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of ^{137}Cs Fallout by Fish¹

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A Technical Progress Report

COO-1795-2

to the
United States Atomic Energy Commission

for the period
June, 1969 to February, 1970

¹The work upon which this report is based was supported in part by funds provided by the United States Atomic Energy Commission

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Effects of Limnological Factors on Uptake
of ^{137}Cs Fallout by Fish

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Introduction

This paper reports the progress for the period from June 1, 1969, to February 1, 1970, of a proposed two-year study. The objectives of the program were to determine the influence of selected water quality parameters on the accumulation of cesium-137 by fish, to determine the influence of trophic position on accumulation of cesium-137 by living components of the aquatic environment, and finally to facilitate the prediction of maximum concentrations of cesium-137 in food fishes when estimated inputs of cesium-137 to the environment are given.

These objectives are based on the hypothesis that fish of a given species have different concentrations of cesium-137 in lakes having different water quality. The water quality parameters that are suspected of having an influence are alkalinity, conductivity, cesium, potassium, ^{137}Cs and the specific activity of ^{137}Cs . It has been reported that lake type influences uptake of cesium by fish and that there exists an inverse correlation between accumulation in fish and the conductivity and alkalinity (Hasanen and Miettinen, 1963, and Kolehmainen, Hasanen and Miettinen, 1966). The influence of the stable isotope concentration and the importance of the specific activity of the water on accumulation has been indicated (Kevern, 1964 and Nelson, 1967).

Scope of the Study

The first efforts of the investigation were to select a number of lakes having the desired range of alkalinity and conductivity. The lakes were to be located as near as possible to each other to minimize differences in fallout patterns and all the lakes were to have adequate populations of largemouth bass, the fish selected for study.

Collections of bass and water samples were undertaken to test the hypothesis that differences among the fish were significant, to determine the water quality parameters and in so doing to test the methodology. Water measurements in the lab or field were to include alkalinity, conductivity, Secchi disk readings, temperature, dissolved oxygen, pH, stable cesium, ^{137}Cs , potassium and sodium. One of the greatest deterrents from field investigations of cesium has been the lack of sensitive, practical, analytical methods. This appeared to be solved in a report by Feldman and Rains (1964) on determination of cesium. Analytical procedures for the other parameters have been refined and standardized for some time.

Given significant differences in cesium-137 concentrations in bass from different lakes the statistical analyses could proceed. Multiple regression analysis would be used to test for relationships between water parameters and accumulation levels in the fish. The assumption that specific activities of fish and water are not different would be tested with analysis of variance.

Results and Discussion

Lake Series and Parameters - The final selection of lakes was made on the basis of various physical and chemical considerations and the abundance of the test species, largemouth bass (Micropterus salmoides). Initial water data gathered during 1967-1968 are presented in Table 1. The series of lakes represent a wide range of specific conductance (36 - 365 μmhos) and alkalinity (6 - 205 ppm CaCO_3).

These lakes appear to be typically dimictic and reflect the influences of the stagnation and overturn periods. Even the lakes that are poor in dissolved salts (Cable L. and Dewey L.) appear to be eutrophic as indicated by the clinograde oxygen profiles (O_2 depletion/depth). This condition probably results from their shallow basins and the reduced hypolimnetic volume relative to the epilimnetic volume.

The chemical and physical data collected during 1969 are contained in Table 2. Comparisons of these data with those from 1967-68 reflect very few changes. The apparent relationship between the concentrations of potassium and ^{137}Cs in the water is difficult to interpret at this time. Additional water quality data to be gathered in 1970 may shed some light on the factors involved. The concentration of ^{137}Cs in the water varies considerably from lake to lake and a general trend of higher concentrations in water of low specific conductance is suggested.

The determinations of ^{137}Cs concentrations in water were obtained by use of ion-exchange columns (potassium hexacyanocobalt ferrate = $\text{K}_2 [\text{CoFe}(\text{CN})_6]$), through which 400 liters of lake water were passed. Due to the extended time required to obtain cesium exchange from large volumes of water, only two determinations were made on each lake. Additional determinations of ^{137}Cs and cesium in lake water will be conducted during 1970.

Table 1. Characteristics of Lakes Selected for ^{137}Cs Study in 1967-1968.

Lake	D.O. (mg/l)	Temp. (°C)	Alkalinity Phth.	(mg/l CaCO_3) M.O.	Sp. Conductance ($\mu\text{mhos}/\text{cm}^3$ 25° C)	pH	Secchi disc (meters)
Schnable (Nov.)							
Surface	10.0	5.5	0.0	203.0	365	8.0	2.44
3.0 M	9.6	5.0	0.0	205.0	365		
bottom (6.5 M)	8.8	5.0	0.0	205.0	365		
Wintergreen (July)							
Surface	12.1	22.0	15.0	109.0	269	8.6	2.14
1.0 M	11.5	22.0	11.0	105.0	---	8.3	
bottom (2.5 M)	8.3	21.0	07.0	110.0	321	8.3	
Wintergreen (Nov.)							
Surface	14.2	4.5	0.0	150.0	286	8.1	2.5
1.5 M	14.8	4.0	0.0	144.0	280	---	
Fine (July)							
Surface	9.3	27.0	6.0	81.0	217	8.7	2.4
3 M	9.4	25.0	10.0	74.0	211	8.7	
bottom (6 M)	2.5	21.0	0.0	1102.0	233	7.5	
Fine (Nov.)							
Surface	12.5	5.0	0.0	88.0	200		2.5
1.0 M	13.0	4.0	0.0	90.0	192	---	
2.5 M	13.0	4.0	0.0	89.0	192		
Fair (Nov.)							
Surface	9.6	4.0	0.0	44.0	106		
2.5 M	9.6	4.0	0.0	41.0	106	7.5	4.0
bottom (4.5 M)	8.7	4.0	0.0	41.0	106		
Dewey (May)							
Surface	11.4	16.0	0.0	18.0	49	7.5	1.68
3 M	11.3	15.5	0.0	17.0	---	---	
bottom (7.5 M)	0.8	14.0	0.0	18.0	48	7.6	
Cable (May)							
Surface	9.8	15.5	0.0	6.0	39	---	3.48
6 M	9.8	14.8	0.0	7.0	---		
bottom (10.5 M)	1.1	10.3	0.0	6.0	36		

Table 2. Characteristics of Lakes Selected for ^{137}Cs Study (1969).

Lake	D.O. mg/l	Temp. °C	Alkalinity Phth.	(mg/l CaCO_3) M.O.	Specific conductance	pH	^{137}Cs pc/l	K^+ mg/l	Na^+ mg/l
Schnablē (Nov.)									
Surface	10.3	8.9	0	203	450	7.6	.057	3.0	2.5
4 M	9.0	7.8	0	203	450	7.7			
bottom (6 M)	8.5	7.8	0	202	460	7.7			
Wintergreen (Oct.)									
Surface	---	9.4	0	133	340	7.5	.191	13.0	8.0
1 M	---	9.4	0	133	350	7.5			
bottom (2 M)	---	9.4	0	130	350	7.4			
Fine (Nov.)									
Surface	10.5	7.7	0	82	210	7.8	.103	2.0	3.0
1 M	10.5	7.7	0	82	210	7.7			
bottom (3 M)	10.5	7.8	0	82	210	7.7			
Fair (Nov.)									
Surface	10.2	7.7	0	41	118	7.4	.170	14.0	3.0
3 M	10.0	7.7	0	41	118	7.5			
bottom (7 M)	9.5	7.7	0	41	118	7.5			
Dewey (Oct.)									
Surface	8.7	8.3	0	15	62	6.6	.040	2.0	3.0
2 M	8.5	7.8	0	15	62	6.7			
bottom (6 M)	8.2	7.8	0	16	60	6.8			
Cable (Oct.)									
Surface	---	11.1	0	6	45	6.6	.110	3.0	3.5
3 M	---	10.6	0	6	45	6.5			
bottom (7 M)	---	10.6	0	6	46	6.5			

Cesium Analysis in Water - Natural systems contain only trace amounts of stable cesium and fallout ^{137}Cs . Due to the extremely low concentrations of these isotopes in lake water, the initial step in cesium analysis must be one of preconcentration. The method described by Feldman and Rains (1964) proved inadequate in providing concentrations of cesium from lake water that could be detected by the flame emission system available (Jarrell-Ash spectrometer equipped with a phototube having 93% of peak absorption at the 8521 Å cesium band).

A number of other methods of cesium analysis have been proposed in the literature, most being some form of ion-exchange. Methods of ion-exchange for cesium using complex ferrocyanide resins as described by Boni (1966), Prout, et al. (1965), Petrow and Levine (1967), and Mohanrao and Folsom (1963) have been considered. Since large volumes of lake water (500-1,000 liters) may be necessary to obtain sufficient quantities of cesium for analysis, batch ion-exchange methods as described by Mohanrao and Folsom (1963) are deemed unsuitable. Consequently, an ion-exchange column has been designed which (1) allows for rapid ion-exchange of cesium (20-30 l/hr.) under field conditions, and (2) can be placed directly into the well of the gamma detector for ^{137}Cs analysis.

Table 3 includes comparative data regarding the column-use of various forms of the complex ferrocyanide resins. Although further testing is in progress; it appears from the data presented that the cobalt ferrocyanide resin yields a more acceptable efficiency of exchange. The ^{137}Cs data from lake water presented in Table 2 were obtained using the cobalt resin ($\text{K}_2 [\text{CoFe}(\text{CN})_6]$).

The final selection of the ion-exchange resin to be used to preconcentrate lake water will depend on a number of characteristics of the resin and the final sample solution: (1) the exchange efficiency for cesium and flow rate must be maximized (Figure 1); (2) to facilitate analysis by flame emission, cesium must be eluted from the resin or put back into solution by digesting the resin; (3) the final solution must be sufficiently concentrated (small volume) for reliable analysis, which suggests the need for a second method of concentrating the sample.

Table 4 includes a comparison of organic extractants for cesium that were tested on acid solutions of the $\text{K}_2 [\text{CoFe}(\text{CN})_6]$ resin. To date, no satisfactory method has been devised to extract cesium from such solutions. Consequently, the method of ion-exchange for cesium in lake water that has provided maximum exchange at high flow rates, and ease of cesium recovery from the resin involves: (1) the use of $(\text{NH}_4)_2 [\text{CoFe}(\text{CN})_6]$ in ion-exchange columns; (2) eluting the cesium from the resin with 1.0 N sodium hydroxide and (3) proceeding with an organic extraction to further concentrate the sample for flame emission.

The many details involved in this ion-exchange procedure are crucial to reliable quantitative measurements of cesium in lake water. Considerable effort will be directed at this aspect of the study during the coming year.

Table 3. Complex Cyanide Ion Exchange Resin X₂ [Y Fe(CN)₆]

Resin Form	Mesh Size	Weight of Resin	Flow Rate	% Uptake ¹³⁷ Cs	Eluting Solution	% Elution
K ₂ [CuFe(CN) ₆]	20-40	2.5 gm	12 L/hr	46%	15 M HNO ₃	39% 35%
K ₂ [ZnFe(CN) ₆]	20-40	2.5 gm	8 L/hr	67%	15 M HNO ₃	29% 25%
K ₂ [CoFe(CN) ₆]	20-50	5.0 gm	15 L/hr	83%	.1 M TiNO ₃	0% 0%
(NH ₄) ₂ [CoFe(CN) ₆]	20-50	5.0 gm	15 L/hr	80%	1.0 M NaOH	81%

Table 4. Extraction of Cesium From Acid Dissolved K₂[CoFe(CN)₆]

Extractant	Solvent	pH Acid solution	% Extraction	Normality
Tetraphenylborate	Henone	3.0	14%	0.1 N
4-sec-Butyl-2-(4 methylbenzyl)phenol	CCl ₄	2.9	5%	1.0 M
Thenoylfrifluoroacetone	CCl ₄	2.5	0	1.0 M
O-phenylphenol	CCl ₄	2.5	0	1.0 M
Picric Acid	CCl ₄	2.5	0	.1 M
2,4,5 Trichlorophenol	CCl ₄	2.5	0	1.0 M
Phenol	H ₂ O	2.5	0	saturated

Figure 1. Comparison of the efficiency of exchange for ^{137}Cs at different flow rates by $\text{K}_2[\text{CoFe}(\text{CN})_6]$ resin from one liter samples.

Fish Sampling - As of October, 1969, all collections of bass have been completed. Samples are being kept frozen until analyzed for ^{137}Cs and cesium. Approximately 150 bass have been collected for analysis.

Cesium in Fish - Although the chemical analysis of bass for cesium isotopes are incomplete, the preliminary data (1968) verify the feasibility of the study by showing a significant difference in the ^{137}Cs activities of bass from different lakes (Table 5). The concentrations of ^{137}Cs in bass appears to be directly proportional to the concentration of ^{137}Cs in the lake water (Figure 2). The concentration factors (^{137}Cs in Bass/ ^{137}Cs in Water) also appears to be proportional to the levels of ^{137}Cs in the water.

The relationship between the mean ^{137}Cs concentration in bass and the specific conductivities of the lake water is plotted in Figure 3. A definite trend over the entire range of conductance is not apparent from the data; however, it is clear that, in general, low conductivity lake water shows a higher concentration of ^{137}Cs in water and bass. The relationship between water quality parameters and ^{137}Cs levels in bass will be more adequately interpreted once the 1969 fish samples have been analyzed.

Stable cesium determinations in bass have only recently been accomplished. Initially, the method of analysis included: (1) a combination of drying (105°C) and ashing (500°C), (2) wet ashing in nitric acid, (3) dissolving the tissue ash (4) cesium collection as described by Feldman and Rains (1964) and (5) flame emission analysis on a small portion of the tissue ash solution. This procedure was attempted many times with no results. It was obvious that the extremely low concentration of cesium in fish would be detected only if larger samples were further concentrated.

In addition, numerous reports in the literature [Blincoe (1962), Kometani (1966) and Martin and Blanchard (1969)] indicate that ashing at 500°C causes the volatilization of cesium. Consequently, a new technique of ashing fish was developed to eliminate the possibility of cesium loss due to thermal volatilization and to decrease the lengthy dry ashing procedure (4-5 days).

The new technique of ashing fish involves a simple digestion in a boiling flask with nitric acid. Once the entire fish has been put into solution, it is treated in a manner similar to that described by Feldman and Rains (1964) whereby ammonium molybophosphate is used as a batch ion-exchanger for cesium. The final step in the procedure (organic extraction with sodium tetraphenylboron) results in a highly concentrated solution that can be analyzed for ^{137}Cs and cesium. This method of ashing fish has: (1) substantially reduced the ashing time and the total number of steps in the procedure, (2) yielded ^{137}Cs determinations that are consistent with those obtained using dry ashing procedures, and (3) provided pre-concentration of cesium to the extent that quantitative measurements in fish have been obtained (approx. 10^{-9} to 10^{-10} gms).

Table 5. Mean ^{137}Cs Concentrations in Bass and Lakewater.

Lake	Sample Size	Mean Wt. gms	^{137}Cs in Bass pc/gm wet wt.	^{137}Cs in water pc/l	Concentration Factor ($\times 10^3$)
Schnable	1	400	0.147	0.057	2.6
Fine	1	157	0.193	0.103	1.8
Wintergreen	9	580	1.116	0.191	5.8
Cable	9	184	1.148	0.110	10.4
Fair	10	174	1.584	0.170	9.3

Figure 2. Comparison of mean ^{137}Cs concentration in bass with specific conductance of water in lakes (October, 1968).

Figure 3. Comparison of mean concentration of ^{137}Cs in bass with mean ^{137}Cs concentration of lake water.

Summary

Bass samples were collected from five lakes during 1968 and from all six lakes during 1969. A new technique of wet ashing fish has been developed which decreases the analysis time and insures against the loss of cesium due to thermal volatilization. A portion of the bass samples have been analyzed for ^{137}Cs and cesium and the results show an inverse relationship with the specific conductance of the water and a direct relationship with the concentration of ^{137}Cs in the water.

Analyses of lake water have been the most elusive aspect of the study. A new technique involving the use of an ion-exchange resin that is specific for cesium has been developed. Preliminary data collected during the fall of 1969 and laboratory testing indicate that reliable analyses of ^{137}Cs and cesium in lake water will be possible.

Although the interpretation of the data cannot be conclusive at this time, the premises upon which the study is based have been supported. An additional year (terminal) of funding is necessary to complete these aspects of the research plan.

Research Time

The principal investigator (N. R. Kevern) has devoted approximately 15% of his time to this research project (June, 1969 - January, 1970). He plans to devote about 10% of his time during the remainder of the study. Two graduate research assistants have devoted 50% of their time to the research during the past and will continue to do so during the proposed contract period.

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