

# Residual Organochlorine Pesticides in the Fat of Mutton Birds of New Zealand

by

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## INTRODUCTION

The presence of residues of organochlorine pesticides in both land and sea birds throughout the world is now well documented (HOLMES et al. 1967; RISEBROUGH et al. 1967, 1968; KOEMAN et al. 1969; PRESTT et al. 1970; BOGAN and BOURNE 1972). The sooty shearwater or mutton bird, Puffinus griseus (order Procellariiformes) nests in New Zealand during the summer months, migrates to the northern hemisphere during May, and returns in September. Eggs are laid during November and December and the chicks are hatched in the following January and February. The mutton birds of New Zealand and the mutton birds of Bass Strait, Australia (slender-billed shearwater, P. tenuirostris) are noted for their very high proportion of body fat. Consequently, large numbers of these birds are caught during the season (April to May in New Zealand) to provide a food delicacy in the diet of the local populations, in particular, the Maori race in New Zealand.

RISEBROUGH et al. (1967, 1968) reported that three mutton birds (P. griseus) migrating in the Monterey Bay area of California during 1966 had 8.4 ppm of total DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane) residues [pp'-DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene)88%, pp'-DDT 5.6%, pp'-DDD (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane)3.8%] and 1.1 ppm PCB (polychlorinated biphenyl) compounds in their lipid extracts. RISEBROUGH et al. (1968) also found 32 ppm of total DDT (pp'-DDE 92%) as well as 2.1 ppm PCBs in the fat of one slender-billed shearwater from Australia. In view of these relatively high levels of DDT and PCBs and since it is also well known that residues of these organochlorine compounds in birds produce effects such as eggshell thinning and consequent population declines (see NATIONAL RESEARCH COUNCIL 1971) it was considered of interest to further identify and measure the levels of these pesticides in the mutton bird. The results of a preliminary investigation of the New Zealand mutton bird are reported in this paper.

## EXPERIMENTAL

Mutton birds (3 adults and 1 chick) were captured by hand on arrival at their burrows in marram grass at their breeding grounds on Taiaroa Head, Otago Peninsula, on 6 March, 1969. Three adult birds were purchased during May 1969 from a retail shop selling frozen mutton birds for eating purposes. These birds were captured during April on Stewart Island, the most southern island of New Zealand. As far as could be ascertained, a DDT superphosphate fertilizer had been used some time previously as a top dressing on fields in the vicinity of the nesting grounds in both locations. The carcasses were kept at 0°C. prior to analysis.

Samples of fat (60-100 mg) were extracted with n-hexane or with acetone and then submitted to a clean-up procedure according to JENNINGS (1968). The PCBs were eluted from the silica gel columns with pentane or n-hexane and the DDT and metabolites were eluted with a hexane/benzene (50/50) mixture and with benzene as described by SNYDER and REINERT (1971). All the extracts were analysed for organochlorine compounds (DDT and analogues, hexachlorocyclohexane isomers (HCH), dieldrin (HEOD), PCBs) by electron-capture gas-liquid chromatography (Micro Tek MT-220 and Varian-Aerograph 660 gas chromatographs with tritium detectors). Glass columns (6' by  $\frac{1}{8}$ " ) were packed with 3% QF-1, 3% OV-210 or 5% SE-30 on 80/100 mesh, acid-washed DMCS-treated Chromosorb G. The operating conditions of the gas chromatographs during analyses were: oven temp. 170°, injection temp. 205°,  $^3\text{H}$  detector temp. 200°,  $\text{N}_2$  flow rate 30 ml/min., standing current  $1.8 \times 10^{-9}\text{A}$ .

All the analyses were made in duplicate and the identities of all the compounds were checked on at least two different columns. Injection volumes were kept constant at 5  $\mu\text{l}$  for both sample solutions and the comparison standards. Where necessary, sample solutions were diluted until the chromatographic responses were within the linear range of the detector. Since all the analyses were carried out under isothermal and isobaric conditions, the peak heights alone were used for quantitation. Identification of PCBs as commercial Aroclor formulations (Aroclor 1242, 1248, 1254, 1260) was based on the best matching of the sample peaks with those of the standard mixtures. The standard Aroclor most closely matching the chromatogram of the sample was used for the quantitation determination.

## RESULTS AND DISCUSSION

The results of the glc analysis of hexane extracts of the fat of seven mutton birds of New Zealand are given in Table 1. The organochlorine compounds DDT and its metabolites DDE and DDD,  $\beta$ -HCH, HEOD and PCBs were found in all the birds, and this is the first reported occurrence of these three latter compounds in the marine wildlife in New Zealand. The mean level of total DDT compounds (17.3 ppm, pp'-DDE 78%) is more than double the value reported by RISEBROUGH et al. (1967). The PCBs were also found (1.83 ppm), again at a higher level than that reported by RISEBROUGH et al. (1968) for birds from the Monterey Bay area of California. It has already been noted in the introduction that these latter workers found 32 ppm of total DDT (92% pp'-DDE) as well as 2.1 ppm PCBs in the fat of a slender-billed shearwater of Australia. More recently, BOURNE and BOGAN (1972) examined the Great shearwater (*P. gravis*) from Trinidad and the Manx shearwater (*P. puffinus*) from Rhum in Inverness, Scotland. These species were found to have small amounts of DDE and PCBs in their liver and muscle tissues; the fat levels were not measured. A chick bird, probably about 4 weeks of age, was also found to have the same organochlorine compounds in the fat as in the adult birds but in much smaller amounts with the exception of  $\beta$ -HCH (Table 1). Since this bird had almost certainly never left its burrow and was being fed by the parent birds, it would seem that these compounds are probably derived from the regurgitated food of the parent birds. No evidence was found for the presence of the fungicide hexachlorobenzene (HCB) in the fat of these birds even though it is used extensively and moreover, it has been reported recently (GILBERTSON and REYNOLDS 1972) to occur in eggs of the common tern (*Sterna hirundo*) which migrates in Hamilton harbour, Ontario, Canada.

The fat samples from the four mutton birds caught on Taiaroa Head, Otago Peninsula, were also extracted with acetone and the extracts after clean-up submitted to glc analysis. The results are given in Table 2 where it will be seen that the levels of pp'-DDE and PCBs are about the same but that the levels of  $\beta$ -HCH are approximately 5 times higher than those found for this compound in the n-hexane extracts (Table 1). This difference is being investigated and will be discussed in a later publication.

It is of interest that all the pesticides reported here, as well as some others in trace amounts, have been found in the fat of some wild birds in the Antarctic regions to the south of New Zealand (GEORGE and FREAR 1966, TATTON and RUZICKA 1967). In view of the presence of relatively high residue levels of six different organochlorine pesticides in mutton birds which are eaten by many New Zealanders, the question of their continued use for this purpose should be closely examined by the appropriate health authorities.

Table 1

Insecticide residue levels (ppm wet wt.) in n-hexane extracts of the fat of seven mutton birds of New Zealand

Bird #	pp'-DDT	pp'-DDE	pp'-DDD	β-HCH	HEOD	PCBs
1	1.04	10.86	0.44	2.72	0.79	1.38
2	1.08	11.18	0.51	4.03	0.97	1.71
3	2.54	16.56	0.98	9.01	0.94	2.44
4 <sup>a</sup>	0.10	1.30	0.04	5.02	0.21	0.05
5	1.20	11.31	0.48	4.12	0.82	1.67
6	1.27	12.85	0.70	5.25	0.93	1.06
7	2.12	18.23	0.73	5.87	1.11	2.72
Mean ±SD <sup>b</sup>	1.54 ±0.63	13.50 ±3.14	0.64 ±0.20	5.17 ±2.17	0.93 ±0.11	1.83 ±0.63
<sup>a</sup> Chick bird						
<sup>b</sup> Excluding bird # 4						

Table 2

Insecticide residue levels (ppm wet wt.) in acetone extracts of the fat of four mutton birds of New Zealand

Bird #	pp'-DDE	$\beta$ -HCCH	PCBs
1	10.56	12.74	1.12
2	13.74	25.04	1.40
3	19.25	39.08	2.05
4 <sup>a</sup>	1.22	18.05	0.11
Mean $\pm$ SD <sup>b</sup>	14.52 $\pm$ 4.40	25.62 $\pm$ 13.18	1.52 $\pm$ 0.48
<sup>a</sup> Chick bird		<sup>b</sup> Excluding bird # 4	

## SUMMARY

The organochlorine insecticides pp'-DDT, its metabolites pp'-DDE and pp'-DDD,  $\beta$ -HCCH, HEOD and PCBs were identified in the fat of mutton birds of New Zealand. The mean levels for six adult birds were: total DDT 17.30 ppm (78% pp'-DDE), pp'-DDT 1.54 ppm, pp'-DDE 13.50 ppm, pp'-DDD 0.64 ppm,  $\beta$ -HCCH 5.17 ppm, HEOD 0.93 ppm, PCBs 1.83 ppm. All the compounds found in the adult birds except  $\beta$ -HCCH, were also present in a chick bird but in considerably smaller amounts.

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