028201 UNITED STATES ENVIRONMENTAL PROTECTION AGENCY 10-18-79 (9)

028201

DATE: 10/18/79

SUBJECT: Meeting with Rohm & Haas on the Univ. Wisc.-Superior Fathead Minnow Study.

FROM: John S. Leitzke, Ecologist
Fred Betz, Aquatic Biologist
Ecological Effects Branch, HED (TS-769)

TO: Richard F. Mountfort, PM 25
Herbicides-Fungicides Branch, Reg. Div. (TS-767)

THRU: Norm Cook
Registration Coordinator
Ecological Effects Branch, HED (TS-769)

THRU: Clayton Bushong
Chief, Ecological Branch, HED (TS-769)

Attendees: Ecological Effects Branch, HED -- Fred Betz; John S. Leitzke
Herbicides-Fungicide Branch, Reg. Division -- Rich Mountfort (PM-25)
Rohm & Haas -- Stephen F. Krzeminski, Ph.D. (Regul. Mar.); Irving L. Adler (Res. Chem.); Morici (F & W Tox)
EG & G, Bionomics -- Kenneth J. Macek (Aq Tox Consultant & Contractor for Rohm & Haas)

At question was the Univ. Wisc.-Superior fathead minnow chronic (or embryo-larvae) study, which showed a Maximum Acceptable Toxicant Concentration of 0.4 to 0.6 ppb compared with a 96-hr LC50 of 3.6 ppm giving an Application Factor of 22,000, and Rohm & Haas' contention that these results are not applicable to currently produced propanil because of alleged impurities in the old technical used by Univ. Wis-Superior.

Krzeminski stated at the outset that he would like to have propanil registered as quickly as possible and would like to have commitments from us as to what EEB is going to do and need.

Adler stated the old technical batch (lot no. 8771) was sent to Duluth for the fathead minnow chronic study in late '77 or early '78. He then submitted data done by Macek with the old technical (lot no. 8771), new technical (lot no. 9287) and purified (99+%) propanil on fathead minnow fry showing that the old technical is 20 times as toxic as the new technical in acute tests (see attached sheet). Adler also stated that current synthesis of propanil [redacted] and that Rohm & Haas is willing to do more acute tests with current batches of technical on fathead fry as a bioassay quality control.

MANUFACTURING PROCESS INFORMATION IS NOT INCLUDED

EPA FORM 1320-6 (REV. 3-76)

~~Krzeminski said that it has all been formulated and probably all used up by now.~~

Macek, noting the differences in the acute tests and the differences in the [redacted] said that potential impurities in the old technical (lot no. 8771), and not in the new technical (lot no. 9287), could account for the differences.

Betz and Leitzke said that Macek should submit his full report and Morici whatever comparative data he had as well.

In looking at the contents data sheet, no significant differences were seen by Leitzke or Adler in the contents of lot nos. 8771 and 9287.

Krzeminski stated that Rohm & Haas is willing to commit to a continuation of quality control aquatic bioassays on fathead fry if different suppliers of 3-4-dichloraniline are found in the future.

Macek then stated that the real question is, what is the chronic toxicity of the current technical, and that perhaps this question could be dealt with by comparing his fry data with the raw fry mortality data from the Univ. Wisc. - Superior study. Leitzke responded that fry are not necessarily the only very sensitive life-stage; Dr. Call of Univ. Wisc.-Superior indicated that the older survivors were greatly swollen and sluggish, and Russian (Popova, 1973) data indicates possible irreversibility of toxicity. (See attached).

Commitments were then made by Rohm & Haas to check consistency of current lots using fathead fry acute bioassay, and by EEB to look at Univ. Wisc.-Superior data and Macek data for possible comparisions. EEb also stated clearly that Rohm & Haas may find it necessary for them to run a chronic embryo-larvae study using new technical. Krzeminski still wanted a commitment about EEB's registration review because he wanted propanil registered on wheat in time for the 1980 application. Plus, he said, the four states where propanil is to be used (Montana, North & South Dakota and Minnesota) seem unwilling to go along with anymore Emergency Exemptions. ~~When asked about projected total acreage should not be that much more than that granted in previous Emergency Exemptions.~~

Leitzke outlined several possible routes EEB was willing to proceed:

1. Proceed with the registration review now with the data available (including the Univ. Wisc.-Superior study), and modify it later if EEB judges that the quality control fathead fry bioassay results (projected to be in to EEB by January, 1980), or any possible additional chronic embryo-larvae test in the future, on current technical batches warrant a revision; or

2. Wait until the fathead fry acute data is in and then do the review; or

3. Have Rohm & Haas the redo the embryo-larvae chronic study on current technical now, wait for its results, and then do the review; or

4. Wait until acute bioassay results are in, if necessary have Rohm & Haas redo the embryo-larvae chronic study, and then wait to do review after results are in.

Rohm & Haas stated that they preferred to go with the first option, i.e. to have EEB proceed now with the review with the data available (including the Univ. Wisc.-Superior study), and modify it later if fathead fry acute bioassay results are judged to warrant such a revision.

To this end EEB must receive: 1) a full report on the recent fathead fry bioassay done by Macek comparing old technical (lot. no. 8771) and new technical (lot. no. 9287), 2) full reports on all subsequent quality control fry acute bioassays using other current batches of technical, and 3) fully listed contents data sheets, listing all components and impurities "present in quantities of 0.01 percent (of the weight of the product) or more" (CFR 163.61-7; Product Chemistry, Product Analytical Methods and Data, Manufacturing - Use Products), for lot nos. 8771 and 9287 and all other batches on which quality control fathead fry acute bioassays are subsequently run.

Table 1

STAM (Propanil): Static LC_{50} (96 hour) in Fathead Minnows

Chemical	LC_{50}, mg/l 48 hr. old eggs	LC_{50}, mg/l ≤24 hr. old fry	LC_{50}, mg/l 30 day old fry
STAM purified, 99+%, WDW 51:26a	≥1.9	8.4(6.8-10.7)	-
STAM Tech, 85.9%, lot 8771[a]	-	0.18(0.01-0.34)	8.6[c] (3.2)
STAM Tech, 85.4%, lot 9287[b]	≈4.0	4.0(3.3-4.9)	-

[a]Lot 8771 was used in the EPA study.
[b]Lot 9287 is typical of current production material.
[c]LC_{50} determined by EPA Laboratory; figure in parenthesis represents the 192 hour LC_{50}.

TELEPHONE MEMORANDUM

Date: 4/29/80 Time: 4:00 pm

To [redacted]: Dan Call

Subject: Methods for Propanil Residue Analysis

Major Points Covered

1) Fathead Chronic test levels of 0.4 and 0.6 ppb were approaching the level of sensitivity and detectability above 'background noise'. These tests were run in relatively clean water

2) Agreed that analyzing pond water (which would be dirtier, i.e. having compounds in that might interfere with and cause more background noise) may not be as sensitive. Suggested using gel permeation chromatography as an additional clean up method, which has proved successful in similar situations.

3) Mentioned recent article in Bull Env Cont Tox (1980. 24: 550-54) which found 3,4-DCA in rice.

4) [redacted] This brought up ~~possibility~~ possibility of looking for 3,4-DCA in these pond waters as well, as evidence of propanil contamination.

TELEPHONE MEMORANDUM

Date: 2/19/80 Time: 4:00 pm

To ~~From~~: Doug Kuehl

Subject:

Progress on residue analysis

Major Points Covered

Sent results + Ray Kent's mixture of 1:1 TCAB: TCA_2OxyB back to Dan Call

Waiting for more residue samples for analysis from Dan Call

Actually, Dan Call can do now what he needs done himself on his own GS since he has now a known source of TCAB + ~~TR~~ A_2OxyB.

TELEPHONE MEMORANDUM

Date: 12/5/79 Time: 2:00 pm

To: ~~From:~~ Doug Kuehl

Subject: Progress on residue analysis

Major Points Covered

Told him I'm not able to arrange things with Rohm & Haas

Said Ray Kent's mixture is 1:1 TCAB : TCA$_2$O$_{xy}$B by Mass Spectral

Is going to check his lab procedures against this known source of TCAB, and then fully reanalyze old technical a second time

TELEPHONE MEMORANDUM

Date: 11/21/79 Time: 10:15 am

To [redacted]: Douglas Kuehl - Analytical Chemist, Duluth Env Res Lab (8-783-9559)

Subject:

Residue analysis of propanil technical (lot. no. 8771)

Major Points Covered

Did not see any azobenzene by following published procedures — but did not have any TCAB to check out his own lab's methods

Rainbow trout metabolism study found TCAB formed in TLC but not found in Mass Spectral — Although he wasn't there at the time of this work, they analytical chemists probably used a different method (one which works well with relatively high concentrations of azobenzene) than that used in the residue analysis of the technical

Dan Call has some material synthesized by Ray Kent (who has since left) which should be TCAB on hand now Willing to try this out on the two methods but would also like some TCAB from Rohm & Haas as well as new technical (that used by Bionomics - lot. no. 9287) to check out his lab procedures.

TELEPHONE MEMORANDUM

Date: 10/23/79 Time: 12:30 pm

From: Dr Dan Call

Subject: Propanil Fathead Minnow Study

Major Points Covered

Started off with 30 fry per duplicated tank, but then cut them back to 20.

Fertilized eggs hatch within about 4 days

Will get back in touch about apparent differences between data sheet (E) + results in 3rd Quart. Rept.

TELEPHONE MEMORANDUM

Date: 10/4/79 Time: 11:30 am

To ~~From~~: ~~Dr~~ Dan Call, Ph.D — Univ Wisc - Superior Ctr Lake Sup Env Studies (zip 54880) (715-392-8101 -ext. 410)
Duluth Lab (218-727-6692 - ext. 503)

Subject: Fathead Minnow Chronic Study on Propanil

Major Points Covered

Got Propanil from Rohm & Haas

Douglas Kuehl of Duluth currently doing analysis - first go-around did not show anything unusual

When asked ~~Mike~~ he tested such low levels of propanil, he said complete mortality soon occurred at higher concentrations in initial runs

Surviving fish were very swollen + sluggish + generally not very good looking at all.

When told about Russian study (Popova, 1973) said he would like a copy of translation (have sent it to him)

Co-worker on fathead minnow study Ray Kent now at EPA Hdqtrs in DC.