Monsanto

re Aroclor Pollution

FROM (NAME & LOCATION) W. B. PAPAGEORGE - ST. LOUIS

DATE January 8, 1971

cc H. S. Bergen
J. Mason

SUBJECT PCB ENVIRONMENTAL PROBLEM
DECEMBER STATUS REPORT

REFERENCE

TO :
P.J.A. Marsh - BRUSSELS
W. S. Clark
J. R. Durland- TOKYO
M. W. Farrar - 2nd Street
E. V. John
R. E. Keller - 2nd Street
R. M. Kountz
T. L. Gossage
P. S. Park
W. R. Richard
J. R. Savage
E. P. Wheeler

MARKETING:

Efforts continue to educate Therminol FR users to control leakage.

Consulting visits to JFQ and WGK plants have brought results - all but one system at JFQ converted from Therminol FR/Aroclor to Therminol 66.

At WGK, two systems converted and four in process of converting from Therminol FR/Aroclor fluid to Therminol 66.

A U.S. Dept. of Agriculture press release announcing the banning of both polychlorinated biphenyls and polychlorinated terphenyls in pesticide formulations has generated a considerable number of inquiries from our chlorinated terphenyl customers. Inquiries made to representatives of the U.S.D.A. to establish reasons for including terphenyls have been answered with vague generalities. Formal protest is being prepared and will be forwarded.

ENGINEERING:

Liquid Incineration - Krummrich - CEA 2415

Final drawings of the incinerator system from John Zink Company were received as well as their fabrication schedule. All additional equipment is on order and design is proceeding on schedule.

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IN 10 REV. 11 65

MCS 1016 - Krummrich - CEA 2417

Additional evaluations with Manufacturing led to a decision to revise the scope of this project. The revised Data Transmittal is now scheduled for mid-January. Definitive design continued on elements not effected and pile driving work for foundations was started.

Tributyl Phosphate - Queeny - CEA 2371

Pre-approval funds were provided to start definitive design and work is in progress.

N-C Phosphate - Queeny - CEA 2451

The preliminary project scope was developed, a safety review was held and the scope was reviewed with Research and Manufacturing. A capital estimate is in progress and the Appropriation Request Data Transmittal will be issued in mid-January.

Solids Waste Disposal - Krummrich - CEA 8042

Analysis on the samples collected during the Enviro-Chem test are still in progress. Meanwhile, a system specification was developed for facilities to remove PCB's from solid waste. Work continued with marketing in an attempt to better establish what we can expect for disposal from our customers.

JAPAN:

No new developments reported.

EUROPE:

No new developments reported.

MEDICAL:

The 18 month status reports on the two-year chronic dog studies with Aroclors 1242, 1254 and 1260 were received. There has been essentially no change in the animals since the 12 month reports last July.

The teratology studies with these same compounds have been scheduled and will be underway shortly.

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PUBLIC RELATIONS:

Three new sources of PCB news appeared during the month. The American Chemical Society syndicated an article, based on Carl G. Gustafson's article in Environmental Science and Technology. The ACS feature appeared mainly in East Coast and New England weeklies. The College Press Service distributed a PCB story to campus newspapers which rounded up previously published material. So far, it has appeared in the Washington University and SIU student dailies. A third article, quoting oceanographers meeting in Rome, criticized Monsanto for refusing to release production figures on PCB.

RESEARCH:

Carbonless Reproduction Paper Solvents

Process assistance was provided Dixie Chemical Co. during initial phases of MIPB-2 production. Operations proceeded well and satisfactory crude reaction product was made which was further refined in the J. F. Queeny Plant.

A process modification proposed by Dixie was shown to be satisfactory regarding performance of MIPB-2 in dye color development.

As a result of an exchange of visits between Nashua and Monsanto, two candidates appear promising as Aroclor 1242 replacements:

XS-276 (HB-40/Aroclor 5442) and XS-310 (MIBP/chlorinated paraffin). XS-276 has received a partial plant trial and a drum of XS-310 has been ordered for more testing. Other coded samples are also under test at Nashua.

G. E. Samples

A second set of plant and stream water samples from G.E.-Pittsfield, Mass. were analyzed for PCB's. The results (< 1 ppm) were similar to the first set analyzed in early December. Additional samples of milk have been received from G.E. for PCB analysis.

J. F. Queeny

The monthly monitoring of the JFQ Plant composite effluent continues. The PCB level found for November was 19 ppb calculated as Aroclor 1248. This level is lower than found for September and October by a factor of about 4X, part of which can be attributed to the current very low laboratory blanks.

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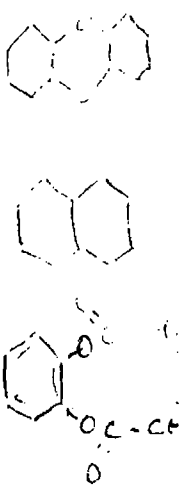
Solid Disposal - Pyrolysis Unit

The analysis of all samples taken during the recent Enviro-Chem PCB solid waste disposal tests have been completed and the results reported for correlation with engineering data. A second sampling of the pond associated with the Enviro-Chem incinerator demonstrated that the PCB disposal tests did not contaminate the site (<10 ppb).

Aroclor 5442 Composition

GC/Mass analysis of a composite sample of materials extracted by water from eleven current Aroclor 5442 lots has been completed. No highly toxic components, furans, dioxins, etc., were identified which could account for the reported higher toxicity of Aroclor 5442 to Daphnia over chlorinated biphenyls. Chlorinated biphenyls and terphenyls were identified as the major constituents of the composite. Previous work had shown that an impurity in Aroclor 5442 gave a low-resolution mass spectrum similar to the spectrum of tetrachlorodibenzofuran. It was later found that tetrachloromethylbiphenyl has a similar mass spectrum.

To determine which of these compounds is present, a high resolution mass spectrum was obtained at the Physical Science Center on a concentrate containing the impurity. This spectrum indicated the empirical formula of the impurity to be $C_{10}H_{12}O_2Cl_4$. The empirical formulae of tetrachlorodibenzofuran and tetrachloromethylbiphenyl are $C_{12}H_3OCl_4$ and $C_{13}H_8Cl_4$, respectively. No reasonable structure has been found for the indicated empirical formula. Another sample has been concentrated and is scheduled for high resolution mass spectrometry to verify the empirical formula of the impurity.



Biodegradation Testing

The expansion of the semi-continuous activated sludge (SCAS) testing facilities from 16 to 26 units was completed. This will allow us to study 24 products, including 10 new ones. Additionally, early in January a fractional replicate of a factorial experiment will be initiated. This preliminary experimental design will be used to determine the effect that seven variables have on the observed SCAS disappearance rates of three model compounds. The model compounds to be studied during the eight week duration of the test are biphenyl (degradable), 2,4'-dichlorobiphenyl (intermediate degradable), and 2,2', 4,4', 6,6'-hexachlorobiphenyl (non-degradable).

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A staggered schedule for all SCAS units has also been laid out which will allow one-third of the 24 units devoted to degradation to be sampled and analyzed (20 data points) during each month of operation. The compounds to be studied during January include TCB, MIPB, HB-40, 2,2'-dichlorodiphenyl ether and Aroclor 1221 as well as the three units devoted to the statistical experiment. The other compounds being fed (but not sampled and analyzed) to the remaining units are MCS 1043, MCS 1016, Aroclor 1242, Aroclor 1254, Arobromoclor 1232, ONCB, PNCB, p-chloroaniline, nitrated orthene, S-711M, hexabromobiphenyl, Aroclor 5432, Aroclor 5442, Aroclor 5460, and Arobrom 5465. Analysis and sampling of these units will begin in February and March. In the meantime, the effects that these materials have on the normal characteristics (pH, growth rate, and settling time) of the activated sludge will be monitored on a daily basis.

The two remaining units are being used to maintain special cultures, a C_2 biphenyl culture from MCL, and a biphenyl culture grown in our laboratories. Very rapid growth on biphenyl as the sole carbon source has been observed with the MCL-C_2 culture.

River Die-Away

River die-away tests with Aroclor 1242, Aroclor 1254, MCS 1016, MCS 1043, Arobromoclor 1232 and TCB at the 100 ppb level were discontinued after several weeks. The highly scattered data obtained indicated that the loo ppb level was too low to achieve meaningful disappearance rates due to procedural problems and/or losses by non-degradation routes (volatilization, adsorption, etc.). Further experimentation is planned during the first quarter.

HB-40 and MIPB Biodegradation

A brief sampling period of the HB-40 and MIPB semi-continuous activated sludge (SCAS) units was completed 11/28/70. UV analysis of the hexane extracts gave mean disappearance rates of 58%/cycle for MIPB and 44%/cycle for HB-40 based on the total material present. A 3X cycle gave disappearance rates of 66% and 55% respectively while a 5X cycle gave 77% and 62% respectively. SCAS work with these materials will be concluded with an extended sampling period in January.

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River die-away tests on HB-40 and MIPB are nearing completion. After a three week exposure at the 1 ppm level to the normal level of micro-organisms in Meramec river water the MIPB concentration has decreased by a total of 85% of which 54% can be attributed to microbial degradation. Similarly for HB-40, the total concentration has decreased by 66% of which 57% can be attributed to microbial degradation.

Aroclor 1221

Feeding of the Aroclor 1221 SCAS unit continues but with only limited sampling of the unit. No quantitative data is available yet but qualitatively there appears to be a rapid disappearance of the lower homologs with a build-up of the higher ones. This unit is scheduled to be sampled for an extended period in January.

Aroclor 5432 Liquid-Liquid Chromatographic Analysis

The liquid-liquid chromatography method for the analysis of SCAS samples containing Aroclor 5432 has been optimized. The liquid-liquid system consists of a 3 ft. column packed with Zysan Permaphaze as the stationary phase and water/methanol (75%/25%, v/v) as the mobile phase. The ultraviolet detector response is linear between 0 and 50μg of Aroclor 5432, absolute, with a lower detection limit of about 1μg absolute. Analysis time is 40 minutes. Optimization of the system to other halogenated terphenyls will be made.

Carbon Adsorption Studies

The pilot unit continues to operate with minimum difficulties at an average flow rate of 6 gpm/ft^2. Effluent quality, at the present flow rate, is <10 ppb Aroclor for average influent concentrations in the range 100-2000 ppb and for occasionally high concentrations of up to 11,000 ppb. There has been no indication of a breakthrough. Present plans are to operate the unit until 12/30 at the present flow. If there is no indication of a breakthrough at that time, all data will be compiled for an evaluation and recommendation by a Pittsburgh carbon consultant.

Filtration Studies

The study conducted to remove the Aroclor containing solids from the effluent of the new neutralization pit by filtration through a sand bed has been completed. At flows greater 200 cc/min the filter tended to blind with the fine solids. The solids could not be success-

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fully washed from the filter. A report will be issued by 12/28 on all the filtration studies.

Solids-Aroclor Removal by Flocculation and Flotation

The clarifier unit from Biodize has been received. Plans are now being made for some necessary alterations on the unit. The complete installation is scheduled to be completed by 1/29/70.

Denver Equipment has completed their study on the removal of solids by flocculation and flotation. The most satisfactory flocculation results from these studies were obtained by conditioning with (200 ppm) CAO, and (10 ppb) $Al_2(SO_4)_3$ to preflocculate the solids and then intensifying the floc with (4 ppm) Separan MGL. Initial solids concentrations in the range (100-1000 ppm) were reduced to 19 ppm in a 120 min. settling time.

Flotation of the same material using 56 ppm of Armac T and 30 ppm of Aerofroth 65 produced a final effluent of 34.5 ppm of solids. Solids removal is more dramatic by flocculation, however, the froth may be more effective in removing the organics.

Betz is scheduled to complete their evaluation and recommendation by 12/21 on the floc study.

A tentative work plan will be issued by 1/4/71.

Pydraul Reformulations

Pydraul 312A

The new Pydraul 312A was formulated using 750 SUS mineral oil with Santicizer 711 as solubilizing agent. Production quantities will be sent to GM Central Foundry in January.

Pydraul 540B

We added 2.5% tributyl phosphate to minimize pump wear in oil gear equipment. We expect satisfactory performance.

Pydraul 135A and Pydraul 230A

We will use 750 SUS petroleum oil plus small amounts of TCB for improved fire resistance in these new formulations. Pump tests were satisfactory.

Pydraul A200B

The V-105C Vickers pump test had excellent wear characteristics. A Tentative Process was issued.

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Pydraul 150A

We do not have a satisfactory candidate. Fire resistance is insufficient.

MANUFACTURING:

W. G. Krummrich Plant

PCB Levels in Sewer

1. Aroclor losses from the Aroclor Department averaged about 0.6 lbs/day and ranged from about 0.2 to 1.4 lbs/day.

   Losses from the Sauget Village Treatment Plant for the period 11/17 - 12/17 averaged 34 lbs/day (177 ppb). Range for 7 samples was 9 to 53 lbs/day (47-280 ppb). Samples taken during the 3-day neutralization test (12/15 - 12/17) are not included. Average for this period was 27 lbs/day.

2. Program to monitor the various plant sewers was begun the last week of December. Plans are to composite samples twice per week for analysis.

3. Sewer samples were taken from the effluents of the other industrial plants. These included:

Midwest Rubber	9 ppb
American Zinc	6 "
Cerro Copper & Brass	9 "
Mobil Oil	54 "
Dead Creek	18 "
Village	2110 "

   The only significant quantity is the PCB's from the Village sewer. This amounts to about 2 to 3 lbs/day. Probable source is Aroclor trailer washes at Rogers Terminal.

Projects To Reduce Sewered PCB's From Aroclor Dept.

1. Design package for project to pave and trench loading areas is 95% complete and will be issued by 1/15/71.

Program To Eliminate Sewered PCB's From Using Depts.

The Plant manager has requested by memo that all General Superintendents proceed at once to change out all Therminol FR units to non-Aroclor heat transfer fluids.

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Removal Of Soluble PCB's From Sewer Stream (Reach 10 ppb)

A 3-day test was run 12/15 - 12/17 in which the entire plant effluent was neutralized with lime. Results indicated no change in the average level of PCB's in either the influent or the effluent at the treatment plant at the 90% confidence level.

At this point, it appears possible to reach the goal of 10 ppb without secondary or tertiary treatment by doing the following:

1. Change out of all plant Therminol FR units to non-Aroclor fluids.

2. Continue control of losses at the Aroclor Department at less than 1.5 lbs/day

3. Clean all contaminated sewers and sewer boxes.

4. Monitor and control Rogers Terminal.

PCB Levels in the Atmosphere

A project premise and estimate for $6,000 were prepared to replace the nitrogen purge with a nitrogen blanket at the mix tanks and to re-route the chlorinator rupture disc lines to the pad.

A sampling station will be shared with the Chlorine Department to monitor PCB content of air downwind from the Aroclor Department. Samples will be taken every other week starting the week of 1/11/71.

PCB Rework Project (Estimate 2095)

Project package is essentially complete and will be issued the week of 1/4/71.

Replacement Products (CEA 2417)

Ground was broken for the fractionator project for production of MCS 1016, replacement for Aroclor 1242 in capacitors.

Newport Plant (October/November)

Removal of Suspended Aroclor From Plant Effluent

Now that all jobs have been completed, a careful check was carried out to correlate PCB content at the interceptors compared with the final effluent discharge tank.

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At the interceptor, the PCB content was 22.6 parts per billion. Simultaneous sampling at the main effluent plant gave 54.0 parts per billion.

Difference of 31.4 parts per billion is arising from spillages from internal heat transfer fluid systems, and from drum leakages from Aroclor stored on drum flats. Evaluation is now in progress to change all internal Aroclor heat transfer fluid systems to Santotherm 66. The two areas involved are Santolube 900 and 4-NDPA. The expansion project for 4-NDPA has been requested to use a Santotherm 66 system.

Incineration

Contact has been made with Dr. J. B. Lewis, Chemical Engineering Division, A.E.R.E., Harwell, and Mr. Higginson who is in Division Engineering Design and Development, Refuse Disposal Branch of the Public Engineering Dept., Greater London Council.

Dr. Lewis is considering offering an incineration service to industry for the disposal of highly toxic wastes. Vodden and Macdonald are scheduled to meet with Dr. Lewis in the near future.

Mr. A. E. Higginson is very much in favor of industrial waste disposal services carrying highly toxic wastes for incineration through special systems provided by the Greater London Council. This appears to be a logical step forward and should be of significant advantage to our customer disposal problems. We intend to follow up with Mr. Higginson following our discussions with Dr. Lewis.

Atmospheric Emission

This investigation is proceeding and T.S.D. should assemble data in progress report issue.

Esturial Dilution

The Monsanto effluent discharge of approximately 1.4 million gallons per day is further diluted in the Severn Estuary by the several rivers discharging into this area. Average daily flow for these rivers have been obtained and are as follows:

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River Usk	535	million	gallons	per	day
River Wye	1319	"	"	"	"
River Severn	1178	"	"	"	"
River Stour	38	"	"	"	"
Bristol Avon	353	"	"	"	"
Somerset Minor discharges	45	"	"	"	"

The average daily flow corresponds to 3,670 million gallons per day.

The lowest dry weather flow for all these discharges has been established at 445 million gallons per day.

These volumes should be looked at in relation to the current discharges from the Newport location.

Used Drum Disposal

Blagden's drum reconditioning plant at Barking, Essex is acceptable for reconditioning used Aroclor drums as a customer service, but is not approved for the incineration and disposal of the washings, and this problem is being further investigated.

Anniston Plant

Current Level - Aroclor Wastes

Aroclor losses during Dec. averaged 1.5 lbs/day (321 ppb). The breakdown of the numbers is:

26	Day average	182 ppb	0.8 lbs/day
2	Day pumping from old Limestone Pit	39	0.2
1	Day detergent wash of Aroclor Dept.	58	0.3
2	Day removal collected PCB & solids in first part of new Limestone Pit	42	0.2
	Total average:	321 ppb	1.5 lbs/day

From this it is obvious that we can no longer detergent wash the Aroclor department. When the second Limestone Pit is completed, the losses from digging and pumping should be eliminated. Two pits will allow switching to a clean pit when one becomes saturated with PCB.

Spills

Shutting the Aroclor department down for the New Years

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Day holiday caused the Therminol system surge tank to overflow when a valve leaked. The Therminol was caught in the department sump and no Therminol entered the plant effluent.

Projects and Evaluations

1. Supplied information to R. F. Seifert of CED covering solids containing PCB generated at Anniston for use in evaluation of PCB/solids incinerator tentatively located at WGK.

2. Laboratory tests conducted by Betz Laboratory representative in our Anniston laboratories indicates that Bentonite Clay and Betz Polymer 1175 combination is very effective in removing solids from Limestone Pit effluent. Some mix will be tried by Denver Equipment Laboratories and then clarifier size recommendations will be developed.

Pilot scale unit utilizing Biodize clarifier under construction. Startup is targeted for February 1.

3. Construction of No. 1 Limestone Pit 90% complete. Will meet 2/1/71 construction completion unless delayed by weather.

4. Approximately 20 tons of inert material pumped from effluent end of pit (along with 260 pounds of PCB adsorbed on the inerts) on 12-18-70. This approach has added one month to the effective pit life at this time and can be repeated several more times.

W. B. Papageorge

W. B. PAPAGEORGE

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