Photochemically Induced Artifact in the Analysis of Soil for Residues of Organochlorine Pesticides

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"Apparent residues" or artifacts, which might mistakenly be attributed to the presence of organochlorine pesticides in soils, have been reported by BOWMAN et al.(1965), PEARSON et al. (1967), OSADCHUCK et al. (1968), DE VRIES et al. (1968), and by FRAZIER et al. (1970). So far, however, the literature has not reported any example of a residue which is "apparent" and simultaneously "increasing" even after the normal clean-up of the soil extract.

In this note we describe observations which seem to be peculiar to an agricultural soil from Modena, Italy, which had to be treated experimentally with alpha-/gamma-chlordane and had to be analysed for its residue content. Our object had been to determine residues of organochlorine pesticides eventually interferring with the analysis of the alpha- and gamma-chlordane (KOVACS et al. 1973); and, whilst this purpose was achieved, our observations showed yet again that what can be determined by gas chromatography apparently as a residue may be due, not to any known residue or metabolite, but to the products of photochemically induced reactions in the solvent phase.

EXPERIMENTAL

The environmental and physico-chemical properties of the soil are given in Table 1.

The soil sample was air-dried, ground in a mortar, and sieved. Then 100-g of this prepared sample was extracted with 1:1 hexane/ iso-propanol following FRAZIER et al. (1970), CARTER and STRINGER (1970), ONSAGER et al. (1970); except that, according to SAHA et al. (1969), SAHA (1970), 20% of water was added to improve recovery. After partition with water, the extract was cleaned up in a Florisil column and concentrated. The Varian Aerograph 1520 apparatus, with tritium foil E.C. detector, was operated with the following parameters:

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column	sylanized glass 180 cm x 3 mm i.d.
packing	10% DC-200 on 80/100 mesh Gas Chrom Q
temperatures	oven 195°C detector 210°C injector 220°C
carrier gas	nitrogen at 100 ml/min
attenuation	10 x 8
injections	5 microlitre by Hamilton 701 microsyringe
recorder	Leeds and Northrup Speedomax W, 1 mv full scale.

TABLE 1

Environmental and physico-chemical properties of the examined soil

Locality	Carpi (Modena) Italy.
Previous crops	Up to 1970 apple orchard, 1970 alfalfa
Sampling date	March, 1971
Sampling depth	0-15 cm
Soil properties	
Bulk density	1.25 g/ml
Organic matter	3.54%
Weight loss at 105° C	1.28%
pH	7.48
Mechanical analysis	clay 28.50%, silt 40.50%, sand 29.92%
Texture	medium-silty soil

Residues of the more commonly occurring organochlorine pesticides, including BHC, heptachlor and its epoxide, pp'-DDT and its derivatives, were found in the soil at concentrations ranging from 0.005 to 0.035 ppm. However, while the final cleaned-up extract was preserved at room temperature in daylight, the height of a peak coincident with that of pp'-DDT increased with time, for example, as between the first injection in the morning and a late afternoon injection. On the next day, upon repeating the injection, the height of this peak became still greater.

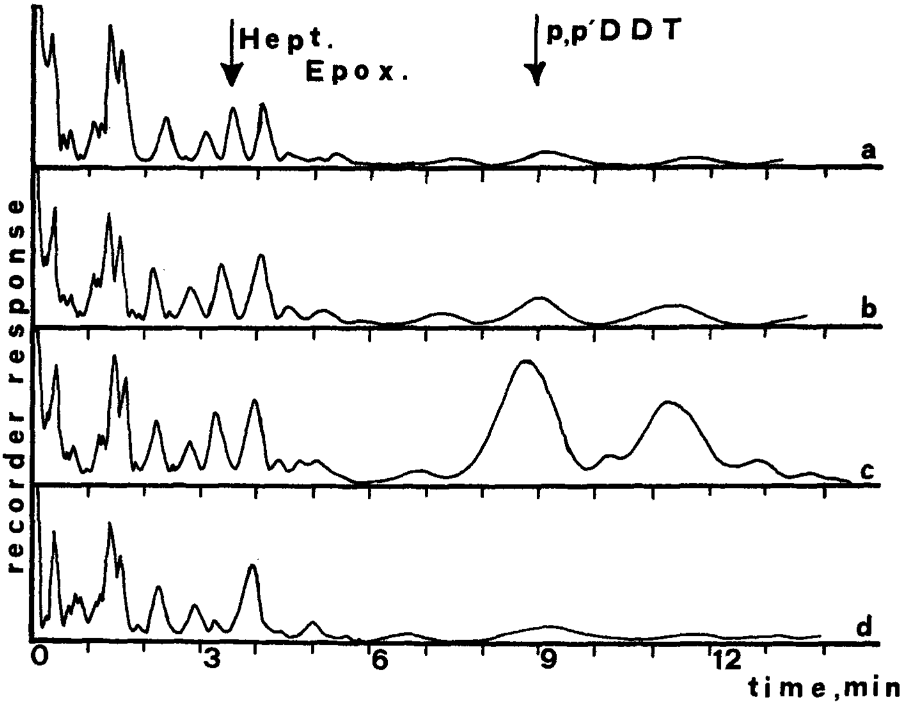

Fig. 1 - GLC behaviour of the extract kept in day light.
a = 0 hrs., b = after 2 days, c = after 10 days, d = the same as in c, but after sulphuric acid treatment and florisil clean-up.

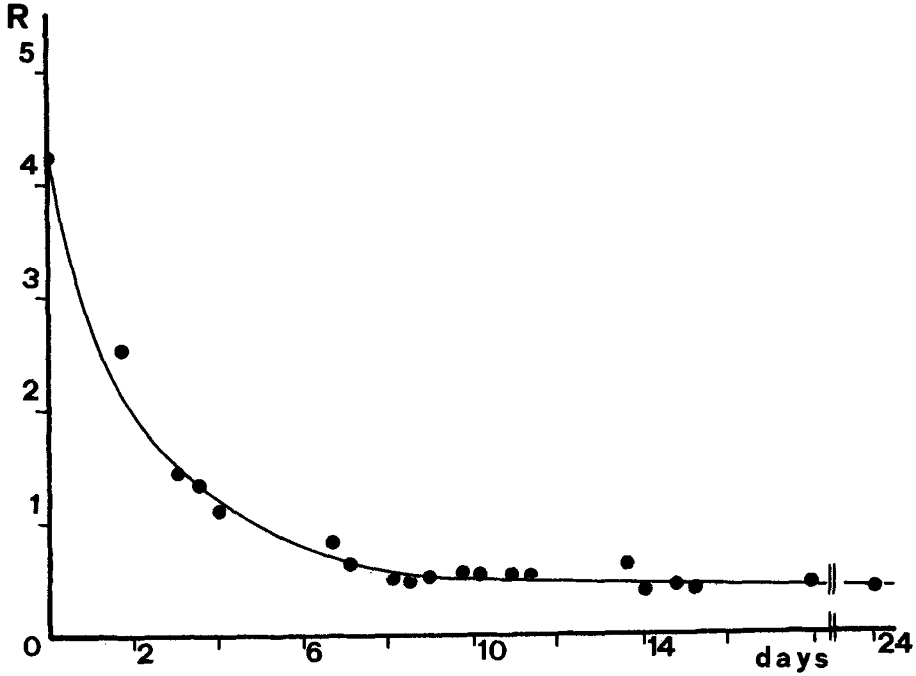

Fig. 2- Heptachlor epoxide/p, p'-DDT height ratio vs. time, for the soil extract kept in day light.

To investigate this phenomenon and the influence of light and temperature, three portions of the soil were separately extracted and the extracts were cleaned-up as already indicated. The final solutions were preserved as follows:

A	at room temperature	(20°C)	in daylight
B	at room temperature	(20°C)	in darkness
C	at -12°C in darkness		

These were injected during the morning and afternoon of each day, except for weekends, during a period of 24 days.

Throughout this period the chromatograms of B and C showed no change for pp'-DDT nor for any other peak. In consecutive chromatograms of solution A the peak coincident with pp'-DDT increased gradually, finally attaining more than ten times its initial height and corresponding to a change (calculated in terms of pp'-DDT) from 0.032 ppm to a constant value of 0.42 ppm on the eighth day after extraction (Fig. 1 a,b,c). By way of further illustration, Fig. 2 shows how the ratio of the heights of the heptachlor epoxide/"pp'-DDT" peaks decrease asymptotically. Meanwhile, where none had been detected initially, other peaks gradually appeared in the consecutive chromatograms of solution A, although their retention times on the DC-200 column did not correspond with any of the more commonly occurring pesticides or metabolites (Fig. 1 b,c). These peaks appeared independently of all others which did not change on the chromatogram. Solution A gradually became brown.

After 24 days solution A was treated with a little concentrated sulphuric acid, and was then cleaned-up again in a small Florisil column as suggested in the VELSICOL procedure for determination of chlordane residues. Thereafter the spurious peaks disappeared, leaving for pp'-DDT a peak identical in height with that of the initial extract at zero time (Fig. 1 d), and when this solution was kept in daylight the peak did not increase again.

DISCUSSION

Although we have not identified the compound(s) formed gradually by photochemical reaction, it is difficult to suppose them to be natural chlorinated organic comounds of vegetable origin in the soil (HYLIN et al. 1969). Probably the compound(s) formed are unsaturated or polynuclear compounds which undergo photochemical reaction.

Some possible effects of u.v. irradiation upon organochlorine residues in solution and in the solid phase have been discussed by BANKS and BILLS (1968) and by GLOTFELTY (1972) respectively, with reference to the identification of pesticides. Under intensive irradiation some variations in composition occurred; however, as one compound was transformed into another, a decrement in one peak coincided with an increment in another. The mechanisms and the products of the photochemical decomposition of DDT were discussed by MOSIER et al. (1969).

With a view to discovering other photochemical effects we have examined samples of soil of many differing physical compositions and of varying organic content, but we have not so far encountered any other spurious peak coincident with that of pp'-DDT. Since DC-200 is commonly used, and since the deliberate storage of solutions and extracts in darkness is uncommon practice, spurious peaks might perhaps photochemically increase and erroneous values might be inadvertently attributed to pp'-DDT. The purpose of this note is to draw attention to such a risk.

SUMMARY

After solvent extraction of soil and clean-up of the extract there is a possibility of reactions being induced photochemically in the solvent phase. In one recent instance such reactions, proceeding relatively quickly during 6-8 days, produced unknown compound(s) whose retention time in a column of 10% DC-200 on 80/100 mesh Gas Chrom Q coincided with that of pp'-DDT. Such interference could be eliminated by later treatment of the extract with concentrated sulphuric acid.

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