Monsanto

FROM (NAME & LOCATION) W. R. Richard - Research Center

DATE October 8, 1969 CC

SUBJECT

REFERENCE

TO D. R. Miller

Attached are the first of several internal papers dealing with various aspects of the "Aroclor pollution" problem. The purpose is to stimulate thinking and encourage an input of ideas as to what steps should be taken to minimize adverse effects on our business.

Anyone wishing to put his oar in is invited to do so, either by writing his own white paper or by commenting on subject matter which has already appeared. Papers may or may not be "in depth" reviews of a specific topic. We anticipate that short concise reports will be of most value, but anything contributing to the stated objective will be satisfactory.

W. R. Richard

ms

MONS 098166

IN-10 REV 11 65

SOME TENTATIVE RULES FOR PREDICTING BIOLOGICAL REFRACTIVITY OF HALOGENATED AROMATICS

Q. E. Thompson

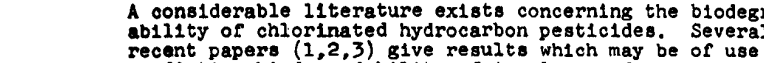
Evidence to date indicates that among chlorinated biphenyls those molecules containing 4 or more chlorine atoms per molecule are the chief offenders insofar as biological contamination is concerned. The higher Aroclors are thus said to be "refractive" with respect to natural degradative processes. The extent to which lower chlorinated biphenyls are refractive remains to be determined.

A considerable literature exists concerning the biodegradability of chlorinated hydrocarbon pesticides. Several recent papers (1,2,3) give results which may be of use in predicting biodegradability of Aroclors and some possible Aroclor substitutes. In brief, the findings may be summarized as follows.

A. Aliphatic Hydrocarbons: Aliphatic materials containing one chlorine atom are not refractive. Additional chlorine substitution markedly increases refractiveness (Dieldrin, Aldrin, Heptachlor, DDT) although the latter may still be somewhat degradable under anaerobic conditions.

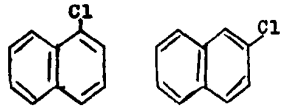
B. A Benzene Nucleus

1. When not substituted with at least one C-atom or one O-atom, a benzene ring becomes refractory with only one Cl-atom attached. DDT and DDD seem to be special cases in which refractiveness is increased by the high degree of chlorination in the aliphatic portion of the molecule, i.e.

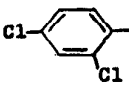


2. A benzene nucleus substituted by one C-atom or one O-atom generally requires at least two chlorines before it becomes refractive.

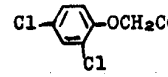
Examples:

a) 

not refractive

b) 

almost but not quite refractive

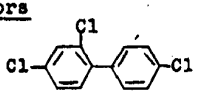
c)  not refractory while the 2,4,6 trichloro analog is.

d) Ar-O substitution alleviates refractivity more than Ar-C substitution (cf b vs. c)

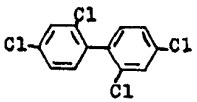
e) An isomer with chlorine closest to the point of substitution will metabolize slower than one with chlorine substitution farther away (1-chloronapthalene slower than 2-chloro isomer, o-chlorobenzoic acid slower than p-chlorobenzoic acid).

Applying the preceding observations to the Aroclor situation permits the following predictions.

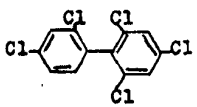
A. Aroclors

1.  probably not refractory - neither ring has more than two chlorines.

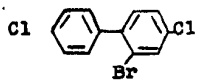
~1242 (41% Cl)

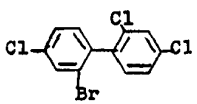
2.  borderline - probably not completely refractory.

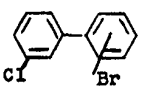
~1248 (48.5% Cl)

3.  refractory -

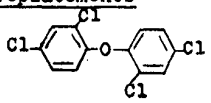
B. Bromochlors - Would conform to the same rules.

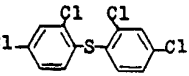
1.  equivalent to Aroclor 1248 would no longer be borderline but should be at least as degradable as the $(Cl)_3$-biphenyl.

2.  equivalent to 1254 in physical properties but approximately the same as Aroclor 1248 in refractivity.

3.  equivalent to 1242 in physical properties but less refractive.

C. Other possible Aroclor replacements

1. Diphenyl ethers -  less refractory than $(Cl)_4$-biphenyl

2. Diphenyl sulfides -  probably still less refractory than the corresponding oxygen ether since $-\ddot{S}-$ is more electron releasing than $-\ddot{O}-$.

Undoubtedly, additional factors such as water solubility, hydrolytic stability as well as oxidative and light stability also influence the extent of environmental refractiveness. Thus, for example, highly chlorinated materials which could hydrolyze readily to chlorophenols (pentachlorophenol, etc.) might be expected to be substantially less serious long term contaminants than a material of similar or lesser chlorine content which resists the initial hydrolytic attack. Specific data on these points are however lacking at present.

October 6, 1969

REFERENCES:

1. R. W. Okey and R. H. Bogan, "The Apparent Involvement of Electronic Mechanisms in Limiting the Microbial Metabolism of Pesticides", J. Water Pollution Control Federation, 37, 692 (1965)

2. D. W. Hill and P. L. McCarty, "Anaerobic Degradation of Selected Chlorinated Hydrocarbon Pesticides", ibid., 39, 1259 (1967).

3. H. G. Schwartz, "Microbial Degradation of Pesticides in Aqueous Solutions", ibid., 39, 1701 (1967).

SCHEMES FOR THE

RECOVERY AND DISPOSAL OF AROCLORS

R. W. Weiss

Improvement of analytical techniques has arrived at a point where parts per billion of stable chlorinated hydrocarbons can be identified. This led to discovery of DDT and more recently of PCB (polychlorinated biphenyl) in the environment, and whereas the harmful effects of DDT are known, PCB's are quite naturally suspected.

This and the current emphasis on pollution prompts the question: what can and should be done to reduce the amount of Aroclor that now finds its way into the environment. Two obvious ways will be dealt with in the following sections: Recovery of Aroclor from the environment by absorption of an organic phase or solute from the medium, air or water. Secondly, the innocuous disposal of spent Aroclor containing fluids will be considered.

I. Recovery of Aroclor dissolved or dispersed in waste water.

Recovery of Aroclors from water or air can be achieved by means of adsorbents or absorbents. Highly selective adsorbents are desirable for an economic process. Active adsorbents are expected to be found under activated clays or earths, zeolites, alumina, dicalite, active carbon, acylated cellulose or other polymers. Aroclor can also be preferentially absorbed on materials like tar, paraffins or waxes. The adsorbing or absorbing agents will be admixed with waste water and allowed to settle in tanks and lagoons. An alternative are suitably packed towers or pipes. The techniques involved are now commonly applied in the treating of industrial or household wastes.

From expensive adsorbents Aroclor will have to be recovered by solvent extraction; cheaper material can be disposed of like any other solid waste after removal from tanks and towers, drying or pressing.

A screening program for the most suitable absorbers will be greatly facilitated by the excellent and sensitive analytical techniques available to identify Aroclors.

II. Disposal of Aroclors

Large amounts of Aroclors will have to be disposed of in the foreseeable future at a rate of 10 million pounds a year. A considerable fraction of this will be contaminated with mineral oil and phosphate esters from our industrial hydraulic business. The following methods for disposal have been suggested.

A. Oxidative Degradation

The simplest method of disposal one would consider is burning in presence of a combustible carrier in a hot furnace. There evolve considerable quantities of highly corrosive hydrochloric acid and chlorine which have to be scrubbed. Hydrochloric acid could in principle be recovered. The combustion can be carried out in presence of chlorine binders. The use of lime for this purpose requires a suitable setup for cleaning the furnace. Also feasible is the use of scrap iron or tin cans as binders. The chlorine from Aroclor presumably could be recovered as ferric chloride and stannic chloride.

B. Pyrolytic Degradation

Pyrolysis under reducing condition with Ni catalyst and ammonia could lead to progressive dehalogenation above 270°. Exhaustive chlorination above 300° should produce lower chlorinated olefins, e.g. C_2Cl_4, C_3Cl_6, etc. The destructive chlorination technique might also be promoted by and carried out in conjunction with a tin recovery operation using tinned cans. Thus pyrolytic overchlorination of waste Aroclor in the presence of scrap Fe° and Sn° would afford $FeCl_3$, $SnCl_4$ and the lower perchlorinated alkanes (i.e. C_2Cl_6) all of which are volatile, separable and have recovery value.

C. Other Miscellaneous Methods

Other methods suggested for disposal of Aroclor include roasting with sulfidic ore, possibly in presence of coke; adsorption on clay and burning, adsorption on suitable carriers and burying and partial condensation on an acidic catalyst increasing the molecular weight to render the material innocuous.

The methods under A. are suitable for contaminated Aroclor whereas the processes under B. and C. are probably only practical with material having a high content of Aroclor.

October 8, 1969

MONS 098172