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Chlorinated hydrocarbons in beef, cow liver and milk products and total mercury in cow liver

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Abstract. The chlorinated hydrocarbons used in pesticides and PCB-compounds (polychlorinated biphenyls) were determined in domestic and imported beef (79 samples), cow liver (195 samples), butter (112 samples), cheese (93 samples) and milk powder (58 samples); mercury was determined in cow liver (163 samples). The domestic samples (320 samples in total) were collected from different parts of Finland. The foreign samples (270 samples in total) came mainly from the Nordic countries and Central Europe.

The chlorinated hydrocarbons were determined by gas chromatography with an E.C. detector. The mercury determinations were made from freezedried samples using a Coleman Analyzer.

In the domestic samples the contents of chlorinated hydrocarbons were low and clearly below the FAO/WHO recommended limits. The pesticide quantities in the foreign samples were often higher, and in two cases the total DDT limit recommended by FAO/WHO was exceeded. The mercury contents of the livers were low and of the same magnitude in all samples examined.

Introduction

The use of pesticides has been limited by law in Finland; the use of mercury has been controlled since the middle of the 1960's and that of chlorinated hydrocarbons since the beginning of the 1970's. However, since the decomposition of many organic compounds in nature is slow, they may accumulate in animals and through them enter into food. A corresponding tendency has been observed concerning many metals which in sufficiently high concentrations in food may be detrimental to human health. In addition to domestic products, fairly large quantities of imported foodstuffs are used, and our knowledge of their contents of harmful compounds is limited. Thus continued research and control in this field is required.

This study deals with domestic and imported beef and cow liver, which is an important imported raw material for the meat industry. As a second group, milk products (butter, cheese and milk powder), which have a large domestic consumption, have been chosen; in addition they are important export articles. Analyses of chlorinated hydrocarbons, including polychlorinated biphenyls (PCB) were taken from all samples. Total mercury determinations were made in cow liver.

Material

Domestic beef and cow liver were obtained from five different slaughterhouses in Southern and Central Finland. Foreign beef and liver samples were obtained in connection with customs clearance of food lots coming from different countries (Table 1).

Butter, cheese and milk powder samples were obtained from dairies operating in different parts of Finland. Foreign milk products were random purchases mainly from other Nordic countries where similar studies have been made. The rest of the material consisted of occasional samples from Central and Southern Europe and the U.S.A. (Table 1).

Table 1. The samples from the various countries.

Country	Beef	Cow liver	Butter	Cheese	Milk powder
Australia	—	21	—	—	—
Canada	—	10	—	—	—
Czechoslovakia	—	—	1	—	—
Denmark	—	—	13	7	—
Finland	64	55	73	75	53
France	—	—	2	9	—
Ireland	5	17	3	1	—
Netherlands	—	—	1	—	—
New Zealand	—	19	—	—	—
Poland	10	52	—	—	—
Spain	—	—	2	—	—
Sweden	—	12	9	—	3
Switzerland	—	—	1	—	1
U.K.	—	—	2	—	—
USA	—	9	3	—	1
West Germany	—	—	2	1	—
Number of samples	79	195	112	93	58

Methods

Chlorinated hydrocarbons

Extraction and cleanup

The fresh sample (beef 10 grams, cow liver 5 grams, butter 1 gram, cheese 2—10 grams, milk powder 4—50 grams) was homogenized with anhydrous sodium sulphate. The homogenate was then shaken in a flask with a glass plug with diethyl ether (25 to 100 ml) about 3 minutes and the extract was filtered through glass wool. The ether was evaporated at room temperature. The fat was dissolved in 5 ml of hexane and decanted into a separatory funnel (250 ml) and rinsed with 3 × 3 ml of hexane. Fifteen milliliters of acetonitrile saturated with hexane were added and shaken vigorously for 1—2 minutes. After the layers had separated the acetonitrile was drained into a 150 ml glass bowl. The shaking was repeated with three 15 ml portions of acetonitrile. The acetonitrile extract was evaporated at 60—70° C by blowing purified nitrogen slowly down into the glass bowl. Methylene chloride was added in a sufficient

amount and the fat in the methylene chloride solution was then applied on a thin layer plate.

The thin layer plates (50 × 200 mm) were covered with Silica Gel G so that the layer was 1 mm thick (Shandon Equipment for Thinlayer Chromatography) (KARPPANEN et al. 1969). The solvent fronts, the border line between the upper and lower section and the origin line were marked on the plates, which were then heated overnight at 200° C. The plates with fat on the origin line were developed with the solvent methylene chloride and n-hexane, 25: 75 (v/v). After drying at 25° C both the upper and the lower sections of the thin layer material were removed and packed into small glass columns. They were then extracted with cyclohexane and diethyl ether, 6: 4 (v/v). The eluates were collected in 1 ml flasks. The solution from the upper section contained PCB compounds, p,p'DDE and p,p'DDT. To separate p,p'DDT and a major PCB peak 0.5 ml of the eluate was treated with a methanol solution of 10 per cent KOH (w/w).

Gas chromatography

Gas chromatograph: Varian 600 and 1 400 with electron capture detector (tritium) and glass columns.

Column packing:

1) Chromosorb W a.w./DMCS. 100/120 mesh; coated with 5 % SF96 methyl silicone.
2) As above but stationary phase 5 % SF96—QF—1, 25: 75.

Carrier gas: Nitrogen 99.999 %.

Reference solutions: Pesticides, purity 99—100 % (Analytical Standards LTD, Sweden).

Reference solutions of PCB:

1) A hexane solution of a 60 %-chlorinated technical PCB-micture (Clophen A 60).
2) A hexane solution of a 42 %-chlorinated technical PCB-mixture (Aroclor 1242).

Calculation of PCB

After the pesticide residues from the sample had been removed, the sum of the heights of all peaks corresponding to PCB peaks was calculated with the exception of the two interfering with p.p'DDE. This sum was compared with the sum obtained from the same peaks in the reference chromatograms.

By using the method of acetonitrile partition (ZWEIG and SHERMA 1972) it has been shown that both pesticides and PCB decrease. Average recovery of pesticides is 95 % and that of PCB 70 %. Organochlorine compounds may decrease during evaporation of acetonitrile.

Total mercury

For determination of total mercury the samples were analysed by an oxygen flask combustion method (GUTENMANN and LISK 1960, RAJAMA et al. 1964) combined with a Mercury Analyzer Coleman 50 (Perkin—Elmer).

Table 2. Organo chlorine content and total mercury in cow liver. Mean concentration, mg/kg fresh sample. (Range in parentheses)

Country	Number	Dieldrin	Total DDT	PCB	Fat-%	Hg
Australia						
1971	13	—[1]	0.007 (n.d.— 0.024)	0.008 (<0.005— 0.021)	3,5 (2,4—6,0)	0,06 (n.d.—0.12)
1972	3	n.d.	<0.005 (<0.005— <0.005)	<0.005 (<0.005— <0.005)	3.2 (2.6—3.6)	0.05 (0.03—0.07)
1973	5	n.d.	<0.005 (<0.005— <0.005)	<0.005 (<0.005— <0.005)	4.5 (3.6—5.5)	0.04 (0.02—0.05)
Canada						
1974	10	n.d.	<0.005 (n.d.— 0.010)	0.006 (<0.005— 0.027)	3.2 (2.6—5.8)	—[2]
Finland						
1971	16	—[1]	<0.005 (n.d.— 0.006)	0.010 (<0.005— 0.079	2.7 (1.5—4.1)	0.04 (n.d.—0.09)
1972	27	n.d.	<0.005 (n.d.— <0.005)	<0.005 (n.d.— <0.005)	3.3 (2.0—9.1)	0.06 (n.d.—0.12)
1974	12	n.d.	<0.005 (n.d.— <0.005)	0.010 (<0.005— 0.025)	3.2 (2.5—4.1)	—[2]
Ireland						
1972	17	n.d.	<0.005 (<0.005— <0.005)	<0.005 (<0.005— <0.005)	2.8 (2.3—4.0)	0.05 (n.d.—0.12)
New Zealand						
1971	19	—[1]	0.005 (n.d.— 0.020)	0.008 (0.005— 0.043)	3.1 (2.0—6.4)	0.02 (n.d.—0.04)
Poland						
1971	8	—[1]	0.025 (0.012— 0.040)	0.012 (0.005— 0.055)	3.1 (2.1—7.1)	0.08 (0.04—0.13)
1972	44	<0.005 (n.d.— <0.005)	0.035 (<0.005— 0.39)	0.006 (n.d.— 0.086)	3.6 (1.6—10.5)	0.07 (0.03—0.11)
Sweden						
1972	2	n.d.	<0.005 (<0.005— <0.005)	<0.005 (<0.005— <0.005)	2.9 (2.7—3.2)	0.10 (0.08—0.11)
1973	10	n.d.	0.006 (<0.005— 0.030)	0.051 (0.029— 0.077)	3.1 (2.4—4.7)	n.a.
USA						
1971	9	—[1]	0.011 (n.d.— 0.024)	<0.005 (<0.005— 0.010)	3.2 (2.3—6.8)	0.13 (n.d.—0.37)
Number of samples	195					

[1] H_2SO_4-method.
[2] Stabel-Taucher et al. 1975.
n.d. = not detected n.a. = not analysed

Results and discussion

In the result tables only those chlorinated hydrocarbons detected in the samples are shown. The sum of DDT compounds was calculated and mentioned in the tables as total DDT.

Dieldrin was found in small quantities only in the Polish liver samples (Table 2). However, parts of the liver samples have been cleaned by the H_2SO_4-method (AHLING and JENSEN 1970), during which the dieldrin dissolves and cannot be detected. The highest total DDT value was also detected in Polish liver. If the results are compared to the suggested FAO/WHO limit of 7 mg/kg fat (ANON. 1973), one Polish liver sample exceeded this value. In the domestic liver samples the total DDT content was low. In one of the domestic samples an abnormally high PCB content was found. The sample was from a cow which during the grazing period had been drinking water from the Kokemäki river; this river belongs to the Finnish water system most seriously polluted by PCB compounds. The mercury contents of the livers were low and of the same magnitude in the different countries. The highest values were found in liver imported from the U.S.A., but the limited material does not justify definite conclusions.

In the Finnish and Irish beef samples examined, only small residues of DDT decomposition products were found (Table 3). On the other hand, the average total DDT in the Polish beef samples examined was considerably higher, exceeding in one sample the FAO/WHO recommended limit of 7 mg/kg fat (ANON. 1973). Small amounts of PCB were found in Finnish beef samples only.

In the Finnish, Swedish, Danish and Irish butter samples analysed, the contents of chlorinated hydrocarbons were of the same magnitude and fairly low (Table 4). Results in agreement with this study have also been obtained in Sweden (WESTÖÖ et al. 1970), Denmark (BRO-RASMUSSEN et al. 1968) and Ireland (DOWNEY 1972). The Danes, however, have recorded considerable BHC-values (β-BHC and lindane), whereas the 13 Danish butter samples in

Table 3. Organo chlorine content in beef. Mean concentration, mg/kg fresh sample. (Range in parentheses).

Country	Number	Total DDT	PCB	Fat %
Finland 1974	64	<0.005 (n.d.—<0.005)	<0.005 (<0.005—<0.005)	5.0 (0.9—14.9)
Ireland 1973	5	<0.005 (n.d.—<0.005)	n.d.	23.8 (17.3—30.2)
Poland 1973	10	0.69 (0.052—4.4)	n.d.	23.7 (12.5—34.1)
Number of samples ...	79			

n.d. = not detected

Table 4. Organo chlorine content in butter. Mean concentration, mg/kg. Range in parentheses.

Country	Number	Lindane	Heptachlor-epoxide	Dieldrin	Total DDT	PCB
Denmark						
1972	4	n.d.	n.d.	0.011 (0.009–0.012)	0.016 (0.007–0.022)	0.15 (0.063–0.24)
1973	9	n.d.	n.d.	0.006 (<0.005–0.011)	0.017 (0.009–0.034)	0.21 (0.090–0.35)
Finland						
1972	42	n.d.	n.d.	<0.005 (n.d.–0.006)	0.011 (<0.005–0.022)	0.065 (0.028–0.18)
1973–1974	31	n.d.	n.d.	n.d.	<0.005 (<0.005–0.006)	0.076 (0.028–0.14)
Ireland						
1973	3	<0.005 (<0.005–<0.005)	n.d.	0.013 (0.011–0.017)	0.012 (0.095–0.15)	0.090 (0.046–0.14)
Sweden						
1972	7	n.d.	n.d.	<0.005 (n.d.–0.012)	0.034 (0.010–0.065)	0.094 (0.075–0.12)
1973	2	n.d.	n.d.	0.011 (0.007–0.016)	<0.005 (n.d.–<0.005)	0.11 (0.086–0.13)
The other countries						
1972	14	n.d.	<0.005 (n.d.–<0.005)	0.021 (<0.005–0.050)	0.051 (<0.005–0.27)	0.090 (0.035–0.24)
Number of samples	112					

n.d. = not detected.

our material did not contain detectable amounts of these compounds. This may depend on differences in the methodology.

There were no significant differences in the average residue contents of the Finnish and Danish cheese samples (Table 5). However, there was in the Danish samples some heptachlorepoxide, which was not found in the Finnish samples. In the cheese samples originating from other countries (France, Germany) clearly higher amounts of dieldrin and DDT were found than in samples from the Nordic countries.

All the examined milk powder samples contained only small residues of chlorinated hydrocarbons (Table 6).

Table 5. Organo chlorine content in cheese. Mean concentration, mg/kg fresh sample. (Range in parentheses).

Country	Number	Lindane	Heptachlor-epoxide	Dieldrin	Total DDT	PCB
Denmark						
1972	5	n.d.	<0.005 (n.d.—<0.005)	<0.005 (n.d.—<0.005)	0.005 (<0.005—0.008)	0.058 (0.042—0.10)
1973	2	n.d.	n.d.	<0.005 (<0.005—<0.005)	<0.005 (<0.005—<0.005)	0.090 (0.085—0.094)
Finland						
1972	26	n.d.	n.d.	<0.005 (n.d.—<0.005)	<0.005 (<0.005—0.007)	0.068 (0.008—0.19)
1973	49	n.d.	n.d.	<0.005 (n.d.—<0.005)	<0.005 (n.d.—0.005)	0.074 (0.007—0.35)
The other countries						
1972	7	n.d.	0.020 (n.d.—0.12)	0.020 (n.d.—0.086)	0.018 (<0.005—0.059)	0.10 (0.069—0.17)
1973	4	0.014 (<0.005—0.022)	n.d.	0.008 (<0.005—0.015)	0.016 (<0.005—0.031)	0.10 (0.023—0.17)
Number of samples	93					

n.d. = not detected.

Table 6. Organo chlorine content in milk powder. Mean concentration, mg/kg. (Range in parentheses).

Country	Number	Dieldrin	Total DDT	PCB
Finland 1972	14	n.d.	<0.005 (n.d.—0.010)	0.017 (<0.005—0.054)
1973	39	<0.005 (n.d.—<0.005)	<0.005 (n.d.—<0.005)	0.005 (<0.005—0.021)
Sweden 1972	3	n.d.	<0.005 (n.d.—<0.005)	0.005 (<0.005—0.007)
Switzerland 1972	1	<0.005	<0.005	0.005
USA 1972	1	<0.005	<0.005	0.022
Number of samples	58			

n.d. = not detected.

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SELOSTUS

Klooratut hiilivedyt naudan lihassa, naudan maksassa ja maitotuotteissa sekä kokonaiselohopea naudan maksassa

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Torjunta-aineiden käyttöä on rajoitettu ja käytön valvontaa tehostettu Suomessa kloorattujen hiilivetyjen osalta 1970-luvun alusta alkaen ja elohopean osalta jo 1960-luvun puolivälistä lähtien. Useiden orgaanisten yhdisteiden hajoaminen luonnossa on kuitenkin hyvin hidasta, joten niillä samoin kuin monilla metalleilla on mahdollisuus rikastua erikoisesti eläinkudoksiin ja sitä kautta elintarvikkeisiin. Kotimaisten tuotteiden ohella käytetään maassamme runsaasti ulkomaisia elintarvikkeita. Tiedot näiden sisältämistä haitallisista yhdisteistä ovat vähäiset.

Tähän tutkimukseen on valittu sekä kotimainen että ulkomailta tuotu naudan liha, josta on määritetty tuhoeläinmyrkkyinä käytetyt klooratut hiilivedyt ja PCB-yhdisteet 79 näytteestä. Naudan maksasta, joka on tärkeä lihateollisuuden raaka-aineeksi käytetty tuontituote, on vastaavia määrityksiä suoritettu 195 näytteestä. Toiseksi ryhmäksi on otettu maitotuotteet, joilla on suuri kotimainen kulutus, ja lisäksi ne ovat tärkeitä vientiartikkeleita. Voinäytteitä on analysoitu 112, juustonäytteitä 93 ja maitojauhenäytteitä 58. Vuosina 1971–1973 on suoritettu kokonaiselohopeamääritykset 163 naudan maksanäytteistä, ja nämä tulokset on liitetty tähän tutkimukseen. Eri puolilta Suomea kerättyjä kotimaisia näytteitä oli kaikkiaan 320. Ulkomaisia näytteitä oli yhteensä 217 ja ne olivat etupäässä Pohjoismaista ja Keski-Euroopasta.

Kotimaisissa näytteissä torjunta-aineina käytettyjen kloorattujen hiilivetyjen pitoisuudet olivat alhaiset ja alittivat selvästi FAO/WHO:n suosittelemat raja-arvot. Ulkomaisten näytteiden pestisidimäärät vaihtelivat suuresti. Joissakin maissa ne olivat samaa suuruusluokkaa kuin Suomessa, toisissa taas huomattavasti korkeampia. Kahdessa tapauksessa FAO/WHO:n kokonais-DDT:lle suosittelema raja-arvo ylitettiin. PCB-yhdisteiden jäämät olivat yleensä pieniä ja vaihtelivat samoissa rajoissa sekä kotimaisissa että ulkomaisissa näytteissä. Maksojen elohopeapitoisuudet olivat kaikissa tutkituissa näytteissä alhaisia ja suuruusluokaltaan samanlaisia.