Stream Pollution by an Organomercury Compound

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Most studies of organic chemical residues in soils have been confined specifically to pesticides or particular industrial chemicals, but in this work we report some general combined gas chromotography - mass spectrometry analysis of various agricultural soils, in which we looked for well known pesticide residues as well as other organic chemical residues in the soils. One aim was to discover the minimum workup procedure necessary for intellegible GC/MS results.

Experimental

Soil samples were collected for fifteen vineyard, cornfield and stream sediment areas, and were extracted (Soxhlet) with both benzene and acetonitrile according to modifications of the Ontario Food & Drug Directorate (1969) methods. The benzene extracts were cleaned up on a Florisil column with hexane, 1:1 hexane/dichloromethane, 1:1 hexane/ether and ether as eluting solvents. Prior to acetonitrile extraction soils were moistened with 15 per cent water. The concentrate was then extracted into 200 ml of hexene in the presence of 10 ml of dichloromethane, 20 ml of phosphate buffer, 50 ml of saturated sodium sulphate solution and 125 ml of water. The concentrated hexene extracts were then treated as were the benzene extracts.

Concentrated extracts were then subjected to a GC/MS analysis using a Pye 104 GC(5 ft x ¼ inch glass column with 3% SE 30 on 100/120 on Varaport 30) interfaced with a silicone membrane separator to an AEI MS-30 double beam mass spectrometer run at 10 seconds/decade, 1000 resolution, 70 ev ionization energy with perfluorokerosene as mass marker in the second beam. The Eight Peak Index of the Mass Spectrometry Data Center (MSDC 1970) was used as a primary mass spectrum reference sourse.

Results and Discussion

Table I shows respectively positively identified, non trivial compounds of pesticidal and probably non-pesticidal origins while Table II show several compounds whose identity is less certain due

Bulletin of Environmental Contamination & Toxicology,
Vol. 16, No. 4 © 1976 by Springer-Verlag New York Inc.

TABLE I

Compounds Positively Identified

Compound	Sample Area Type	No. of occurances (15 areas
Pesticidal Origin		
DDT	vineyard, cornfield	7
DDE	vineyard, cornfield	10
DDD	vineyard, cornfield	6
4,4'dichlorobenzophenone	vineyard	1
Linuron	vineyard	1
dichloroaniline	vineyard	2
3,4 dichloroformylanalide	vineyard	2
Atrazine	cornfield	1
Elemental sulphur	vineyard, cornfield & stream sediments	15
Non-pesticidal origin		
di-nbutylphthalate	vineyard, cornfield & stream sediments	7
diallylphthalate	vineyard, cornfield	3
triphenyl phosphate	vineyard	1
ethyl benzene	vineyard	2
tridecane	vineyard	2
phenylα -naphthylamine	vineyard, cornfield	3

TABLE II

Other Compounds Detected

Triphenylene	vineyard	1
2,6 di-tbutyl-4methylphenol	vineyard, cornfield	6
4,6,8 trimethylnonene	vineyard	1
n-alkanes	vineyard	1
n-butylbenzene	vineyard, cornfield	4

to small ammounts present, but where spectra correspond to those of known compounds.

DDT and three of its degredation products, DDE, DDD, and 4,4'dichlorobenzophenone were detected four years after the last application of DDT to any of the areas sampled. As Linuron, dichloroaniline and 3,4dichloroformylanilide were detected in the same sample area, this arroused suspicion that the three might be related, though laboratory photolysis of Linuron did not produce either of the other two compounds. Further study of the 3,4dichloroformylanilide, first reported by KEARNEY and PLIMMER (1972), is probably warranted in relation to urea type herbicides such as Linuron and Diuron, the latter, but not the former having been used in the area sampled. The presence of atrazine, but none of its known metabolites suggests the persistance of this herbicide. Elemental sulphur, found in all samples collected was probably of agricultural pesticidal origin.

The presence of a series of phthalates is not surprising in view of their widespread industrial use as plasticisers etc. Their occurance is common in biological and environmental samples, and no single source is likely identifiable, although FUKUTO and SIMS (1971) have suggested possible routes to their formation in soils. The remaining compounds again cannot be traced to one specific source. The triphenyl phosphate may have its origin in many manufactured products which may have been used in the field, but the detection of phenylαnaphthylamine, a potentially carcinogenic material, has never been reported in soil extracts.

None of the compounds in Table ii have any particularly apparent source and none seem particularly dangerous. Ammong other compounds which could not be identified were three having apparent molecular ions at m/e 360, 436, and 451 respectively containing 2, 2 and 1 bromine atom.

Conclusion

A GC/MS study of residues in general can be very rewarding as shown by some of our unexpected discoveries, but due to the vast ammount of data collected, the best way to effectively use the technique for routine survey work must be with the aid of an interfaced computer complete with library search capabilities.

Acknowledgements

The Government of Ontario and the National Research Council of Canada are thanked fo financial support.

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