Return to FM 3422 File

Form 6747-11-A

TECHNICAL REPORT SUMMARY

Date: 5/22/79

TO: TECHNICAL COMMUNICATIONS CENTER – 201-2CN

(Important – If report is printed on both sides of paper, send two copies to TCC.)

Division: Environmental Laboratory (EE & PC)	Dept. Number: 0222
Project: Decatur, Alabama - Tennessee River Fish	Project Number: 78-2740
Report Title: Bioaccumulation of Fluorochemicals in Tenn. River Fish	Report Number: 001
To: D. L. Bacon	
Author(s): James E. Gagnon	Employee Number(s): 213531
Notebook Reference: 51568	No. of Pages Including Coversheet: 10

SECURITY ▶ ☐ Open (Company Confidential) ☒ Closed (Special Authorization) — 3M CHEMICAL REGISTRY ▶ New Chemicals Reported ☐ Yes ☒ No

KEYWORDS: (Select terms from 3M Thesaurus. Suggest other applicable terms.)

EE & PC
Decatur

CURRENT OBJECTIVE: Qualitative and quantitative determination of ~~FM-3923~~, FM-3925, and FM-3422 in fish taken from the Tennessee River above and below Wheeler Dam at 3M's Decatur plant. Analyze for organic and inorganic fluoride in the same samples.

Should be F 6309

Everywhere mentioned in report according to JEG on 7-22-81

REPORT ABSTRACT: (200-250 words) This abstract information is distributed by the Technical Communications Center to alert 3M'ers to Company R&D. It is Company confidential material.

Channel catfish *(Ictalurus punctatus)* had the largest combined total, 2.74 ppm and 1.13 ppm, of FM-3923, FM-3925, and FM-3422, as determined by gas chromatography. It was shown that the three fluorochemicals of interest bioaccumulated more readily in the gastrointestinal tract, fat and reproductive system of the channel catfish, while no fluorochemicals were observed in the muscle layer. A white bass *(Roccus chrysops)*, taken from below Wheeler Dam, had a combined FM-3923, FM-3925, and FM-3422 concentration of 0.40 ppm. A white crappie *(Pomoxis annularis)*, from above Wheeler Dam, was found to contain only FM-3923, 0.004 ppm.

Total organic fluoride ranged from 9.7 ppm, channel catfish, to 16.2 ppm, white crappie. Inorganic fluoride ranged from 6.2 ppm, white bass, to 24.6 ppm, channel catfish.

Future Studies: TLC on above fish samples.
GC/MS on channel catfish samples.
Background fluorochemical analysis on a crappie from a Minnesota Lake.

cc: D.Ricker-236-2B
A.Welter
A.Mendel

Information Liaison Initials: SKW

3M CONFIDENTIAL

INTRODUCTION

It is known that 3M's Decatur, Alabama plant effluent has high organic fluoride levels, 10.9 ppm (1)(2). It has also been shown that fluorochemicals can bioaccumulate in fish in a laboratory environment (3)(4). With these combined factors, the next step was to see if fish caught in the Tennessee River near the Decatur plant had detectable levels of fluorochemicals.

RESULTS AND DISCUSSION

Table 1 lists the concentration, in ppm, in fish of compounds which have the same retention time as the three fluorochemicals of interest (FM-3923, FM-3925, and FM-3422).

Analysis of the results for the dissected channel catfish, Sample 3A, shows that the fluorochemicals bioconcentrate to a greater extent in the gastrointestinal tract, reproductive system, and fat. It can also be seen that the muscle layer was found not to bioaccumulate the three fluorochemicals of interest. These results agree with earlier reports (3)(4).

When comparing the total fluorochemical content (TFC) for the two whole fish samples, the larger channel catfish contained more than twice the fluorochemical content, 2.74 ppm vs. 1.13 ppm. Since both fish were caught in the same area, a reasonable explanation for this may be related to the high partition coefficients for channel catfish. Fluorochemicals bioaccumulate in fatty tissue, and since more fatty tissue is present in the larger fish, more fluorochemicals would be expected.

FM-3923 is present at higher concentrations in the dissected channel catfish, sample 3A, than other samples. Since bioaccumulation rates have not been determined for FM-3923, no explanations for the higher concentrations can be offered.

The two fish samples which had cores taken from them will not be rigorously compared to whole fish samples. The reason for this is that the core samples may not have representative concentrations of fluorochemicals (whole fish values may be higher or lower). Since core samples were taken from the approximate same location, the results can be rigorously compared.

The white bass from below Wheeler Dam, sample 1B, had a whole fish TFC of 0.40 ppm, while the white crappie from above Wheeler Dam, sample 2A, had a whole fish TFC of 0.004 ppm. With such small statistical samples, it would be difficult to say that the larger TFC is due only to the white bass living in the presence of higher fluorochemical concentration, downstream from the plant. Other possible explanations for the higher TFC could be the following:

TABLE 1

FLUOROCHEMICAL CONCENTRATION (ppm)
IN TENNESSEE RIVER FISH

Sample	FM-3923	FM-3925 & FM-3422 (1)	Total Combined FC in Fish (ppm) (2)
1A - Whole fish	0.40	0.73	1.13
1B - Core (3)	0.82	3.31	0.40 (4)
2A - Core (5)	0.06	N.D. (6)	0.004 (4)
3A - Gills	1.48	0.80	
3A - Liver	2.17	0.38	
3A - Parts (7)	1.33	0.43	2.74 (9)
3A - Muscle	N.D.	N.D.	
3A - Fat (8)	13.85	6.12	
3A - Gall bladder	1.57	0.74	
Water blank	N.D.	N.D.	
Ethyl acetate blank	N.D.	N.D.	

Footnotes to Table 1:

(1) FM-3925 and FM-3422 cannot be resolved with GC parameters used; therefore, a combined value is reported.
(2) Based on frozen weight of the fish.
(3) Sample core, 3.61 cm, id contained skin, filet, reproductive organs, and parts of kidney, rectum, and backbone.
(4) Assumes that the concentrations obtained in the core are representative of the rest of the fish.
(5) Sample core, 3.61 cm id contained filet, vertebrae, skin, and bile.
(6) N.D. = Not detected.
(7) Consisted of muscle, skin, blood, bone, and cartilage.
(8) Consisted of gastrointestinal tract, reproductive system, and fat.
(9) Based on the actual weight of sample used, 18.8% less than frozen weight, and weight percent of each part.

1. Longer river residence time, older fish.
2. Longer location residence time.
3. Different species
   a) Different feeding and life stylos
   b) Contains larger weight percent of organs which tend to bioaccumulate fluorochemicals
   c) Larger fluorochemical partition coefficients

If the core samples are representative of whole fish concentrations, then it can be postulated that channel catfish bioaccumulate fluorochemicals to a greater extent than either white bass or crappie. Reasons for this are the same as listed above.

Table 2 gives the results of the organic (RF) and inorganic fluoride (F^{θ}) concentration, in ppm, in the fish samples.

TABLE 2 (5)

ORGANIC (RF) AND INORGANIC (F^{θ}) FLUORIDE CONCENTRATIONS (ppm)

Sample	RF	F^{θ}
1A	9.7	24.6
2A	16.2	13.3
1B	10.5	6.2
Water	N.D.	0.01

Jon Belisle points out that the high inorganic fluoride values seem rather surprising. His only explanation was that fish flour previously analyzed, for a different requestor, was shown to have inorganic fluoride values higher than organic fluoride. Jon also states that high inorganic fluoride values would make it difficult to calculate low levels of organic fluoride.

Comparison of the organic and inorganic fluoride content shows that samples from above Wheeler Dam have just as high, if not higher, values than for the sample from below the dam. There are no clear cut explanations for this observation. An earlier analysis of Tennessee River water showed high organic fluoride concentrations upstream from the plant. At that time, it was thought the samples may have been mislabeled. With these results,

it would seem to indicate that the concentration of fluorochemicals may actually be less below Wheeler Dam. This may be caused by volatilization of the fluorochemical when going over the dam (1), settling of fluorochemicals before the dam.

Comparison of organic fluoride values from Tables 1 and 2 show no correlation. For example, the highest organic fluoride value, 16.2 ppm for sample 2A, had the lowest TFC, 0.004 ppm, for the fluorochemicals analyzed. A possible explanation is that there are organic fluorides present in very high concentrations which were not analyzed for individually. The species which had the highest fat content, channel catfish, had the lowest organic fluoride concentrations.

With limited sample population (2 fish of one species and one of each of two other species), it is difficult to draw any meaningful conclusions. The only definite conclusion is that the fluorochemicals studied do appear to bioaccumulate in river fish under natural conditions.

EXPERIMENTAL

1. Sample materials

Fish

1A - Small channel catfish *(Ictalurus punctatus)*, caught above Wheeler Dam in Tennessee River.

1B - White bass *(Roccus chrysops)*, caught below Wheeler Dam in Tennessee River.

2A - White crappie *(Pomoxis annularis)*, caught above Wheeler Dam in Tennessee River.

3A - Large channel catfish *(Ictalurus punctatus)*, caught above Wheeler Dam in Tennessee River.

Standards

FM-3923, FM-3924, and FM-3422.

Ten ppm standards of FM-3923, FM-3925, and FM-3422 were prepared by diluting 1 ml of a 100 ppm standard, in ethyl acetate, to mark with ethyl acetate in separate 10 ml volumetric flasks.

2. Analysis Instruments/Materials

Blender:

Waring Commercial blender, Model #91-263, available from Waring Products Division, Route 44, New Hartford, CT 06057.

Tissuemizer:

Model #SDT, available from Tekmar Company, P. O. Box 37202, Cincinnati, OH 45222.

Dinker Die:

3.61 cm id AISI-02 high carbon steel cutting die made by Jerry Guthrie in Central Research Labs, described in 3M Technical Notebook #51568-35.

Mixer:

"Vortex Genie" Model #K-550-G, available from Scientific Industries, Inc., Bohemia, NY 11716.

Centrifuge:

Damon-IEC Model #B-20A, available from Damon-IEC Corporation, Needham Heights, MA.

Bottles:

Four-ounce widemouthed clear glass bottle sealed with aluminum foil and aluminum foil-lined caps.

125-ml linear polyethylene (LPE) plastic bottle with polyseal caps.

Gas Chromatograph:

Chromatograph - Hewlett-Packard Model 5713 GC.
Integrator - Hewlett-Packard Model 3380A integrator-printer.

Both of the above available from Hewlett-Packard Co., 150 Page Mill Road, Palo Alto, CA 94304.

Column - Six-foot, 1/8 inch OD, stainless steel, packed with 10% CW20M on 60/80 Chromasorb W-AW.

Column Temperature - Isothermal 180° C.
Injector - On-column at 200° C.
Detector - Electron Capture at 300° C.
Flow - ~40 cc/minute of Argon:Methane (95/5).

Ethyl Acetate:

"Li Chrosolv" chromatography solvent available from MC/B Manufacturing Chemists, 2909 Highland Avenue, Norwood, OH 45212, as Catalog #6008688M.

Water:

Deionized water.

3. Procedure (6)

Procedures used below, except for minor modifications, were obtained from earlier 3M Technical Report summaries (7).

Samples 1A through 3A and 1B were removed from the freezer and placed in large aluminum pans, in a fume hood, and allowed to thaw.

A whole channel catfish, sample 1A, was cut into 5 sections and homogenized in a blender with 200 ml water.

Sample 1B had a dinker die core sample taken just off the lateral line behind the gill plate. Contents of the 20.591 gram sample were skin, filet, small part of backbone, reproductive organs, part of kidney, and rectum.

Sample 2A had a dinker die core sample taken behind the gill plate. The 16.684 gram sample contained filet, vertebrae, skin, and bile. Samples 1B and 2A were homogenized with 10 ml of water in a "tissuemizer."

Sample 3A was dissected, and the various individual parts were homogenized with water. Individual parts weighing more than 25.0 grams were homogenized in a blender, while those of lesser weight were homogenized in a "tissuemizer." Table 3 lists the sample, sample weight, and amount of water added for homogenizing each sample.

All of the above samples, after homogenization, were divided into five aliquots and placed in precleaned bottles, (dichromate/acid, water rinse, dry, toluene, dry). Three aliquots were placed in LPE bottles, while the other two were placed in glass bottles. Samples were stored in a refrigerator at 4.5° C. until needed.

Samples analyzed for FM-3923, FM-3925, and FM-3422 were prepared according to the following procedure. See Table 4 for weight of sample and milliliters of ethyl acetate used for extractions.

A previously homogenized sample, stored in a glass bottle, was weighed (no larger than 4.00 g) and added to a 30-ml precleaned glass centrifuge tube. A volume of ethyl acetate was added at the rate of 1.0 ml ethyl acetate per gram of homogenate. The ethyl acetate/fish homogenate were mixed for 1.5 minutes in a mixer at a speed setting of 3. The samples were removed and centrifuged at 1500 rpm at

21° C. for 10 minutes. After centrifuging, the ethyl acetate layer was separated, by use of a pipet, and placed in a vial. Five µl of sample (standard) was injected for gas chromatographic analysis.

Samples 1A, 2A, and 1B homogenates, plus a water blank, in LPE bottles, were sent to Jon Belisle of the Central Research Laboratory for organic and inorganic fluoride analysis.

REFERENCES

(1) 3M Technical Report Summary, August 30, 1978, Arthur Mendel to R. L. Bohon, "Fate of Fluorochemicals Project - Progress Report."

(2) Central Research Laboratory Report Number 6902, April 20, 1978, Jon Belisle.

(3) "Bioconcentration of FM-3422 in Bluegill Sunfish and in Channel Catfish," M. T. Elnabarawy to A. N. Welter, May 17, 1977.

(4) 3M TRS, August 16, 1978, A. N. Welter to D. L. Bacon, "Evaluation of the Bioconcentration Potential of FM-3422."

(5) Central Research Laboratory Report on Request #A72199 by Jon Belisle, May 7, 1979.

(6) Experimental work done in cooperation with A. N. Welter of the Environmental Laboratory (EE & PC), who performed the dissections and homogenizations.

(7) 3M Technical Report Summary, November 15, 1977, A. Mendel to D. L. Bacon, "Analytical Methodology on FM-3422."

James E. Lagnon
JEG/cen

TABLE 3

FISH WEIGHTS AND WATER VOLUMES USED FOR HOMOGENIZATION

Sample Description	Initial Whole Frozen Weight	Actual Sample Weight Used	ml Water Used
1A	146.0 g	Whole fish (1)(2)	200
2A	266.5 g	16.684 g (3)	10
1B	210.0 g	20.591 g (3)	10
3A - Muscle	752.0 g	209.93 g	200
3A - Gall bladder	752.0 g	1.378 g	10
3A - Liver	752.0 g	5.949 g	10
3A - Fat	752.0 g	52.230 g	100
3A - Parts	752.0 g	321.57 g	300
3A - Gills	752.0 g	19.38 g	100

Footnotes:

(1) A fish hook, with no apparent rust or line, was found in fish and was removed before homogenization.

(2) The fish appeared to be slightly dehydrated (possibly due to constant air flow over surface of fish) so the actual weight of fish used may have been less than frozen weight.

(3) Sample core 3.61 cm id.

TABLE 4

FISH WEIGHTS AND ETHYL ACETATE VOLUMES USED FOR EXTRACTIONS

Sample Description	Weight of Fish Homogenate (grams)	% Water in Homogenate	Actual Fish Wt. Extracted (mg)	ml EtOAc
3A - Gall Bladder	1.20	87.9	145.2	1.2
3A - Liver	2.20	62.7	820.6	2.2
3A - Muscle	2.40	48.8	1228.8	2.4
3A - Fat	2.40	65.7	823.2	2.4
3A - Parts	3.00	48.3	1551.0	3.0
3A - Gills	3.00	83.8	486.0	3.0
Water Blank	2.40	100.0	--	2.4
1A	2.40	57.8	1012.8	2.4
1B	2.40	32.7	1615.2	2.4
2A	2.40	37.5	1500.0	2.4