

3M Report: Bioaccumulation Studies

AR226-0351

J.W. Gillett

- ① 1. Report No. 1 (5/17/77) "Bioconcentration of FM3422 in Bluegill Sunfish and in Channel Catfish" and Progress Report No. 2 (10/14/77) "Fate of Fluorochemicals"

A modified (from what?) exposure (?) technique was used to estimate BCF to bluegill and channel catfish (whole body) and particular tissues following exposure to a supersaturated solution (suspension) of FM 3422 (N-Et FOSE alcohol). Experimental detail are lacking in many areas for which there are text statements and conclusions. Even for its time this set of experiments was only marginally useful, at best. Problems include the following:

- a. The character and source of the FM 3422 is never stated, particularly with regard to purity; similarly, the assay technique is undocumented as to precision and sensitivity for the purposes to which it was applied.
- b. The material taken up and bioaccumulated was never identified as the nominal toxicant to which the fish were exposed, as far as readers are concerned. Could it be a metabolite and/or bound residue?
- c. Geo. Chapman and Chuck Warren at Oregon State Univ. had demonstrated the utility of saturated glass bead delivery in a flow-through system in the early 1970's. In the course of those experiments they were able to demonstrate the presence of a very much more highly toxic component of tech. dieldrin which was not the nominal compound (HEOD). Their method was to saturate the glass beads with tech. dieldrin by removal of acetone solvent in the flash evaporator, then place the beads in a large column over glass wool and a portion of clean beads. The water-jacketed column was brought to experimental temperature and portions of the water stream assayed for dieldrin (as HEOD) by extraction and GC/EC. A compound with lower EC response than HEOD for its toxicity (or much more toxic for its EC response) came off the column during the equilibration phase (1-2 weeks), but was not detectable by 3-4 weeks when the HEOD concentration was stabilized (it remained constant for ca. 10 weeks). Use of the Brungs-Mount diluter with this saturated solution produced consistent results if the diluter apparatus was equilibrated with the test solution. The point is that the column can generate suspensions and solutions of changing composition and toxicity, as well as concentration. The static system employed in these papers cannot equilibrate in the same sense as does a flow-through system.
- d. The authors used the "air-off" concentrations as that for the BCF calculation, although they clearly had a problem with values of FM 3422 15-300% (!) higher with "air-on." The latter was probably the "well aerated" water to which test fish were exposed. This underlines the extensive problem supersaturation creates.
- e. It is likely that the values reported have little to do with bioaccumulation or even uptake per se, at least as exposed within the reports. Whole body residues might include entrapped material (colloidal particles in the gills); tissue residues depend upon not only correct dissection, but also protection from surficial contamination.
- f. The number of fish constituting a sample, the number of fish per tank, the size (length, weight) of each fish, and whether measured fish were live or among the dead removed all are alluded to but never detailed by the authors. Nevertheless, they proceed to note that larger fish accumulate more FM 3422 than smaller fish and that some (3) of the controls died. Heavier fish might have a higher percentage of fat than younger, leaner fish. It would be useful to know if the test subjects had about the normal lipid content.
- g. It is not clear why fish were dipped for 2 min, then analyzed. The experiment is without much meaning with respect to protection, toxicity analysis, etc. I know of no database including such a measurement for comparison with other toxicants.
- h. The cited value for K_{ow} appears in error; it may involve mis-measurement.

006234

- i. Some of the tissues show no increase in BCF between 1 and 4 weeks; others (gills and gut) increase dramatically. The data in tissues do not support the assumption that a true equilibrium is reached between the fish and its environment or within the fish between tissues.

Analytical From Fish Bioconcentration Studies

PROJECT NO. 9970612000

3M TECHNICAL NOTEBOOK NO.

41947 21

Subject: Bioaccumulation of FM-3422 in channel catfish Date: 1/15/76

Object:

Reference:

A significant problem with this work is that no where was it demonstrated that solvent extracts of fish tissue were quantitative. SARC-3-4-83

Three groups of 5 channel catfish were exposed for 32 days to Control water, 400ml acetone on marbles, and 16g FM-3422 + 400ml Acetone sprayed on marbles in 16L Tank.

The fish after 32 day exposure were dried and wt taken

Control
3.95g

Acetone only
4.65g

FM-3422 + Acetone
4.77g

The three (5 lot) groups were digested with ~25ml 20% KOH at 50°C for 1 hr. The three digested samples were then diluted to ~50ml and extracted with 10ml N-Octanol. G.C. for FM-3422

50ml aliquots of the tank water was extracted with 10ml octanol also for G.C. analysis,

All samples G.C.ed see FC 1/19/76 to yield

Water - mg/l FM-3422
Control - Nil

Acetone - Nil

FM-3422 - 0.17mg/l

Fish - mg/g - dried fish
Control - 0.0015mg/g

Acetone - 0.0006mg/g

FM-3422 - 0.161mg/g

006236

Signature

E. J. Vraspi

Date:

3/8/78

14712

2 22 20

PROJECT NO. 99 706 12600

3M TECHNICAL NOTEBOOK NO.

PAGE

Subject:

41947 23
Date: 2/18 - 2/20/76

Object:

Reference:

LR 3114 was to determine the uptake of FM-3422 by channel catfish in a 1,000 ppm tank (static) 33 day exposure. Verify the fish test. Page 21

~~Test~~ Samples submitted - Test Water (1,000 ppm)

Fresh gutted wt.
Fish were gutted { Fish ① - 3.20g
Fish ② - 3.46g
Fish ③ - 2.58g

Test water sample was extracted with 10ml Oct per 10ml H₂O

Fish were digested in 10ml each of 20% KOH by heating to ~50°C for 1 hr. Then extracted with 10ml Oct.

~~Extracts~~ G.Ced See integrator reports 043-048

to yield ~~Test~~ Water 4.86 mg/l

Fish ① - 0.31 mg/g - Fresh gutted wt.

Fish ② - 0.24 mg/g - " " "

Fish ③ - 0.46 mg/g - " " "

The test water was filtered through a Millipore 0.22µ filter and 50ml water extracted with 2ml Oct. G.Ced integrator report 049-051 to yield 0.011 mg/l.

006237

Signature

M. D. Vreep

Date:

3/8/78

PROJECT NO. 9970612600
 Subject:

3M TECHNICAL NOTEBOOK NO.

Date:

11947 24
2/23 - 2/25/78

Object:

Reference:

LR 3114 - The second part of the uptake bioassay was the removal of the fish from the FM-3422 tank and placement of them into ~~the~~ a tank of clean H₂O to determine the cleaning effect if any.

Samples submitted - Control Water

Recovery tank Water

Fresh gutted wt.

Control Fish #1

4.63g

Control Fish #2

4.80g

Exposed fish #1

3.90g

Exposed Fish #2

3.66g

Water samples extracted 2ml / 10ml Oct / H₂O

Fish digest as earlier and extracted with 10ml Oct.

Sample ext. G Ced Ing reports - 061-067 to

yield Control Water - <0.01mg/l FM-3422

Recovery Water - 0.033mg/l

"

Fish

C-1

-

0.00067mg/g

"

C-2

0.00097mg/g

"

F-1

0.029mg/g

"

F-2

0.031mg/g

"

006238

Signature

M. D. Vraspir

Date:

3/8/78

PROJECT NO. 9970612600

3M TECHNICAL NOTEBOOK NO.

41947 25

Subject:

Date: 2/73 - 2/24/76

Object:

Reference:

Same question was raised to the validity of the
1ml/50ml Oct/H₂O extraction ratios used to
obtain the lower detection limits.

A. 0.5mg/l soln of FM-3422 in H₂O was made by
dispersing the FM-3422 via acetone

1st, 2nd, & 3rd extractions were made with the
1ml/50ml ratio G.C. - Int. reports - 052-057

The yield was 1st - 86%

2nd 13%

3rd 2%

} Total = 0.438mg/l

100% recovery
in 35ccm dec
1:50 ml extracts of
H₂O

Same procedure was tried on a sat water soln
of FM-3422. G.C. int. reports 058-059

To yield 1st ~~86%~~ 89% 7.5mg/l

2nd ~~13%~~ 10% 0.84mg/l

3rd 1% 0.06mg/l

} 8.4mg/l

006239

Signature

A.D. Vraspin

Date:

3/8/78

PROJECT NO. 9970612600

3M TECHNICAL NOTEBOOK NO.

41947 41

Subject:

Date: 3/8/77

Object:

Reference:

3 samples were drawn from the FM-3422 fish tank. These samples were taken at the same levels as the initial samples and will be analyzed for FM-3422

Samples ① ^{Day 8} ~~Fish~~ ② ^{Day 8} ~~Fish~~ ③ ^{Day 8} ~~Fish~~

Mo gave me 2 digested bluegill fish samples

Day 8 Control fish 1.15g Exposed Fish 0.977g.

Water samples and fish samples were taken on 3/14/77 - 14 days of exposure.

Control 3/14/77 - 3 fish wt. = 1.434g.

Exposed 3/14/77 - 3 fish wt. = 1.172g.

Fish samples were extracted with 2 - 10ml portions of ethyl Acetate and then the 2 - 10ml aliquots were diluted to 25ml. Digested fish sample were pH adjusted with H₂SO₄ conc. to pH 7-8

Fish samples G.C. Integrator reports - 051-054

Results: Control fish - No background

	Total wt. fresh fish	Total ^{FM-3422} mg	
Exposed Fish 8 days 3/8/77 -	0.977g	0.115mg	- 0.118 ^{FM-3422} mg/g F

Exposed Fish 14 days 3/14/77 -	1.172g.	0.137mg	- 0.117mg/g Fat
--------------------------------	---------	---------	-----------------

See page 54 for 21 day Exposure.

Signature

Greg Vrospir

M.T. Shokri

Date:

3/21/77

00624

3/20/77

PROJECT NO. 99706126003M TECHNICAL NOTEBOOK NO. 46269 35Subject: FM-3422 Uptake in Channel Cat FishDate: 2/1/78Object: G.C. analysis of water and fish samples submitted by Al Welter for FM-3422. ~~Electron~~ Electron Capture

Reference: G.C. conditions used for study: Column 6'x8" SS on column injection. Chromosorb W A.W. 60/80 mesh CW 20m - 10% Flow Argon Methane 240 ml/min. Temp. Inj. Port 200°C Det. 300°C Oven 170°C Isothermal

Standards run on each day of analysis. Std. w/v in ethyl acetate.
 Water samples extracted with two portions of ethyl acetate.
 10ml of sat NaCl soln added to salt out organics. 100ml water sample extracted & diluted to 10ml.

Tissue sample finsumized in ethyl acetate prior to submittal for G.C. analysis. The ~~to~~ ethyl acetate was transferred to volumetric flasks and subsequent washes made with E.A. then diluted to vol. The study involved uptake - coded "U" and clearance coded "C".

G.C. analysis of 2/1/78

Stds. 10ppm FM-3422 1ppm
 Integrator ~~12,107~~
 Values Ave. 1,261,386 126,838
 Uptake

Water Sample

20hr.	Sample size	Final Vol.	ppm FM-3422	
Bottom	100ml	10ml	0.347	
Middle	100ml	10ml	0.342	0.309
Top	80ml	10ml	0.514	0.478

Fish

20hr.	Wt.	Final Vol.	FM-3422 (µg/g)	
Whole 1	10.309g	50ml	62.0	60.6
Whole 2	10.111g	50ml	75.2	73.0
16hr				
Whole 1	13.678g	"	53.0	48.4
Whole 2	13.185g	"	59.6	53.6

006241

Signature

GO Vrospir

Date:

3/7/78

Read and Understand

175 E. P. LARSEN11-7-78