SF
Aroclors

From Report of the DDT Advisory Committee to Ruckelshaus

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ANALYTICAL INTERFERENCE WITH THE DETERMINATION OF DDT BY POLYCHLORINATED BIPHENYLS IN THE ENVIRONMENT

A number of polychlorinated biphenyls (PCBs) have been commercially available in the U.S. since 1930. Currently PCBs are being marketed by Monsanto Chemical Company under the trade name of Aroclor with the percentage chlorine designated by the last two digits of their four digit identification number. The first two digits indicate the type; for example, the 1200 series for the biphenyls which are the most common. In the environment, PCBs behave like DDT and many other organochlorine pesticides. PCBs are very stable, resist degradation, are insoluble in water and highly soluble in lipids. It is inevitable, therefore, that PCBs would be concentrated in biological systems since they possess all the characteristics associated with DDT and its metabolites. PCBs are extracted and detected by the same techniques employed for the organochlorine pesticides and consequently residue chemists have had to develop adequate analytical procedures to separate them from associated chlorinated pesticides, prior to quantification.

Prior to 1967, PCBs were either misidentified as specific pesticides such as DDT or viewed as unidentified compounds, possibly unknown pesticidal metabolites. PCBs were previously evident as extraneous, unidentified peaks in GLC chromatograms of extracts of marine fish and birds, until identified in 1966 by Jensen and by Widmark in 1967 and Holmes et al. (1967). It was not until a year or two later that federal monitoring and surveillance sample analysis began to include any routine screening for PCBs, in addition to the usual screening for chlorinated pesticides. The timelag between use and the detection of

PCBs in the environment can be attributed to accumulative concentration over the years and/or recent sophistication in analytical techniques and instrumentation.

The presence of PCBs, DDT and DDT-like moieties in environmental samples presents the residue chemist with both a qualitative and quantitative analytical problem. Because of the similiarity of retention times of gas chromatographic peaks, concentration of certain PCBs can interfere with the accurate determination of p,p'-DDT, p,p'-DDD and p,p'-DDE depending on the type of GLC column employed. One of the most common PCBs found in the U.S. environment, Arcolor 1254, interferes with the GLC peaks associated with p,p'DDT and p,p'DDD and p,p'DDE. Another common PCB, Aroclor 1260, interferes the least with peaks associated with p,p'DDE. The seriousness of the PCB interference or bias in DDT, DDD, and DDE quantifications per se by gas chromatography is dependent on several interrelated factors such as the polarity of the gas chromatographic column packing, the percentage of chlorine in the particular Aroclor being chromatographed, and the concentration and ratio of PCB and DDT and metabolites in the extract.

Considering the most common Aroclors found in the environment, such as 1254 and 1260, unless the ratio for PCB:DDT concentration in the sample is greater than 2:1, the PCB bias to accurate quantifications of DDT and its metabolities by electron capture gas chromatography will be relatively negligible. The PCB bias will interfere and can become serious if the ratio of PBC:DDT concentration in the environmental sample approaches 5:1 or higher. One reason for

this is that electron capture detector usually employed in the gas chromatography is considerably less sensitive to the PCB mixture than to individual DDT compounds on a comparative weight basis.

The analytical problems associated with separating PCBs from DDT, DDD and DDE have largely been overcome in the past few years. It cannot be said that the extraction and isolation recovery of PCBs is absolutely quantitative but it can approach 80-90% if adequate preliminary procedures are carefully followed. Separation of PCBs by column chromatography using Florisil has been reported for several pesticides by Reynolds (1969), but p,p'-DDE is eluted along with the PCBs. Armour and Burke (1970) have developed a separation of the DDT analogs and PCBs by employing a silicic acid column. Identification of these interfering PCBs by combined gas chromatography - mass spectrometry has been reported by Widmark (1967) and more recently by Bagley et al. (1970) using a thin-layer chromatography preliminary separation followed by GLC-mass spectrometry. Separation and identification of DDT analogs in the presence of PCBs by two dimensional TLC has recently been proposed by Westfall and Fehringer (1970).

Based on current data, results obtained from environmental monitoring and market surveillance sampling of various foods and other published data, it appears that the most serious chronic PCB contamination is in fish and fish-eating birds. Apparently PCBs are widely distributed among marine birds which are the terminal carnivors of a complex mesh of food chains in the sea. Concentrations of DDT and PCB in marine birds tend to be an order of magnitude higher than in marine fish according to Risebrough et al. (1968). Occasional acute PCB contamination occurs in various areas of our environment leaving the

mistaken impression that serious PCB contamination is a universal problem. Most of the acute residues of PCBs found to date can be attributed usually to inadvertent or accidental industrial causes. A recent example of acute PCB contamination in poultry was traced to contaminated fish meal resulting from unnoticed leakage of PCBs in the sterlizing vats. The PCB contamination found currently in fruits, vegetables, and in most samples of milk, cheese and eggs appear to be relatively insignificant, at least as to posing a serious analytical bias to DDT or DDE determinations of these samples.

Undoubtedly, prior to recent cognizance by the chemists of possible PCB interference, some of the peaks or portions of them could have been erroneously attributed to DDT, DDD or DDE presence in the sample, particularly if adequate conformation procedures were not followed. In many environmental samples, the seriousness of the PCB bias on the DDT quantification is dependent on the significance of the DDT concentrations in the sample. According to Risebrough et al. (1969), although p,p' DDE is the most abundant of the DDT compounds in the environment, there appears to be no significant PCB interference in DDE quantifications. Consequently, he concludes that total DDT residues in the past, before the extent of PCB interference was known, would not be greatly changed after correction for this interference.

In summary and based on the rather limited knowledge currently available, it would appear that generally the PCB bias to the analytical determination of DDT, DDD or DDE has been and continues to be insignificant in most foods, feeds and environmental samples. An exception, where it

appears there may sometimes be serious analytical bias due to the presence of high ratios of PCB:DDT, would be fish and fish-eating birds and any associated byproducts.

Recent reports of PCB content in human adipose tissues indicated that the PCB problem is not of widespread concern. Undoubtedly isolated cases of abnormally high PCB levels will continue to be reported but these are considered to be the exception rather than the rule.

The degree of carcinogenicity of the various common environmental PCBs remains to be elucidated as well as a more complete evaluation of their relative toxicity to mammals. There is limited information that toxicity is associated with the percentage of chlorine but generally the Aroclors are less toxic to mammals than DDT and its metabolites.