

Monsanto

SP
arrollor

FROM (NAME & LOCATION) J. C. Weber - B2SK (St. Louis)

DATE : August 30, 1976

CC: R. E. Keller

SUBJECT : PCBs - EPA 307(a) HEARING

C. Paton

D. Wood

REFERENCE :

TO : J. P. Mieure

Dick Rollins of Jard, a member of EIA's PCB Task Force to oppose the proposed 307(a) standard for PCBs asked that we critique the testimony of two EPA witnesses on the subject of sampling and measuring PCBs. The witnesses and their subject matter are:

Witness

Selman Veith, Ph.D.
EPA Water Quality Lab
Diluth, Minn.

Subject

Bioaccumulation and transport of PCBs in fresh water aquatic environment; chemistry of PCBs; measuring methods and capabilities.

Thomas O. Munson, Ph.D.
EPA Region III Field Office
Annapolis, Maryland

Transport and persistence of PCBs in the Upper Chesapeake Bay Area, measuring technology and capabilities.

I said we would and volunteered your services.

Dick said he will mail me copies of their testimony today and would like our response by September 20th. I will get the copies to you as soon as they come in.

Cole

J. Coleman Weber

mg

Cole :

9-10-76

Attached are my comments along with the original copies of Veith's and Munson's testimonies.

Jim

DSW 379870

STLCOPCB4100642

Monsanto

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

MONSANTO COMMENTS ON THE EPA HEARINGS ON PCBs EPA EXHIBIT B - AFFIDAVIT OF GILMAN D. VEITH, PH.D.

The first 9 pages consist of a rudimentary discussion of hydrocarbon chemistry concluding with a description of PCBs. The text has many typographical errors and is not clearly written, but is basically correct.

Page 10 begins an equally vague but essentially correct description of gas chromatography as applied to determination of PCBs. The definition of gas chromatography in the last sentence of the first paragraph on page 10 is very poor. For example, his definition could also apply to distillation. Exhibit 10 has been oversimplified to the point that it is incorrect. The "non-volatile liquid" coated onto "crushed firebrick" is actually packed uniformly throughout the column and the "nitrogen carrier gas" flows through the coated packing.

Exhibit 15 is a modification of a Monsanto tabulation of percentage compositions of Aroclor 1221, Aroclor 1016, Aroclor 1242, and Aroclor 1254. However, Veith's testimony in the first paragraph on page 15 incorrectly refers to Exhibit 15 as a list of relative retention times of major components in a chromatogram. There are no retention times in Exhibit 15, no major components, no chromatograms, and no reference to Aroclor 1428 (sic. presumably Aroclor 1248) or Aroclor 1260.

In discussing the EPA prescribed method for analyzing water for PCBs, Veith states on page 17 that "Although the basic method suggests a detection limit of approximately 1 $\mu\text{g}/\ell$ using a sample of 100 ml to 1,000 ml, the method can readily be adapted to larger sample volumes to provide reasonable reliability at much lower water concentrations".

This argument is theoretically correct if no interferences are present in the water and if the reagents and glassware contain no contaminants which show up as "background". In actual practice with

real effluents, interferences are present. The EPA method makes no provision for removing most industrial chemical interferences such as polychlorinated naphthalenes and polychlorinated paraffins. Also, even pesticide grade reagents contain trace impurities which contribute a background when a large volume of solvent is concentrated by evaporation.

For these reasons, it is not always possible to attain a detection limit of 1 $\mu\text{g}/\ell$ for PCBs. In such cases, starting with larger samples will not lower the detection limit. Many laboratories located at manufacturing sites where PCBs are used experience a "laboratory background" corresponding to about 1 $\mu\text{g}/\ell$, which precludes analyses at lower levels.

On page 20, Veith claims that "At 1 $\mu\text{g}/\ell$, a standard deviation of 10 to 20 percent of the mean concentration can be expected". No data are presented to substantiate this claim. Is this for inter- or intra-laboratory comparisons? See related remarks in the section commenting specifically on the reproducibility of the EPA method.

On page 21, Veith introduces a mathematical model to approximate bioconcentration and makes predictions based on the model. What place do predictions based on models have in EPA hearings?! Experimental evidence is more credible than models and should take precedence.

The text on page 21 does not indicate whether the study presented in Exhibit 17 was conducted as a static or a flow-through test. There is considerable controversy among aquatic biologists over whether static tests are as reliable as flow-through tests. This might be a point to pursue. The whole concept of extrapolating laboratory bioconcentration studies to the environment assumes that PCBs in pure laboratory water behave the same as PCBs in natural water. This is not a good assumption if sediment or suspended solids are in the natural water. PCBs absorb onto the sediment and are less available to fish membranes. Hence, laboratory bioconcentration values may be higher than environmental values.

Monsanto

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

MONSANTO COMMENTS ON THE EPA HEARINGS ON PCBs EPA EXHIBIT E - AFFIDAVIT OF THOMAS O. MUNSON, PH.D.

On page 3 and 4 and in Appendix A of Exhibit B, Munson understates the difficulties in determining PCBs at 0.1 - 0.05 ppb concentrations in effluents and at 1 ppt in landfill leachates.

His statements about detection limits are theoretically true for waters containing no interferences and for pristine laboratory conditions which contribute no laboratory background. However, in our experience, most effluents and leachates contain interfering components which are difficult to remove. We agree with Dr. Munson, "that not all laboratories..... can routinely achieve these results....".

To illustrate this point, we learned through private communication that a competent EPA laboratory analyzed two aliquots of the same sample submitted by a capacitor manufacturer and reported concentrations of 1 and 3 ppb, respectively. Hence, the variability for that laboratory at that time was 2,000 ppt. Without more information on the cause of this variability, it is questionable whether this EPA laboratory could reproducibly measure 1 ppt.

We are not aware of any multilaboratory studies of the reproducibility and accuracy of the EPA method for PCBs at these low levels. Unless multilaboratory testing has been conducted, Munson's claimed detection limits should not be extrapolated to other laboratories.

On page 3 of Exhibit B, the material of construction of the sample bottles and bottle caps are not given. Unless the bottles were glass and the cap liners aluminum foil, significant contamination and/or sample loss could have occurred.

A more significant deficiency exists on page 3 of Exhibit E. The sampling gear was fabricated from PVC pipe. Plastic tubing or pipe is a known source of contamination by organic compounds which could interfere with PCB analysis (see Junk et. al., Environmental Science

DSW 379873

and Technology, 8, 1100 (1974)). These contaminants may represent impurities from the manufacture of the plastic or desorbed residues from previous analyses. In either case, this deficiency sheds doubt on the validity of all data for samples obtained with this equipment.

DSW 379874

Monsanto

SPECIALTY CHEMICALS DIVISION

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

MONSANTO COMMENTS ON THE ANALYTICAL METHOD SPECIFIED IN THE PROPOSED TOXIC POLLUTANT EFFLUENT STANDARDS FOR POLYCHLORINATED BIPHENYLS

The analytical method specified in the Proposed Standards is unsatisfactory for measuring PCBs at water concentrations approaching 1 µg/l. At higher concentrations the method may have adequate specificity and accuracy for monitoring effluents. It has the inherent sensitivity to detect and measure PCB levels below 1 µg/l. However, at PCB concentrations of about 1 µg/l the precision and accuracy of the method, when applied to actual industrial effluents, has not been demonstrated. The method has not been subjected to adequate multi-laboratory testing to define the accuracy, precision or limits of applicability. Multi-laboratory round robin testing of the precision of a similar method, American Society for Testing Materials Method D-3304, "Analysis of Environmental Materials for Polychlorinated Biphenyls," has been carried out. This test by twelve laboratories showed that the 95% confidence level for precision agreement between any two participating laboratories was greater than a factor of two. Using the ASTM method, the only method subjected to government and industrial multi-laboratory testing, if one laboratory measures PCB in a sample containing only PCBs and water and reports a value of 1.0 µg/l, a second laboratory could expect to measure a

DSW 379875

value in the range of about 0.5 to 2.0 µg/l. This precision variability very likely applies also to the method specified in the Toxic Pollutant Effluent Standards. However, if you are trying to measure PCBs in an industrial effluent you would not be able to achieve the sensitivity or reproducibility reported in ASTM^D 3304. The accuracy of neither method has been adequately testing^{ed} in industrial effluents.

Since the precision and accuracy of the recommended method for real effluents are unknown, this uncertainty should be reflected in the Proposed Standards.

An abbreviated procedure is needed for routine monitoring of PCBs at the sources covered by the Proposed Standards, namely PCB manufacturers and capacitor and transformer manufacturers. Effluents from these facilities typically have a very low ratio of pesticides to PCBs. Potential interferences likely to be in these effluents are not pesticides and are not materials classified as toxic pollutants. Therefore, we propose that these facilities should be allowed to use a straightforward procedure designed to measure only PCBs.

The method specified in the Proposed Standards is not such a procedure. It contains elaborate and time-consuming separation schemes to isolate each potential interference and permit its measurement. However, as pointed out above, this is beyond the scope of the Toxic Pollutant Effluent Standards and represents an undue hardship for those monitoring source effluents.

DSW 379876

We propose ASTM Method D-3304 as an alternate procedure for these source effluents. This method was developed specifically for PCBs and omits the elaborate separation procedures for organochlorine pesticide interferences. Instead, pesticides and many other potential interferences are eliminated by a simple chemical treatment. Hence, the method is more direct, less prone to handling errors and less time-consuming.

The following specific comments apply to the EPA method:

1. The method title should be changed to reflect the intended dual application of this method to PCBs and organochlorine pesticides.
2. When the observed PCB level is significantly above laboratory and reagent background, background subtraction should be permitted.
3. In Section 4.1, reference to a glass lined injection port should be rephrased to insure that it includes on-column injection into glass columns.
4. Acetonitrile partitioning similar to that described in Section 10.2 leads to incomplete recovery of PCBs as well as pesticides. Recoveries of various PCB product mixtures during this partitioning should be carefully examined.
5. Confirmation of PCBs using the second GC liquid phase referenced in Section 4.4.4.2 should be clarified in the experimental portion of the method.
6. Total peak areas should be used for quantitation of each PCB product mixture. This technique is equally accurate and much more rapid than using peak weight factors for calculating effluent concentrations.

7. Chromatograms of Aroclor 1016 should be included with the reference chromatograms of the other PCB products.

Sampling and sample storage procedures are even more important than the analytical method for establishing accurate effluent concentrations. Random "grab" samples, for example, are inadequate for determining daily or monthly average concentrations. Improper sampling or storage can introduce order of magnitude errors in measured concentration values. Proposed Standards and the analytical method specified therein completely ignore sampling and storage. It is important that samples be representative of the average effluent and be properly preserved. Accordingly the Standard must specify precisely how samples are to be obtained. It must also impose limitations on sample storage conditions, including containers.

DSW 379878