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OTHER LOCATIONS	GENERAL OFFICE	W. G. KRUMMRICH PLANT
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TITLE: Polychlorinated Biphenyl (PCB) Residues in Surface Water

PERSONNEL:

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PROBLEM:

Analyze various river water samples with sufficient sensitivity to reach sub-parts per billion levels.

JUSTIFICATION:

Data needed for Krummrich Plant PCB strategy as related to possible Federal water quality requirements.

SUMMARY:

Analytical procedures have been applied to river water samples capable of reaching PCB levels compatible with the EPA guideline of 0.01 ppb.

Results from sampling sites on the Mississippi River north of the Plant out-fall show positive PCB levels of at least an order of magnitude larger than 0.01 ppb. Data from a Missouri River sampling is inconclusive and re-sampling is recommended.

See Table 1

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Details

Foreword

The Environmental Protection Agency (EPA) guideline for PCB in receiving waters is expected to be 0.01 parts per billion (ppb). Calculations based on current Krummrich losses would indicate a level, in the Mississippi River, at less than this concentration. However contamination from non-plant sources is expected, due to the wide use of PCB in the past -- plasticizers, solvents, insulators, etc. At present no data is available, relating the PCB levels in the Mississippi (or other near-by rivers) north of the Plant outfall.

Three (3) one-gallon samples of river water were taken at sites at or near the Chain of Rocks (Mississippi), north of the Illinois river (Mississippi) and at St. Charles (Missouri River). Analyses were performed using techniques adapted or developed in this laboratory, during recent months, for reaching PCB levels compatible with the EPA guideline.

Experimental

Two different procedures were used to examine the samples. Both utilize a minimum one-gallon sample size, giving at least a four-fold increase in detection limit over our present analytical method. The basic difference in these techniques is the manner in which the PCB's are collected or isolated from the water sample. A brief description of the procedures follow.

A. Charcoal Column Filtration

This procedure is an adaptation of Berg's charcoal method for separation of PCB's from DDT group pesticides. Our technique is based on the fact that PCB's are adsorbed from water onto charcoal and can be quantitatively removed with cold benzene. The choice of charcoal is critical - only Fisher cocoanut charcoal for decolorizing will work.

Recoveries of 75% for Aroclor 1242 and 92% for 1254 were obtained, and presented no observed alteration to overall GC peak profile. Using a filter column containing about 1.5 gram of charcoal the thru-put is 1.5 liters of particulate-free water per hour. The system can handle up to 5 microgram of PCB. Practically, the filtration is limited to 2-3 gallons of sample as much larger volumes would become quite time consuming.

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Experimental (Continued)

B. Aluminum Sulfate Sedimentation

This method is currently under examination in our laboratory, and as such can only be considered as semi-quantitative at best. It is based on observations - in this lab and of other workers - that low levels of PCB and some organochlorine pesticides are almost completely removed from surface waters by sedimentation techniques (contaminants are adsorbed on slowly descending particulate matter).

In this work, 1.2 grams of $Al_2(SO_4)_3 \cdot 18\ H_2O$ per gallon was added to the water sample and sedimentation allowed to proceed over night. Although clarification is apparent in several hours total "settling-out" requires much longer periods of standing. The sediment or precipitate is collected by filtration after decantation of the supernatant, and analyzed for adsorbed PCB using standard procedures.

As indicated, this method is now under evaluation, and capacity and recovery data have not been obtained at this time. The volumes of water that can be treated and analyzed in this manner, although more than that of the charcoal filtration, is also limited in that very large quantities would become too cumbersome to handle in ordinary laboratory equipment.

C. Analytical Background (Blanks)

Analytical blanks were obtained periodically to establish the apparent laboratory and reagent PCB-background at the times of the analyses. This involved working thru all steps of each procedure, in addition to examining several individual chemicals and pieces of equipment for contamination.

Results - Discussion

The most critical point in this work was to be able to reach PCB levels that are compatible with the EPA guideline of 0.01 ppb. This has been achieved in part by being able to analyze large volumes of water. In addition, changes in gas chromatographic operational parameters have resulted in an improved instrumental sensitivity. With the AR&D instrument 0.03 nanograms per micro liter can be detected over base-line noise. This provides a lower detection limit, taking the equivalent of one-gallon of water as sample, of 0.01 ppb. Unfortunately our laboratory background of apparent PCB's limits our lowest reportable level to about 0.05 ppb at best.

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Results - Discussion (Continued)

The analytical data obtained by the two procedures are summarized in the attached Tables I and II. Results from the charcoal-column filtration (Table I) have been corrected for the appropriate analytical blanks. Both sites on the Mississippi River, north of the Plant show positive levels at least an order of magnitude above the 0.01 ppm guideline. The PCB's found were essentially of the Aroclor 1254 type. The result, by charcoal filtration, of the sample from the Missouri River indicates that it is almost free of PCB residue. The amount was approximately equal to our analytical background.

Table II shows the range of the quantities found by the sedimentation procedure - the values are uncorrected for analytical background. Unfortunately during the period of analysis by this technique, the PCB background was inconsistent and varied over a greater than normal range. We felt that under such circumstances, the assignment of any given background value to a set of analyses is unrealistic.

Except for one sampling site the remainder were run in duplicate, using a fresh gallon sample for each analysis. The background range reported gives the highest and lowest value obtained during the analytical interval. It can be seen that all the samples are positive with respect to this background. It should be noted also, that by the sedimentation technique, a definite PCB residue is indicated in the sample from the Missouri. The reason for this disparity between procedures is not apparent.

An evaluation of the data from either of the two methods indicates the presence of PCB residues in the Mississippi north of the Krummrich out-fall. The sampling sites were far enough up-stream to preclude any contribution from our waste discharges. Results from the Missouri River analyses are inconclusive at this time, and when practicable additional sampling should be undertaken.

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Table I

PCB's by Charcoal Column Filtration

Sample	ppb - corrected for anal. blank
Miss. at Chain of Rocks, 12/13/72	0.22
Miss. north of Illinois River, 12/20/72	0.19
Missouri River, 12/13/72	<0.05 (1)

Table II

PCB's by Sedimentation with $Al_2(SO_4)_3$

Sample	range in ppb - uncorrected for anal. background
Miss. at Chain of Rocks, 12/13/72	0.21 to 0.39
Miss. north of Illinois River, 12/20/72	0.39 (2)
Missouri River, 12/13/72	0.24 to 0.31
Anal. Background	0.05 to 0.17 (3)

1. or less than twice anal. blank.
2. single analysis only.
3. based on one-gallon sample size.

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