Plasticizers as Interferences in Pollutant Analyses

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The growth of the synthetic organic chemical industry in the past fifty years has led to great increases in both amounts and numbers of organics incorporated in many new products released for use. The dispersal of organics from the site of use to the total environment is well exemplified by chlorinated hydrocarbon insecticides. However, the polychlorinated biphenyls (PCB's) were then found to have dispersed in like manner to mislead analysts in their work on chlorinated hydrocarbon insecticides (FISHBEIN, 1972). With ever improving sensitivity of analytical methods and instruments, other synthetic organics ought to appear as interferences or real pollutants, especially when GCEC is used. Several investigators (BEVENUE, et al., 1971; GIAM & WONG, 1972; LEVI & NOWICKI, 1972) found contaminants in laboratory reagents, adsorbents, filter paper and glassware easily detected by GCEC, but did not identify compounds to aid others encountering the contaminants. Recently, phthalic acid esters (PAE's) have been reported as laboratory contaminants (ASAKAWA & GENJIDA, 1970; MAYER, et al., 1972; OGNER & SCHNITZER, 1970) and environmental pollutants (CORCORAN, 1973; GROSS & COLONY, 1973; THOMAS, 1973). Soon after work was begun on some of the above pollutants or contaminants in aqueous solution, interferences were encountered under conditions not associated with the usual sources of contamination. Consequently, examination of the laboratory for new routes and sources of contamination had to be carried out, and the identity and analytical behavior of any contaminants found had to be determined.

MATERIALS AND METHODS

Gas Chromatography, Electron Capture Detection. Varian 1400 and 1700 gas chromatographs with tritium foil were used with 0.32 cm i.d. glass columns mentioned in the text except for the column of OV-17, which was in a Varian 2100 with nickel foil.

Gas Chromatography, Mass Spectroscopy. A Finnigan Model 3000 Gas Chromatograph Peak Identifier with 0.32 cm i.d. x 152 cm column of 2% OV-1 on 60/80 Chromsorb G was used to confirm PAE's in air fallout samples following standard procedures.

Chemicals. DBP and DEHP were commercially available products and BBP and BPBG were supplied by Monsanto, St. Louis, Mo.* These PAE's had essentially one peak on GCEC although both mixed PAE's had traces of DBP. Aroclor 1254 and 1242 (Registered Trademarks, Monsanto Co.) were from samples supplied to others by Monsanto.

Chlorinated insecticides were analytical standards in use at

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the Davis laboratory (only p,p' isomers of the DDT group were tested). Phenoxy herbicides were analytical standards for technical material supplied by Dow Chemical Co., Midland, Mich.**

Solvents of C.P. grade were distilled through an all glass system having a 60 cm column of glass beads into glass bottles with an aluminum foil shield over the receiver-bottle joint. Usually such distilled solvents could be concentrated 100 fold without interferences from PAE's but the solvent peak on GCEC tailed considerably. Consequently distilled solvents were used for cleaning glassware and unconcentrated samples. Pesticide grade solvents were used for samples requiring concentration. Solutions of the pollutant standards were made in pesticide quality hexane for comparisons of retention times and responses on GCEC.

<u>Collecting and Sampling for Analysis of Contaminants</u>.

1. <u>Reagents</u>. Various grades of solvents were tested by GCEC either as is or after 100 fold concentration if no interferences occurred when unconcentrated. Contamination of diethyl ether, anh., was checked by taking 2 ul samples from several cans in use and a number of cans immediately after opening.

Inorganic reagents mentioned were tested by first extracting the dry reagent and analyzing the extract using several columns on GCEC. Then sufficient water was added to dissolve the reagent, and the solution was shaken with hexane, which was analyzed again by GCEC.

2. <u>Air and Air Contamination Sources</u>. The air conditioning outlet in the laboratory, the air conditioning inlet to the building and one of the filters for the system were sampled by rubbing hexane rinsed applicator swabs over the surfaces and soaking swabs in hexane. Fabric from two filters was cut loose using scissors and tweezers, and the pieces were extracted in hexane. Analysis of PAE's in the hexane was done by GCEC. A piece of caulk from metal window frame-wall joint in the laboratory was cut loose and placed in hexane, which was then analyzed by GCEC.

Glass beakers or dishes were rinsed with distilled acetone and Nanograde hexane. A 5 ul injection of the residual hexane after pouring off the bulk showed no contaminants detectable on GCEC. An oil filmed collector was prepared by spreading 10 ml of 1% Squibb mineral oil in hexane on an 20 x 20 cm Pyrex baking dish and allowing the hexane to evaporate with gentle rocking of the dish. After being exposed on laboratory tables for 20 hr or more, the dishes were rinsed with Nanograde hexane, and samples collected for analysis by GCEC on several columns. Combined samples from unfilmed dishes gave sufficient material for confirming the PAE's by Finnigan GCMS.

3. <u>Hand to Glassware Transfer</u>. Five, 10 ul syringes in five laboratory rooms were taken by tweezers and placed in centrifuge tubes containing 10 ml of hexane, which rinsed the whole barrel. Analysis was done by GCEC with all but the OV-17 column in Table 1. Another syringe was handled after the hand was rubbed over a plastic sandwich bag, Tygon tubing and electric cord. This syringe was then rinsed in hexane, which was analyzed by GCEC.

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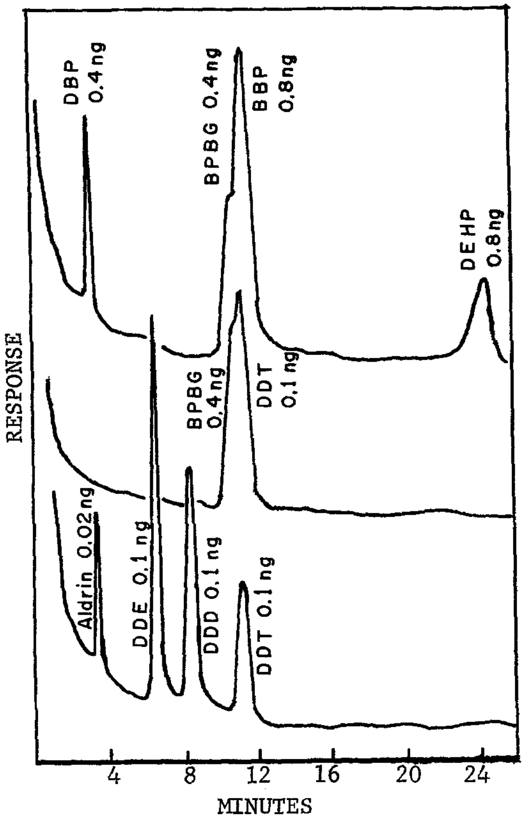

Fig. 1. GC separations of phthalates and insecticides on 4% SE-30 on 60/80 Gas Chrom Q.

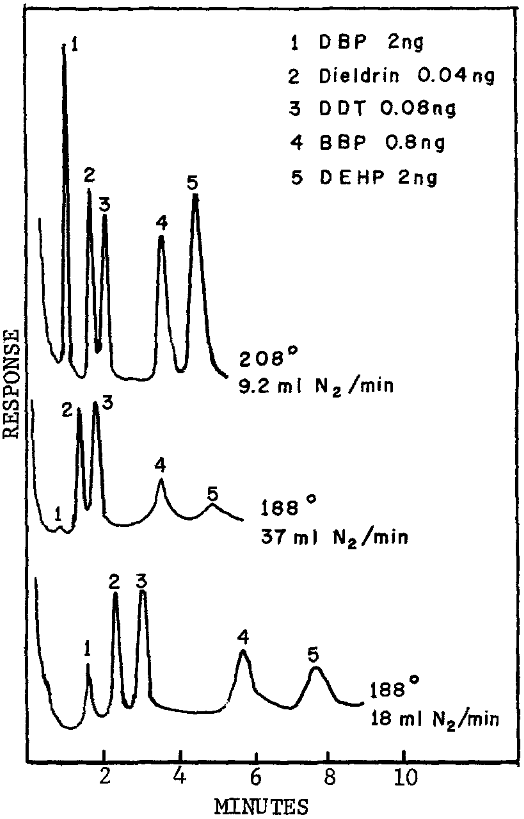

Fig. 2. GC behavior of phthalates and insecticides on 2% QF-1 on 60/80 Gas Chrom Q.

RESULTS

As soon as the chromatograms in Fig. 1 are seen, PAE's are revealed as being extremely serious interferences in environmental p,p'-DDT analyses for both butyl benzyl phthalate (BBP) and butyl phthalyl butyl glycolate (BPBG) are reported to be used in considerable quantities (FISHBEIN and ALBRO, 1972). Four liquid phases listed in Table 1, other than the standard methyl silicones were found to separate BBP cleanly from p,p'-DDT, but BPBG's retention time was within 6% of p,p'-DDT's on all except the QF-1 column. With such close retention times, low level quantitation and identification of p,p'-DDT and BPBG using 2 or even 3 columns on GCEC becomes a dubious proposition.

Lindane, heptachlor and its epoxide, dieldrin, chlorobenzilate and methoxychlor did not interfere with the four PAE's on the column of 4% SE-30. However, interferences between several of these PAE's and esters of the herbicides 2,4-D and 2,4,5-T did occur as Table 2 shows two cases in brackets where identification would be obstructed and two cases underlined where quantitation might be hindered, when using a column with a methyl silicone liquid phase.

TABLE 1
Columns Tested for Separation of p,p'-DDT from Interfering PAE's

Column + Temperature	Relative retention times compared to DDT taken as 1 BPBG	 BBP
4% Se-30 on 60/80 Gas-Chrom Q, 185 cm, 220°C	0.96	1.02
1.5% OV-17 on 100/120 Varaport HP Chromsorb, 185 cm, 190°C	0.97	1.21
2% QF-1 on 100/120 Chromsorb G, DMCS, 185 cm, 190°C	2.1 (DBP, 0.52; p,p'-DDE, 0.54)	1.8
2% Neopentyl glycol succinate on 60/80 Gas-Chrom Q, 123 cm, 210°C	1.05	1.27
5% Carbowax 20M on 60/80 Gas-Chrom Q, 123 cm, 200°C	0.94	1.25

TABLE 2
Relative GC Retention Times of Phthalates and Major Peaks of Technical Esters of 2,4-D and 2,4,5-T on 4% SE-30 Column

Phthalates		Ester	2,4-D	2,4,5-T
DBP	1.8	Butyl	1.15; 1.35	2.0; 2.25
BPBG	{5.9}	Butoxyethyl	3.5	4.9 {5.7}
BBP	{6.4}	Isooctyl	4.0; 4.7	{6.4} 7.5
DEHP	13.3	Butoxypropyl	3.0	4.7; 12.0

From Fig. 1, relative responses for the chlorinated insecticides on GCEC would appear 0.5-2 orders of magnitude greater than the responses for PAE's. However, further work using a column of 2% QF-1 on 60/80 mesh Gas Chrom Q revealed that PAE responses are very dependent on nitrogen flow while the responses of chlorinated insecticides are essentially independent (Fig. 2). This variable response may explain why PAE's are not always interfering in analyses, and may be worth further examination for reducing PAE interferences in pollutant analyses using GCEC.

With two PAE's obviously being serious interferences with p,p'-DDT, sources of PAE contamination in the laboratory needed to be defined as peaks corresponding to dibutyl phthalate (DBP), BBP and di-2-ethylhexyl phthalate (DEHP) were appearing on GCEC chromatograms when background samples were run. Checks of several non-chlorinated solvents of U.S.P. or C.P. grade revealed major responses on GCEC corresponding to these PAE's similar to solvent problems encountered by ASAKAWA & GENJIDA (1970). Distilling such solvents through a 60 cm column of glass beads appeared to remove the PAE's, but 100 fold concentrations still showed variable traces suggesting recontamination was occurring easily. Two opened cans of diethyl ether, anh. were found with ppm levels of BBP and DEHP, but a number of other cans had levels after concentration that could not be differentiated from recontamination levels seen from 100 fold concentrations of several other solvents. Plastic caps for the ether cans did not exhibit more than traces of BBP and DEHP so sloppy lab technique seemed to be responsible. However, HALL (1973a) indicated that his tests revealed some cans of diethyl ether, anh., had severe contamination by these PAE's when tested immediately after opening, but most cans were essentially PAE free, thus locating the source of this contamination.

The inorganic reagents, sodium chloride, several grades and containers; sodium sulfate, anh., several grades and containers; sodium bicarbonate, anh., ACS grade in plastic bottle, potassium carbonate, anh., ACS grade in plastic bottle, magnesium sulfate, anh., reagent grade in plastic bottle, frequently showed low levels (0.01-0.1 ppm) of DBP but not much of the other PAE's matching a report of MAYER, et al. (1972). No correlation between grade or container appeared, but some indication that used or older bottles had higher levels appeared. The cleanest sodium sulfate was a low nitrogen grade in a plastic bag. However, a major difference was found between the extracts of the dry sulfates and their solutions as several prominent early eluting peaks appeared only in solution extracts on GCEC. One of the peaks matched with diethyl phthalate on one column, but not on another. The last prominent peak was thought to be due to sulfur, a reported contaminant in sodium sulfate (PEARSON, et al., 1967), but did not disappear when the extract was treated with copper powder. Attempts to get pure compounds from the water extracts were thwarted when concentrated extracts passed through a GC decomposed in even a cold thermal conductivity detector.

As soon as the air conditioning system samples passed thru the GC, sources of BBP and DEHP were revealed as impregnated air conditioner filters used in the building. One type of filter had BBP, another DEHP and a third little if any PAE's. The grime on the outlet in the laboratory had large quantities of both PAE's. The caulk was revealed as a source of Aroclor 1254 by an exact match with standard. Previous work (SINGMASTER, 1973) had revealed that caulk containing PCB's in metal, glass and marble joints on buildings could led to the entire exterior surface being filmed with PCB's. However, the caulk around the laboratory window was on rough concrete and had not filmed the glass, which probably prevented high levels of contamination in the laboratory.

Several attempts to trap the levels of these plasticizers in air by passing it through solvent did not indicate a very high load of them, but trapping efficiency may have been poor. The simple exposed dish technique proved quite effective, and the difference between oil film dishes and clean dishes was startling. In Fig. 3, the chromatogram A from an oil film dish contains many more early eluting peaks than the chromatogram B from a clean dish, which looks almost like the chromatogram C of PAE standards. Combined samples of clean dish fallout were checked on two other columns

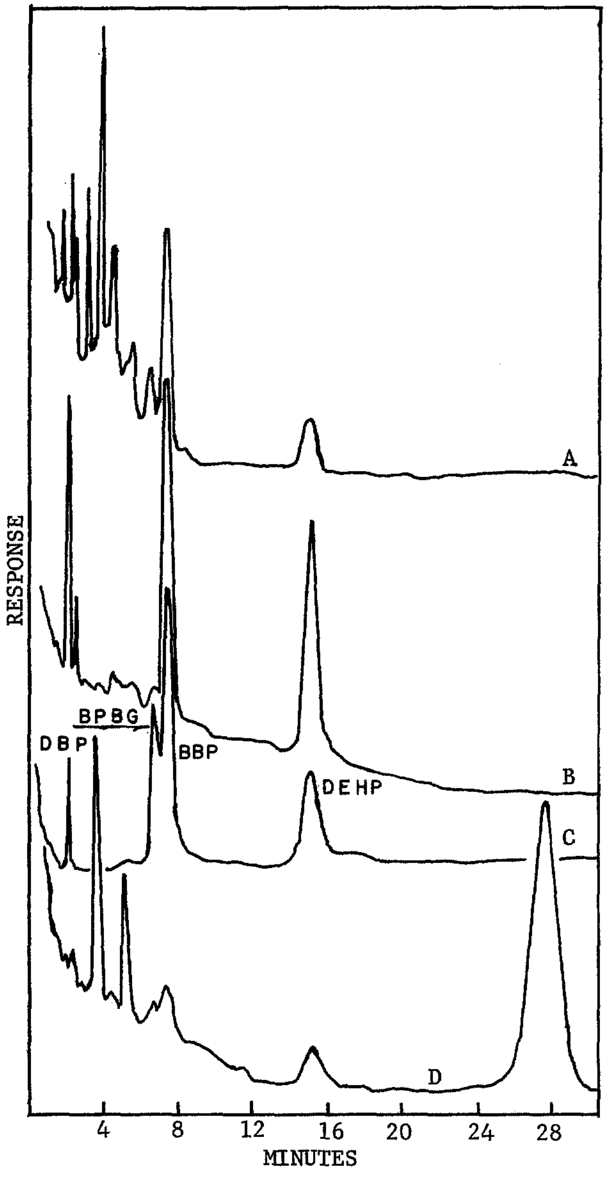

Fig. 3. Air fallout and phthalate chromatograms on GCEC, column of 4% SE-30.

A. Oil filmed dish.
B. Composite, clean dishes.
C. Phthalate standards.
D. Air conditioning inlet.

using electron capture detection to confirm the presence of PAE's, and GCMS of the combined samples showed little more than the three PAE's, which had mass spectra matching standards. Chromatogram D of the hexane soluble grime on the air conditioning inlet to the building does not compare well with chromatogram A suggesting that most of the fallout indicated in chromatogram A is generated within the building. In 24 hr, lab fallout at Davis was in excess of 2 ng cm^{-2} for BBP and 3 ng cm^{-2} for DEHP while DBP was lower and variable.

The caulk containing Aroclor suggested comparisons between the oil film samples and various Aroclors should be made at a somewhat slower elution rate such as shown in Fig. 4 which reveals quite a close correspondence for the peaks in Aroclor 1242 and most of the early eluting peaks in the oil film sample. In the clean dish sample DBP did not show up this time. Since DBP was not found in the air conditioning system, it appears to be escaping from another source in a variable manner. The peak just short of 6 min in the oil film sample appears to match one in the extracts of sulfate reagent solutions. In 24 hr the fallout of this apparent Aroclor was in excess of 2.5 ng cm^{-2}.

On several occasions samples without detectable levels of DEHP suddenly showed very detectable levels. The experiment on rinsing syringes quickly revealed that the glass barrels of syringes are coated with DEHP as all five syringes were positive with levels between 0.2 and 0.55 ug found. No other peak in the syringe rinsings had 0.1 the response of the DEHP found on GCEC even though one syringe was being used with trifluralin and parathion, two good electron captors. Several small peaks did appear, and the QF-1 column was needed to resolve that one peak was due to p,p'-DDT and not BPBG. The deliberately contaminated syringe had 0.9 ug of DEHP, only about 3 times the average contamination of syringes in everyday use indicating hand to glassware contamination by this phthalate is occurring almost anytime glassware is handled.

DISCUSSION

These results suggest many of the environmental analyses finding PCB and DDT compounds at parts per trillion levels and possibly higher may be finding more than the environmental levels of these pollutants especially when minimal cleanup and GCEC is the methodology used as in some reports (HARVEY, et al., 1973; PAREJKO, et al., 1975). Even after proper extraction and cleanup to separate the various types of compounds, lab air contamination with PAE's and PCB's could be incorporated into samples during solvent stripping or other air exchanging processes to distort the analyses if GCEC is used for quantitation of low levels of pollutants in oil containing substrates.

PAE's including BPBG have been reported in environmental samples (MAYER, et al., 1972; THOMAS, 1973), and HALL (1973b) indicated BBP and DEHP elute to some extent in the DDT fraction from Florisil. Consequently, environmental PAE's may be mistaken for DDT and other similar chlorinated pollutants even without the lab contamination reported herein. Qualitative confirmation such as base treatment causing DDT disappearance without quantitative DDE appearance (COX, 1971; MacINTYRE, et al., 1974; WILLIAMS & ROBERTSON, 1975) is meaningless as PAE's will also disappear. In the laboratory at Davis, contamination by DEHP alone indicated hand to glassware transfer; by DBP alone indicated dirty inorganic reagents; and by BBP, DEHP and usually DBP indicated collection of air fallout if

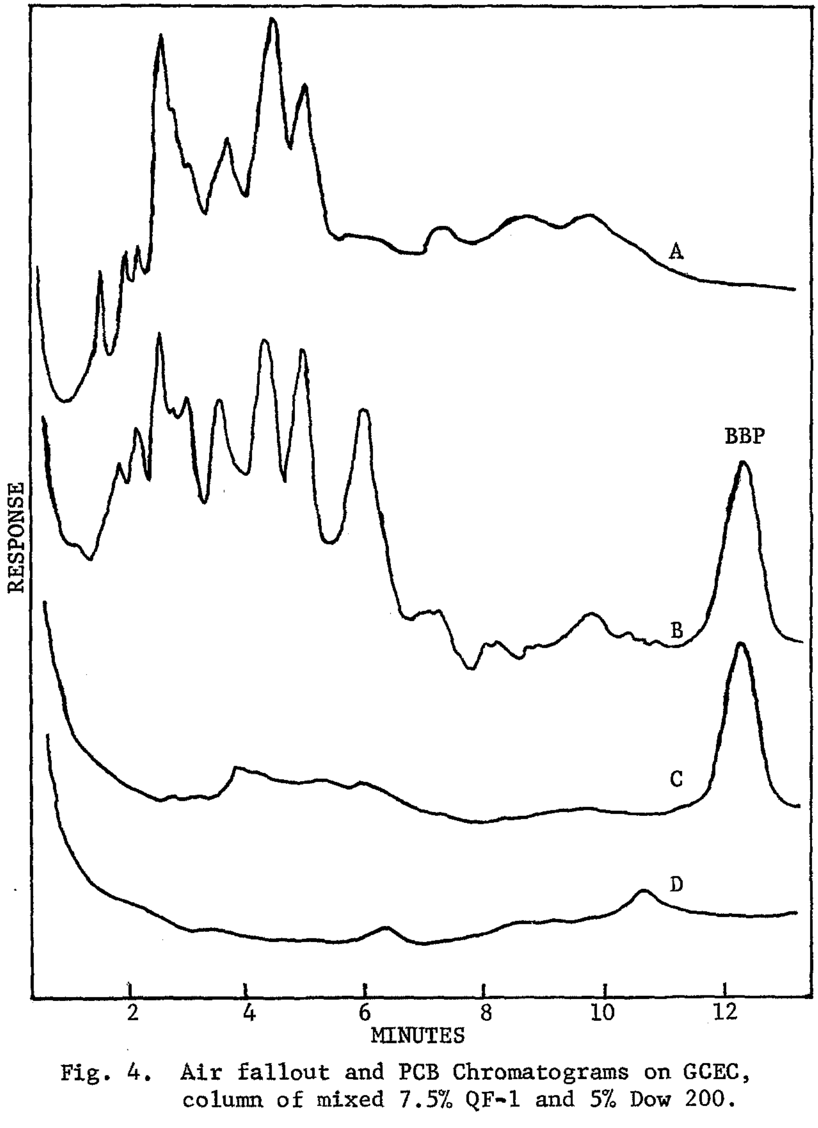

Fig. 4. Air fallout and PCB Chromatograms on GCEC, column of mixed 7.5% QF-1 and 5% Dow 200.

A. Aroclor 1242.
B. Fallout on oil filmed dish.
C. Fallout on clean dish.
D. 1% oil (Squibb mineral) in hexane.

at low levels and dirty solvents if at easily detected levels. Of the many other PAE's commercially available (FISHBEIN & ALBRO, 1972), several that might also be interferences have been reported as contaminants (ASAKAWA & GENJIDA, 1970; OGNER & SCHNITZER, 1970), but DBP, BPBG, BBP and DEHP ought to be first for consideration as interferences.

With the apparent Aroclor 1242 fallout found on oil film dishes, confirmation appeared difficult with the high oil background, but another column (2 parts, 2% QF-1 on 60/80 mesh Gas Chrom Q mixed with 1 part of 1.5% OV-17 on the same support) also revealed a close correspondence between sample and standard on GCEC. Such confirmation appears to be all that was needed in several reports (DUCE, et al., 1972; HARVEY, et al., 1973), and no chromatograms are presented for others to evaluate the correspondence. The apparent Aroclor in oil film dishes only suggests that the compounds involved are essentially free in air and require the oil to adsorb them while the PAE's collected on the clean dish are associated with particulates.

While direct contact with plastics has often been cited as the source of plasticizer contamination especially for PAE's used in polyvinyl chloride (MATHUR, 1974), these results would suggest that sufficient contamination occurs by other routes. Probably the low level air contamination creates a more serious problem in pollutant analyses than direct contact, because the samples may not be considered contaminated, while the very blatant distortion of results from direct contact will bring immediate discrediting of samples as contaminated. Various combinations of lab contamination by PAE's and/or PCB's and environmental pollution by PAE's may explain the widely varying analyses for DDT and PCB compounds in ocean samples (COX, 1971; MacINTYRE, et al., 1974; WILLIAMS & ROBERTSON, 1975).

SUMMARY

Airborne compounds from two groups of plasticizers used in air conditioner filters and caulks as well as flexible polyvinyl chloride and related plastics have been identified as major sources of low level laboratory contamination that can cause serious interferences in pollutant analyses especially at the low levels requiring GCEC for quantitation. Two compounds from the phthalic acid ester group (PAE's) of plasticizers that are environmental pollutants as well were found incorporated on air conditioner filters leading to contamination of clean and oil filmed dishes from air fallout. Solvents, inorganic reagents and hand-to-glass transfer were found to contribute to sample contamination by PAE's. Several PAE's are easily detectable at 0.1 ng levels under some conditions on GCEC and have retention times on several columns of differing polarities that can interfere with analyses of chlorinated pollutants especially p,p'-DDT. Aroclor 1254, a member of the polychlorinated biphenyl group (PCB's) of plasticizers, was found in a caulk around a laboratory window. On oil filmed, but not clean dishes, the compounds collected from air fallout produced chromatograms on GCEC with a close correspondence to Aroclor 1242.

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