxaphene (cotton seed 29%). In processed (canned, dried or frozen) food, toxaphene residues were 6th most frequent in occurrence of all presticides, but few were in excess of the 7 ppm limit. From 1965 to 1970 the average daily intake was calculated to be 0.0015 mg/day.[31] Further total diet studies of the National Pesticide Monitoring Program from 1966 to 1974 revealed a frequency of 9 times/1000 samples with a range of residue levels from a trace to 0.20 ppm.[24]

SUMMARY AND CONCLUSIONS

1) Toxaphene is a complex mixture (>177 C_{10} polychloro compounds) from which five components have been chromatographically isolated in the indicated yields and identified by ^{1}H-NMR and MS (5, 6, 7, 8 and 11) or by these procedures plus X-ray crystallography

(5 and 11). Two additional octachlorobornanes (Toxicant A), isolated as a ca. 50/50% mixture (9 and 10), are identified by ^{1}H-NMR and MS. A nonachlorobornane (20), isolated in undefined yield from toxaphene, is identified by ^{1}H-NMR and MS. Chlorination of 5 yields a product mixture suitable for isolating 10-Cl and 3-exo-Cl derivatives (18 and 19), identified by ^{1}H-NMR and MS, which are chromatographically identical with two toxaphene compounds. These ten compounds or fractions account for ca. 20–25% of the toxaphene components as approximated by GLC-EC of toxaphene or partially fractionated toxaphene. The most toxic of the identified components to houseflies, goldfish and mice is 2,2,5-endo,6-exo-8,9,9,10-octachlorobornane (5). This octachlorobornane, which is estimated to represent about 3% of technical toxaphene, contributes a significant portion of the overall toxicity of toxaphene to these organisms.

2) Toxaphene is slowly to rapidly degraded in various environmental systems. It has been found in soil, in air, and in waters. Bioaccumulation is lower than for various other organochlorines. Occurrence in human tissues has not been reported. Due to relatively high vapour pressure (about 10^{-6} mm Hg), it is apparently volatilized rapidly from plants, soil, or water. This volatility results in lower residues in these media than for other chlorinated pesticides.

3) Analytical methods for determining the consistency of the technical product are sufficiently developed.

4) Available analytical methods for detection in environmental samples are, because of the high number of components, metabolites and degradation products, not sufficient.

5) Although main commercial products manufactured in the western world may have reproducible and constant composition, some products produced in other countries may differ in their composition.

Recommendations

1) Other components of technical toxaphene should be identified and their insecticidal and mammalian toxicities should be determined.

2) In practise the number of constituents should be as low as possible to avoid unnecessary contamination.

3) Analytical methods should be improved for detection in environmental samples.

4) Metabolism and ecotoxicological investigation should be enhanced.

References

1. D. Tishchenko and I. Uvarov, *J. Gen. Chem. USSR* **23,** 1473 (1953).
2. B. H. Jennings and G. B. Herschbach, *J. Org. Chem.* **30,** 3902 (1965).
3. G. Ghiurdoglu, C. Goldenberg and J. Geeraerts, *Bull. Soc. Chim. Belges* **66,** 200 (1957).
4. M. L. Anagnostopoulos, H. Parlar and F. Korte, *Chemosphere* **3,** 65 (1974).
5. J. E. Casida, R. L. Holmstead, S. Khalifa, J. R. Knox, T. Ohsawa, K. J. Palmer and R. Y. Wong, *Science* **183,** 520 (1974).
6. W. V. Turner, S. Khalifa and J. E. Casida, *J. Agric. Food Chem.* **23,** 991 (1975).
7. F. Matsumura, R. W. Howard and J. O. Nelson, *Chemosphere* **4,** 271 (1975).
8. P. F. Landrum, G. A. Pollock, J. N. Seiber, H. Hope and K. L. Swanson, *Chemosphere* **5,** 63 (1976).
9. R. L. Holmstead, S. Khalifa and J. E. Casida, *J. Agric. Food Chem.* **22,** 653 (1974).
10. A. Michna, *Dissertation, Synthesis of low chlorinated bornane derivatives* (Technical University of Munich, 1977).
11. M. A. Saleh and J. E. Casida, *J. Agric. Food Chem.* **25,** 63 (1977).
12. H. Parlar, S. Gäb, A. Michna and F. Korte, *Chemosphere* **5,** 217 (1976).
13. J. O. Nelson and F. Matsumura, *Bull. Environ. Contam. Toxicol.* **13,** 464 (1975).
14. J. O. Nelson and F. Matsumura, *J. Agric. Food Chem.* **23,** 984 (1975).
15. P. S. Chandukar,' F. Matsumura and T. Ikeda, *Chemosphere* **6,** 123 (1978).
16. H. Parlar, S. Gäb, S. Nitz and F. Korte, *Chemosphere* **5,** 333 (1976).
17. H. Parlar, S. Nitz, S. Gäb and F. Korte, *J. Agric. Food Chem.* **25,** 68 (1977).
18. FAO/WHO, 1968 Evaluations of some pesticide residues in food, p. 267–283 (1969).
19. H. Maier-Bode, Pflanzenschutzmittel-Rückstände, Insektizide. Verlag Eugen Ulmer, Stuttgart (1965).
20. F. J. Carlin, J. J. Ford and R. G. Kangas, 168th ACS National Meeting, Atlantic City, New Jersey, Sept. 9–13, 1974.
21. R. G. Nash, M. C. Beall and W. G. Harris, *J. Agric. Food Chem.* **25,** 336 (1977).
22. L. C. Terriere, U. Kiigemagi, A. R. Gerlach and R. L. Borovicka, *J. Agric. Food Chem.* **14,** 66 (1966).
23. G. E. Guyer *et al.*, *Toxaphene Status Report* (U.S. Environmental Protection Agency, Washington, D.C. 1971).
24. L. J. Stevens, C. W. Collier and D. W. Woodham, *Pestic. Monit. J.* **4,** 145 (1970).
25. C. W. Stanley, J. F. Barney II, M. R. Helton and A. R. Yobs, *Environ. Soc. Technol.* **5,** 431 (1971).
26. D. B. Manigold and J. A. Schulze, Pesticides in water—pesticides in selected streams—a progress report, *Pestic. Monit. J.* **3,** (2), (1969).
27. T. F. Bidleman and C. E. Olney, *Nature* **257,** 475 (1975).

28. C. A. Edwards, Persistent pesticides in the environment. Critical Reviews in Environmental Control 1, 1. (CRC Press, Cleveland, Ohio, 1970).
29. C. J. Durant and R. J. Reimold, *Pestic. Monit. J.* **6,** 94 (1972).
30. Anon. EPA, Preliminary assessment of suspected carcinogens in drinking water. Report to Congress. Environmental Protection Agency, Washington, D.C., December 1975.
31. M. L. Schafer, J. T. Peeler, W. S. Gardener and J. E. Campbell, *Environ. Sci. Technol.* **3,** 1261 (1969).