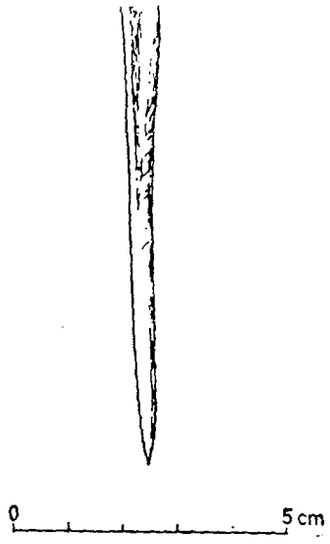

Fig. 2 Bone point found in Pleistocene deposits in Cave Bay Cave.

abundant. There were also some larger marsupials, some of which are not now found on Hunter Island, including the native cat (*Dasyurus* cf. *viverrinus*). A bone point and two pieces of flaked quartz—convincing evidence of the presence of man—were found between 80 and 100 cm below the surface. The bone point is a ground and polished piece of macropod fibula (Fig. 2). Associated charcoal has been carbon dated to 18,550±600 b.p. (ANU-1361).

The final maximum of the last glaciation was responsible for lowered sea levels about 18,000 yr BP and Hunter Island would have been a hill on a land bridge between Tasmania and the Australian mainland[4].

Similar sites in southern Australia with Pleistocene dates, bone artefacts and good faunal preservation are Clogg's Cave at Buchan in south-eastern Australia (17,720±840 b.p., ANU-1044)[5], the Seton site on Kangaroo Island, South Australia (16,100±1,000 b.p., ANU-1221; ref. 6 and R. J. Lampert, personal communication), and the Devil's Lair, Western Australia (24,600±800 b.p., SUA-31)[7]. All of these sites have been the haunt of non-human predators who have contributed their own share of faunal remains. In the Cave Bay Cave, the abundant remains of rodents and small marsupials in the lower levels were probably deposited as pellets regurgitated by owls, and the native cat has probably contributed the bones of larger animals such as bandicoots and possums, which show distinct signs of non-human gnawing.

At Clogg's Cave, the Seton site and the Devil's Lair, there is evidence of the presence of the Tasmanian wolf and devil (*Thylacinus cynocephalus* and *Sarcophilus harrisii*) although there is so far no sign of them at the Cave Bay Cave. The immediate difficulty generated by the presence of these carnivores is that of discriminating the food remains of man from those of the other predators.

A more intriguing problem is suggested by a comparison between these sites and post-Pleistocene cave sites; for instance, the Rocky Cape sites of north-western Tasmania[1]. There, a total of 6 m of shell midden deposit has built up over the last 8,000 yr and there is no evidence of the presence or action of predators other than man (ref. 1 and Rhys Jones, personal communication). There is generally much sparser evidence of human occupation at the older sites in terms of artefacts and stratigraphic features than at Rocky Cape. It seems that [illegible] Australia made less intensive use of cave and shelter sites than his post-Pleistocene descendants. Another important human occupation site of Pleistocene age and with faunal remains preserved is at Lake Mungo—an open site where people camped on the beaches of a lake[8].

The Cave Bay Cave has implications not only for an understanding of the ancestry and development of the unique Tasmanian culture[2], but also for the ecology of Pleistocene man in Australia.

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Identification of metabolic dechlorination of highly chlorinated biphenyl in rabbit

CHLOROBIPHENYLS with one to four chlorine atoms per molecule are metabolised by certain animals, plants and microorganisms but the more highly chlorinated biphenyls are rather resistant to metabolic change[1].

Organochlorine compounds may be identified at low concentrations in crude extracts of natural samples by a high resolution mass spectrometric method involving photoplate detection[2–4]. The method is based on the facts that first, in conditions of high resolution each ion of unique molecular composition is recorded individually and, second, the relatively large mass deficiencies (the actual mass being lower than the closest nominal mass) of both chlorine isotopes. The accurate mass for ^{35}Cl for instance is 34.9688 which accounts for a mass deficiency of -31.1×10^{-3} mass units (m.u.), the corresponding value for ^{37}Cl being -34.1×10^{-3} m.u. These mass deficiencies cause the exact mass of ions which contain these atoms to be at lower masses than ions of the same nominal mass which contain only atoms (that is C, H, N, O) present in most biological molecules. Thus, the high resolution photoplate technique is capable of detecting chlorine-containing mass deficient ions in crude biological extracts. As the photoplate acts as an integrating ion detector it is possible to identify compounds present in low concentrations (≤ 0.01 p.p.m.).

This method has now been applied to the unambiguous identification of metabolites from organochlorine compounds[5] including the detection of trace components. After the usual dosing of the animal, urine, faeces or organs to be examined were extracted with a suitable solvent and a small portion (10–20 μg) of the dried extract was placed in the mass spectrometer sample tubes. Mass spectra from the sample were then obtained by exposing photoplates to ions derived from the crude extract for up to 30 min or

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longer, each at different temperatures (fractional distillation). The developed photoplates were then screened for metabolites (mass deficient ions) manually or by using an automatic photoplate reader coupled with a computer.

Rabbits were fed a diet of food pellets containing 1% 2,2',4,4',5,5'-hexachlorobiphenyl. The feeding time was 7 d and the total concentration of chlorobiphenyl administered was 1 g kg^{-1}. The urine, which was collected during the entire feeding period, was extracted with ether and the extract treated in the manner described earlier. Manually measured data (perfluorokerosene as internal standard, experimental values < 10 p.p.m. from calculated values) showed the presence of two major metabolites (Fig. 1, I, II) formed from the hexachlorobiphenyl by hydroxylation and hydroxylation with concomitant dechlorination respectively. A third, minor, metabolite corresponding to a molecular composition III was detectable only in a limited number of photoplate exposures at about 60° C.

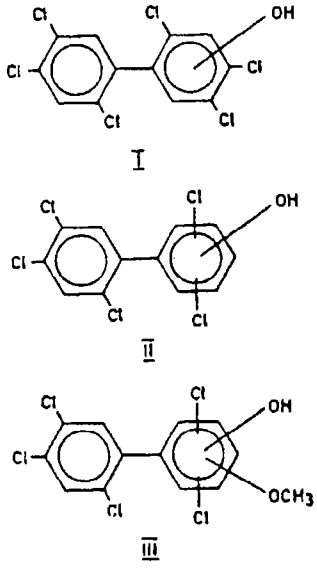

Fig. 1 Metabolites of 2,2',4,4',5,5'-hexachlorobiphenyl.

Figure 2 shows the partial mass spectrum (enlarged photoplate record) of the crude ether extract exposed for 10 min at 60° C. The very mass deficient ions (> 0.1 m.u.) corresponding to the organochlorine metabolites are seen, clearly resolved at lower mass in each cluster of lines corresponding to ions of the same nominal mass. At *m/e* 370 and *m/e* 372 the molecular ion (M$^+$; that is molecular weight calculated with ^{35}Cl) and M+2 ion for compound III are visible. Measurement of the exact mass of the ^{37}Cl isotope peak (M+2 ion) further confirmed the composition of the compound. At *m/e* 374 in addition to the weak M+4 peak of compound III a strong line corresponding to compound I is evident. At *m/e* 375 and *m/e* 376 lines for the ^{13}C and ^{37}Cl isotope peaks of I are obvious.

The advantages of this method in the study of metabolism of organochlorine compounds seem to be first, that no radioactive labelling is necessary because the chlorine atoms act as tracer, second, the method is simple and rapid with unambiguous results so that large scale screening is possible, and third, the danger of loss of metabolite or degradation during separation procedures is minimised and non-volatile products can be detected much more readily than by GC–MS. The usefulness of the method may be considerably improved in this respect by the use of field desorption techniques.

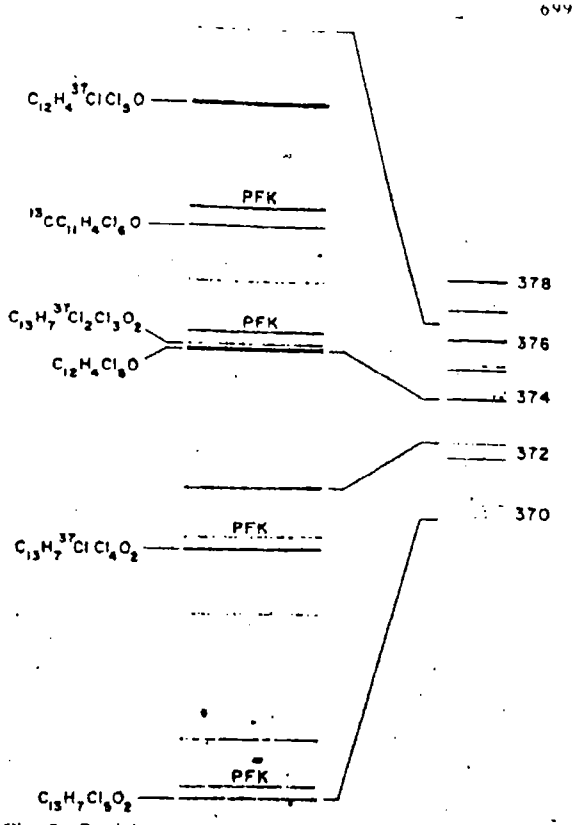

Fig. 2 Partial mass spectrum (*m/e* 370–376; enlargement of photoplate record) of crude ether extract from rabbit urine. Animals were dosed with 2,2',4,4',5,5'-hexachlorobiphenyl. Lines corresponding to compound III are $C_{13}H_7Cl_5O_2$(M$^+$; *m/e* 370); $C_{13}H_7{}^{37}Cl\ Cl_4O_2$(M$^+$+2; *m/e* 372). Lines corresponding to compound I are $C_{12}H_4Cl_6O$(M$^+$; *m/e* 374); $C_{12}H_4{}^{37}Cl\ Cl_5O$(M$^+$+2; 376); $^{13}CC_{11}H_4Cl_6O$(^{13}C isotope peak of M$^+$; *m/e* 375). Lines marked with PFK correspond to ions derived from the mass-marker perfluorokerosene. All unmarked lines correspond to mass positive ions from coextracted natural products.

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