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DETECTION OF FALLOUT ^{155}Eu AND ^{207}Bi IN A ^{210}Pb-DATED LAKE SEDIMENT CORE

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Management Perspective/Executive Summary

The title radionuclides are produced in nuclear weapons' testing in varying amounts.Their modes of formation are as yet not clearly defined.We report the FIRST detection of both these radionuclides in a freshwater lake,McKay Lake in Ottawa,using high-resolution low-energy gamma-ray spectroscopy for Eu-155 and high-energy gamma-ray spectroscopy for Bi-207.We could trace Eu-155 back to mid 1960's.By comparing the fission yields with Cs-137,we propose that Eu-155 is formed via simple thermal neutron fission of U-235 and discount an earlier suggestion that it is formed via fast neutron fission in U-238.

The amounts detected are too small to cause any concern.

This work was done in collaboration with the Geological Survey of Canada.

DÉTECTION DES RETOMBÉES DE Eu^{155} ET Bi^{207} DANS UNE CAROTTE DE SÉDIMENTS LACUSTRES DATÉS AU Pb^{210}

S.R. Joshi et R. McNeely

À présenter au J. Radioanal.Nucl.Chem., Articles

Analyse de gestion/résumé

Les radionuclides mentionnés dans le titre sont produits en diverses quantités lors des essais d'armes nucléaires. Nous ne connaissons pas encore très bien leur mode de formation. Nous signalons ici la PREMIÈRE détection de ces deux radionuclides dans un lac d'eau douce, le lac McKay à Ottawa, à l'aide de la spectroscopie des rayons gamma de faible énergie et à fort pouvoir de résolution pour le Eu-155 et de la spectroscopie des rayons gamma de haute énergie pour le Bi-207. Nous avons pu retracer le Eu-155 jusqu'au milieu des années 1960. En comparant les rendements de fission avec le Cs-137, nous supposons que le Eu-155 est formé par simple fission thermique des neutrons de U-235 et nous écartons l'hypothèse antérieure selon laquelle il est produit par la fission rapide des neutrons de U-238.

Les quantités décelées sont trop faibles pour causer des préoccupations.

Ce travail a été fait en collaboration avec la Commission géologique du Canada.

Low-energy γ-ray spectrometry is used to detect fallout ^{155}Eu and ^{207}Bi in a ^{210}Pb-dated sediment core from McKay Lake, Ottawa, Canada. Unlike ^{207}Bi which is detected only in two core sections deposited in the mid 1970's, ^{155}Eu is consistently detectable to mid 1960's. A comparison of corresponding ^{137}Cs and ^{155}Eu inventories in the sediment core indicates that fallout ^{155}Eu derives primarily from the thermal neutron fission of ^{235}U. The derived flux of unsupported ^{210}Pb at the sediment/water interface is in agreement with previously estimated flux of atmospheric ^{210}Pb in the Great Lakes region.

La spectrométrie à rayons gamma de faible énergie est utilisée pour déceler les retombées de Eu-155 et Bi-207 dans une carotte de sédiments datés au Pb-210, prélevée dans le lac McKay à Ottawa, Canada. Contrairement au Bi-207 qui est décelé seulement dans deux sections de la carotte déposées vers le milieu des années 1970, le Eu-155 se retrouve de façon constante jusqu'au milieu des années 1960. Une comparaison des inventaires correspondants de Cs-137 et Eu-155 dans la carotte de sédiments indique que les retombées de Eu-155 proviennent principalement de la fission thermique des neutrons de U-235. Le flux dérivé de Pb-210 non supporté à l'interface sédiments-eau est conforme au flux déjà estimé de Pb-210 atmosphérique dans la région des Grands-Lacs.

INTRODUCTION

Europium-155 (T = 4.96y) and ^{207}Bi (T = 38y) are produced both in nuclear reactor operations and in nuclear weapons testing. Following extensive atmospheric testing of nuclear weapons in the late 1950's and early 1960's, fallout ^{155}Eu was readily detected in environmental samples[1-3] in the mid 1960's. Although the production of ^{207}Bi during nuclear weapons testing was demonstrated[4] in the early 1960's, the unambiguous detection of fallout ^{207}Bi in terrestrial environmental samples has only recently been reported[5]. The present communication perhaps constitutes the first reported detection of both these radionuclides in freshwater sediments. The sediment core inventories of ^{155}Eu and ^{137}Cs are used to trace the mode of production of fallout ^{155}Eu. Contiguous sections of the sediment core, retrieved from a small lake known to display negligible mixing effects, were also assayed for atmospherically derived ^{210}Pb to assign precise dates and to derive an estimate of the flux of atmospheric ^{210}Pb in the study area.

EXPERIMENTAL

Study area

McKay Lake is a small (8.0-ha), 10.5 m deep, cup-shaped body of water within the village of Rockcliffe Park (Ottawa), Ontario (74° 27.2'N,

75° 40.3'W). Although the lake has a catchment of 1.4 km^2 most overland flow is intercepted by local sewers and the basin receives only minor surface runoff via two small streams. The lake level is maintained by groundwater infiltration through the calcareous bedrock cliffs along the southwest side of the basin and through the sands on the southeastern side. A small intermittent outlet stream, cutting through Leda clays, flows northwesterly for about 1 km into the Ottawa River[6]. This hardwater lake thermally stratifies and undergoes spring meromixis each year which promotes strong anoxia in the bottom waters. During the summer there is no oxygen in the hypolimnion and H_2S is prevalent in the bottom waters. For a short period in the fall the water column mixes, but the period of complete mixing is very brief, 1 to 2 weeks, just prior to freeze-up. Once ice cover is in place the bottom waters rapidly become anoxic and the water column is devoid of oxygen below 5 to 6 m throughout the winter. This oxygen and thermal regime within the lake creates a depositional basin which is excellent for the preservation of the sedimentary record. There is little or no oxidation of organic materials, no bioturbation, and very little or no physical disturbance. Sediment cores taken from the deepest part of the basin have corroborated the foregoing assessment of an undistrubed depositional environment in that the structural details, including marl and silt laminae, are evident both visually and in X-radiographs. Microfossil analysis of the core material also supports the thesis that the sediment is not disturbed after deposition[7].

Sediment samples

A surface sediment core was taken, through the ice, in March 1985, using a modified Finnish 'freeze-corer'[8]. The frozen core was prepared for radionuclide analysis by cutting the frozen sediment into 1 cm thick slabs parallel to the sediment/water interface. The sediment was sectioned in a freezer room (-2°C) using a table saw with a diamond blade. To eliminate the contamination which results from the penetration of the corer into the sediment, approximately 0.5 cm was cut from the 'plate' side of each core slab to remove the 'water freeze' and draped sediment. Then all possible surface contamination resulting from storage or cutting was removed by cleaning all surfaces with a 'shaping' tool. The volume of each slab was estimated by immersing the slabs in a graduated cylinder of purified mercury and measuring the displacement (all measurements were reproducible to within 1 cc). The frozen slabs were weighed at -2°C, then freeze-dried, and re-weighed. Bulk density estimates were also made.

Analytical procedure

The dried, powdered and weighed sediment samples were assayed on low-background Aptec planar and coaxial hyperpure germanium detectors as described earlier[9,10].

Assignment of dates

Two models are used to derive ^{210}Pb dates for sediment core sections. In the first[11,12], the constant rate-of-supply (CRS) of ^{210}Pb model, the age (t) of a sediment slice at a mass depth m in units of g cm^{-2} is given by

$$t = -\frac{1}{\lambda} \ln \left[1 - \frac{\Sigma Am}{\Sigma A\infty}\right],$$

where ΣAm is the integrated unsupported ^{210}Pb (i.e. total ^{210}Pb less that supported by ^{226}Ra in sediment) activity from the surface to the mass depth m, $\Sigma A\infty$ is the total integrated unsupported ^{210}Pb activity per cm^2, and λ the decay constant of ^{210}Pb (0.0311 y^{-1}). In the second, the constant initial concentration (CIC) of ^{210}Pb model, the age of a core section is given, as shown earlier[13], by

$$t = \frac{x}{S_o(1 - \phi_o)} \left[1 - \phi_o \left\{\frac{(1 - e^{-\beta x})}{\beta x}\right\}\right]$$

where S_o is the surface sedimentation rate in cm/yr, ϕ_o is the porosity at sediment/water interface, x is the depth in core in cm and β a constant. These parameters are obtained by linear regression analysis[14] of measured profiles for porosity and unsupported ^{210}Pb activity per g in sediment core.

Results and discussion

The results of more pertinent analytical measurements are given in Table 1 though all core sections were assayed by gamma-ray spectrometry. Although the decay of ^{155}Eu is accompanied by two major[15] γ-emissions at 86.4 (32.7%) and 105.3 (21.8%) keV the preponderance of several X- and γ-rays around 86 keV precludes application of the former emission for low-level measurements. The 105.3-keV γ-emission from ^{155}Eu, on the other hand, is relatively free of potential interferences except that care must be exercised in distinguishing it from the possible presence of $K_{\beta 1}$ Th X-ray (1%) of the same energy[16]. The presence of 42.3- and 43.0-keV Eu X-rays in the γ-ray spectra obtained with a planar detector (Fig. 1) clearly establishes[16] the presence of ^{155}Eu. The two longer-lived europium isotopes, ^{152}Eu (T = 12.7 y) and ^{154}Eu (T = 8.5 y), which are mainly generated as activation products were not detected.

The unambiguous presence of ^{207}Bi in the sediments is established by the 1063.6-keV γ-emission (77%) from this radionuclide[15] (Fig. 2). The other major γ-ray from this radionuclide (569.6 keV, 98%) can have interference from ^{134}Cs (T = 2.1 y; 569.2 keV, 15.4%) and/or ^{234}Pa-^{238}U (568.7, 3%; 569.2, 10.4%). Two possible modes for the formation of fallout ^{207}Bi have been discussed. In the first[4], it is suggested that this radionuclide is produced as ^{209}Bi (n, 3n) ^{207}Bi, while the second proposal[5] assumes that the formation occurs via

deuteron capture in lead. In their investigation of the (n, 3n) reactions in a thermal neutron reactor, EASTWOOD and ROY[17] have demonstrated the occurrence of the ^{209}Bi (n, 3n) ^{207}Bi reaction. The threshold of 14.3 MeV for this reaction appears to be too high for the 14.1 MeV neutrons from the thermonuclear bombs to be responsible for its formation. It would also require the presence of ^{209}Bi in the bomb material. Similarly, the reaction ^{206}Pb (d, n) ^{207}Bi also requires high-energy deuterons and ^{206}Pb as has been assumed by AARKROG et al.[5] The observed occurrence of fallout ^{207}Bi, therefore, leads to the reckoning that neutrons or deuterons of sufficient energy were produced in some thermonuclear explosions and that sufficient amounts of ^{209}Bi or ^{206}Pb, as applicable, were present in the explosive devices no matter how implausible it may seem.

In order to examine the historical patterns of deposition of the two radionuclides, the sediment core was dated by the ^{210}Pb method using both the CRS and CIC formulations. The nearly similar dates afforded by the two models (Fig. 3) reconfirm lack of mixing effects in the bottom sediments and suggest near constancy in sedimentation rates at least up to this depth since, unlike the CRS model, the CIC model used does not account for variations in the sedimentation rate. Having ascertained the consistency of the ^{210}Pb-derived dates (Fig. 3), an examination of the data given in Table 1 reveals that peak concentrations of both ^{137}Cs and ^{241}Am approximately reflect their increased

inputs to the atmosphere as a result of extensive weapons testing in the early 1960's. Surprisingly, ^{207}Bi is detectable only in core sections deposited in the mid 1970's. Europium-155, on the other hand, is consistently traceable to about the mid 1960's and shows deposition pattern more or less similar to that for ^{137}Cs (Fig. 4). Besides confirming the decay of ^{155}Eu, the absence of the 105.3-keV photopeak in sections deposited prior to about 1964 shows that the $K_{\beta 1}$ Th X-ray has negligible, if any, contribution to this gamma emission.

Numerical integration of ^{155}Eu activity per cm^2, obtained by multiplying the activity per g in Table 1 by the amount in grams of dry sediment per cm^2 in the core section, gives cumulative inventory of about 5.2 mBq cm^{-2} in the sediment core. The inventory of ^{137}Cs in the corresponding sections is about 128.2 mBq cm^{-2}. The total ^{137}Cs inventory in the core is about 155 mBq cm^{-2} or about 41% of the expected 380 mBq cm^{-2}. Assuming both ^{155}Eu and ^{137}Cs are generated by the thermal neutron fission of ^{235}U and behave similarly throughout their transport to sediments, we may estimate the expected activity of ^{155}Eu in sediments using the relation

$$A_{155} = A_{137} \cdot \frac{\lambda_{155}}{\lambda_{137}} \cdot \frac{y_{155}}{y_{137}},$$

where A denotes the integrated activity, λ is the decay constant and y the thermal neutron fission yield of the radionuclide. Taking A_{137} to be 128.2 mBq cm^{-2} and y_{155} and y_{137} to be 0.0326 and 6.2%, respectively, a value of about 4.1 mBq cm^{-2} is inferred for A_{155}. This estimate is within about 20% of the measured inventory of ^{155}Eu in the sediment core. The near agreement between the calculated and measured inventories strongly suggests that fallout ^{155}Eu primarily originated during the thermal neutron fission of ^{235}U. AARKROG and LIPPERT[3], on the other hand, have inferred that ^{155}Eu in debris from nuclear weapons originated from the fast neutron fission of ^{238}U. More measurements are, therefore, required to ascertain the origin of fallout ^{155}Eu.

The ^{210}Pb data were also used to derive the flux, P, of unsupported ^{210}Pb at the sediment/water interface since a knowledge of the flux of atmospheric ^{210}Pb may have direct bearing on the expected behaviour of pollutants with similar properties. For example, our recent measurements on rainfall samples[18] suggest that the same processes were responsible for the removal of the Chernobyl cesium and ruthenium radioisotopes, ^{210}Pb, and cosmogenic ^{7}Be from the atmosphere. TUREKIAN et al.[19] have pointed out that physical redistribution of sediments and supply of ^{210}Pb-enriched top soil are two major problems in the use of lake sediment ^{210}Pb measurements for deriving estimates of flux of atmospheric ^{210}Pb. In the present case, however, both of

these factors are not expected to limit such use of ^{210}Pb data since, as pointed out earlier, McKay Lake receives only minor surface runoff and shows negligible mixing. The validity of this reasoning is reflected in the values of 31 and 27 mBq cm^{-2} y^{-1}, afforded by the application of the CIC[13,14] and the CRS ($P = \sum A_\infty \cdot \lambda$) models, respectively, to the present data, which are comparable to the independent estimate[13] of 25 mBq cm^{-2} y^{-1} for the flux of atmospheric ^{210}Pb in the Great Lakes region.

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Table 1

Radionuclide levels in the McKay Lake sediment core

Depth in core (cm)	Concentration[a] (mBq/g dry sediment)					
	Total ^{210}Pb	^{226}Ra	^{137}Cs	^{155}Eu	^{207}Bi	^{241}Am
0- 1.05	1472±99	152±44	31±16	8± 7	ND	ND
1.05- 2.10	1538±56	99±25	35±10	15± 7	ND	ND
2.10- 3.15	1564±47	43±14	148±14	12± 6	ND	ND
3.15- 4.20	1501±41	61±13	167± 8	42±19	ND	ND
4.20- 5.25	837±23	102± 9	148± 5	6± 3	10±5	ND
5.25- 6.30	664±20	51± 9	178± 5	5± 2	5±4	ND
6.30- 7.35	631±20	52± 7	326± 5	14± 3	ND	2±1
7.35- 8.40	631±20	46± 8	595± 7	8± 3	ND	9±1
8.40- 9.45	525±18	24± 7	304± 5	3± 2	ND	7±1
9.45-10.50	405±14	33± 6	175± 4	ND	ND	6±1
10.50-11.55	245±10	26± 4	34± 2	ND	ND	2±1
11.55-12.60	226±11	41± 4	12± 1	ND	ND	ND
12.60-13.65	223±11	46± 5	2± 1	ND	ND	ND
13.65-14.70	273±13	48± 6	7± 1	ND	ND	ND
14.70-15.75	247±13	48± 6	4± 2	ND	ND	ND
15.75-16.80	320±14	39± 6	6± 2	ND	ND	ND
16.80-17.85	316±15	50± 6	6± 2	ND	ND	ND
17.85-18.90	282±14	62± 6	ND[b]	ND	ND	ND
18.90-19.95	211±10	44± 6	ND	ND	ND	ND
19.95-21.00	160±11	43± 6	ND	ND	ND	ND
21.00-22.05	181± 9	48± 5	ND	ND	ND	ND

[a] Errors are based on counting statistics of ±1σ
[b] ND, not detected

FIGURE CAPTIONS

Fig. 1 The γ-ray spectrum of a McKay Lake sediment core section obtained with a hyperpure germanium detector in planar configuration. Energies are in kiloelectronvolts.

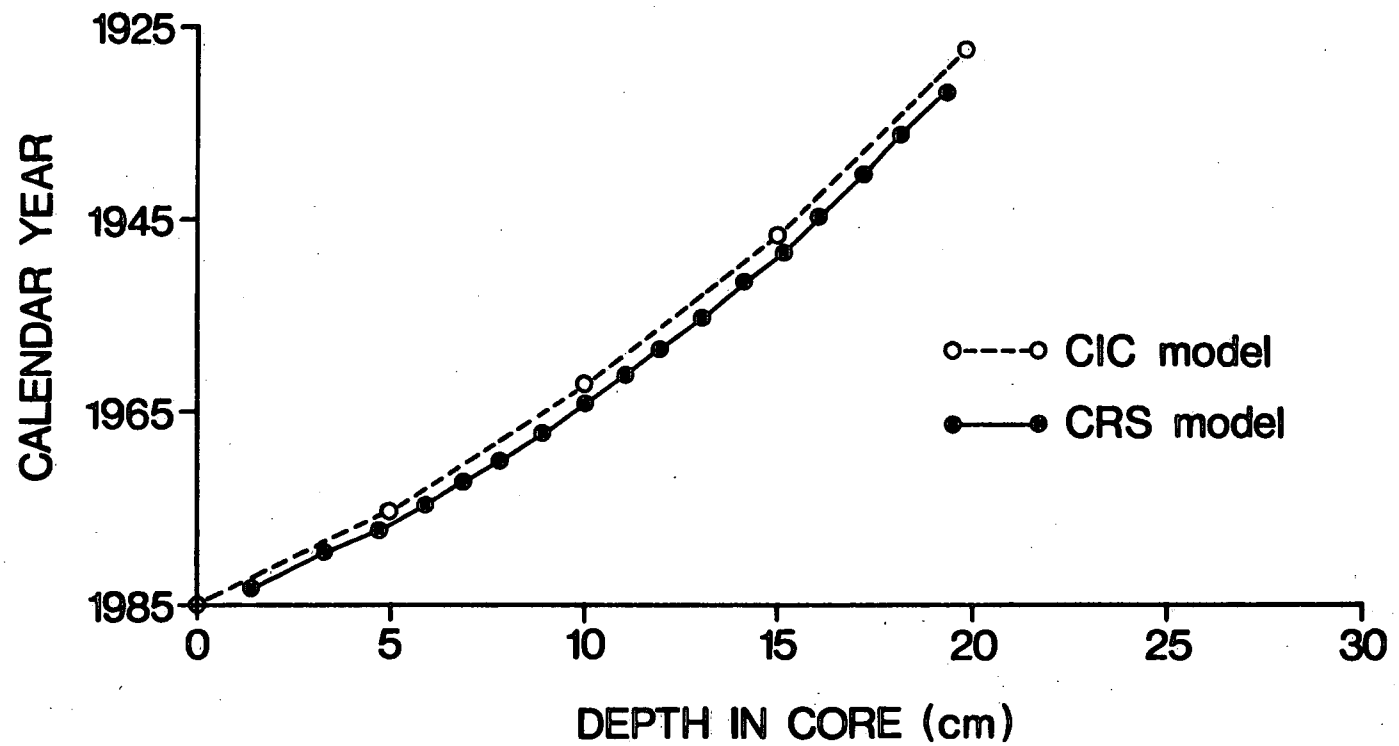
Fig. 2 The γ-ray spectrum of a McKay Lake sediment core section obtained with a hyperpure germanium detector in coaxial configuration. Energies are in kiloelectronvolts.

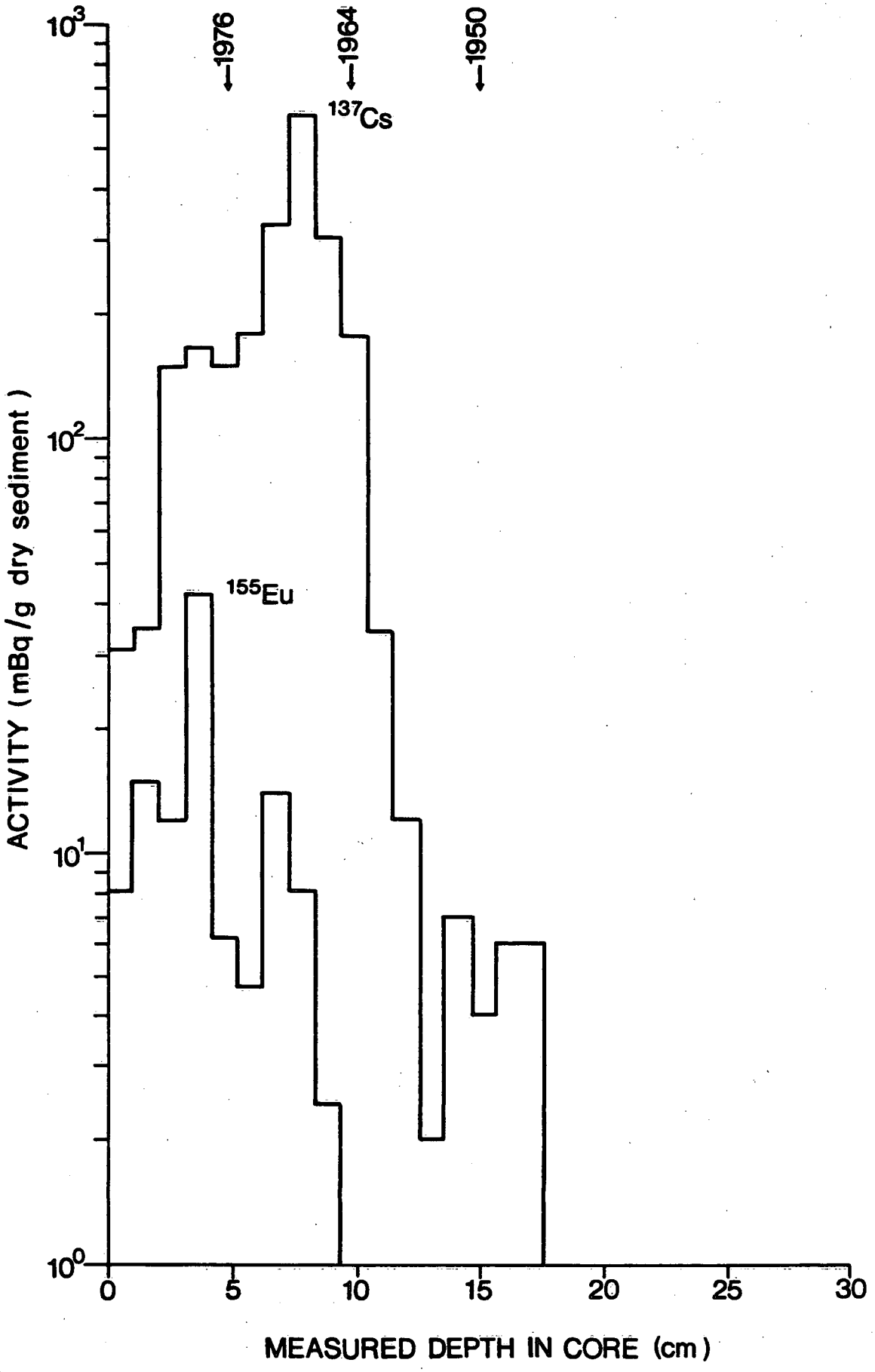
Fig. 3 ^{210}Pb dates for the McKay Lake sediment core using the constant initial concentration (CIC) and constant rate of supply (CRS) of unsupported ^{210}Pb models.

Fig. 4 ^{155}Eu and ^{137}Cs profiles in McKay Lake sediment core.

COUNTS PER CHANNEL
960
800
640
480
320
160
0
0
200
400
600
800
1000
1200
1400
1600
1800
CHANNEL NUMBER
36.4 Cs X-rays
32 Cs/Ba X-rays
39.9 212Bi
42.3, 43.0 Eu X-rays
46.5 210Pb
62.9, 63.3 234Th; 63.9 232Th; 63.9 231Th
74.8 231Th; 74.8-79.3 Pb and Bi X-rays
84.2 231Th; 86.4 155Eu; 87.2-94.7 Pb, Bi, Rn and Th X-rays
105.3 155Eu
185.7 235U; 186.2 226Ra
238.6 212Pb
241 224Ra; 242 214Pb
295.2 214Pb
351.9 214Pb

COUNTS PER CHANNEL
1500
1000
500
0
0
200
400
600
800
1000
1200
1400
1600
CHANNEL NUMBER
} 74.8–94.7 Pb, Bi, Th, Pa and Rn X-rays
185.7 235U; 186.2 226Ra
238.6 212Pb; 241 224Ra; 242 214Pb
295.2 214Pb
338.4 228Ac
351.9 214Pb
510.8 208Tl: 511 ANNIHILATION
583.1 208Tl
609.3 214Bi
661.6 137Cs
911.1 228Ac
969.1 228Ac
1460.7 40K
1063.6 207Bi
80
72
64
56
48
40
1100
1050


1925
1945
1965
1985
CALENDAR YEAR
0
5
10
15
20
25
30
DEPTH IN CORE (cm)
CIC model
CRS model


1976
1964
1950
137Cs
155Eu
ACTIVITY (mBq/g dry sediment)
MEASURED DEPTH IN CORE (cm)
10^3
10^2
10^1
10^0
0
5
10
15
20
25
30

16
7