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THE STRONTIUM AND CALCIUM RELATIONSHIPS IN CLINCH AND TENNESSEE RIVER MOLLUSKS

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INTRODUCTION

When the distribution and abundance of stable strontium are known for an environment, it should be possible to predict the distribution of strontium-90 released to that environment. The behavior of strontium-90 released to the environment due to nuclear weapons testing and radioactive waste disposal has created some concern because of its potential hazard to man. A portion of the released strontium-90 enters natural surface water streams but its fate is not well known because the releases have been small and, when small volumes of contaminated water are diluted in large volumes of uncontaminated water, quantitative determinations are exceedingly difficult. Oak Ridge National Laboratory, Oak Ridge, Tennessee, has released small amounts of strontium-90 to the Tennessee River via White Oak Creek and the Clinch River since the Laboratory was established in 1943 (Morton, 1961).

Strontium occurs most abundantly in nature with calcium, its closest chemical relative. Since an abundant mollusk fauna occurs in the Tennessee River system, the calcium carbonate shells of clams collected downstream from the Laboratory could be expected to contain concentrations of strontium-90. Clams are excellent index organisms for strontium-90 in surface water streams because they are relatively immobile on the river bottom and the strontium-90 content of the shell should be representative of the localities from which the individuals are collected. Clams are active to a certain extent all year, pumping water through their siphons, and clam shells after formation, unlike the bone of vertebrates, are not affected by subsequent metabolism. New layers of shell are laid down as the clam grows; a section through the shell contains a history of mineral deposition in successive annual layers. The shells of a number of species were analyzed for strontium, calcium, and strontium-90 to determine: (1) the content of elements and the radioisotope of strontium as a function of species, age, and location in the Clinch and Tennessee Rivers, and (2) by considering the strontium-90 released from the Laboratory as a tracer, to test whether clams may be used as biological indicators of the strontium-90 concentration in the river system.

THE DISTRIBUTION OF STRONTIUM IN THE ENVIRONMENT AND BIOSPHERE

Strontium is considered one of the rare elements in the environment. The average amount in the earth's crust is 35 micrograms per gram and in surface waters less than 0.1 micrograms per gram (Vinogradov, 1959). In the United States, rivers in the Pacific Northwest, Northeast, and the Central Lowlands contain less than 0.5 micrograms per gram. From 0.5 to 1.5 micrograms of strontium per gram are found in the rivers of southeastern United States, the Great Plains Region, and western United States. More than 1.5 micrograms of strontium per gram are found in western and northern Texas and southern New Mexico and Arizona (Skougstadt and Horr, 1960). The data available from the Clinch and Tennessee Rivers suggest that at most times there is less than 0.1 micrograms of strontium per gram in the water and also the strontium to calcium atom ratio is relatively constant (Tennessee Valley Authority, 1948; Skougstadt and Horr, 1960; Carrigan, 1961). (Strontium to calcium relationships are frequently expressed as atom ratios. The strontium to calcium atom ratio is determined in the following manner:

$$\left(\frac{\text{strontium content of sample}}{\text{atomic weight of strontium}}\right) \Big/ \left(\frac{\text{calcium content of sample}}{\text{atomic weight of calcium}}\right)$$

The current knowledge of the distribution of stable strontium in the biosphere is based largely on two papers in which the investigators analyzed a wide variety of living and nonliving materials. Thompson and Chow (1955) analyzed 250 species of marine organisms and two unidentified fresh-water clams. These authors emphasized the constancy of the strontium to calcium atom ratios within certain taxonomic categories and stated that varying environmental conditions such as temperature, salinity, and locality had no effect on the ratio. They also concluded that the strontium to calcium ratio of growing shells in marine organisms was independent of age. Odum (1957) analyzed 900 samples including a number of freshwater clams. He concluded that the principal factor which determined the ratio in calcareous materials was the strontium to calcium atom ratio of the external medium, or food supply, and that strontium occlusion was passive and incidental to other functions of the organisms. In laboratory experiments Odum (1951) also noted a proportionality between the strontium to calcium atom ratios in snail shells and that of the environments in which they grew. In testing his analytical techniques, Odum (1957) found no differences in the ratio between nacreous and prismatic layers of clam shells and between young and old portions of the clam shell. Swan (1956) suggested that growth and environment may be important in the determinations of the ratios in bivalve-mollusk shells. He postulated an inverse relationship between growth rate and strontium to calcium atom ratio because thick-shelled specimens of Modiolus modiolus, Mytilus edulis, and Mya arenaria contained more strontium in relation to calcium than did thin-shelled specimens.

METHODS

Clams were collected during the summer and fall of 1960 from seven different sites (Table 1, Figure 1) in the Tennessee River system, and the shells were identified and analyzed for strontium, calcium, and strontium-90. A reference collection was used for identifying the clams. A few preliminary analyses were based on dry-shell weight, but most shells were ashed at 500° centigrade for two hours to destroy organic matter, and all values were reported on an ash-weight basis. After ashing, the shells were covered with distilled water and dissolved by the gradual addition of concentrated hydrochloric acid. The solution was filtered and aliquots were used for chemical analyses. Analyses of the residue retained on the filters showed inconsequential amounts of strontium and calcium; therefore, filtration did not affect the subsequent analyses for strontium and calcium. A reagent blank was used for each ten samples and these invariably contained less than detectable amounts of strontium and calcium. All clams

Table 1. The strontium and strontium-90 content of Tennessee River system clams with calculated strontium-90 to strontium atom ratios and strontium to calcium atom ratios.

Specimens collected	Collection site[1]	Strontium: Number analyzed	Strontium: Average micrograms per gram of shell	Strontium: Average strontium to calcium atom ratio x 10^{-3}	Strontium-90: Number analyzed	Strontium-90: Average micromicrocuries per gram of shell	Strontium-90: Strontium-90 to strontium atom ratio x 10^{-11}
Unionidae							
Anodontinae							
Anodonta corpulenta	CRM 4.7-14.5	7	382 ±40.8[2]	0.435±0.046[3]	7	99.08±17.9	176.1 ±25.3
	Grassy Creek[4]	4	324.5±27.8	0.370±0.032	4		
Unioninae							
Dromus dromas	CRM 66	1	202	0.230			
	CRM 47	2	183 ± 6.00	0.208±0.007			
Quadrula metanevra	CRM 47	1	162	0.184			
	TRM 425	3	161.7± 1.22	0.184±0.001			
Quadrula pustulosa	CRM 47	2	186.0± 6.00	0.212±0.007	2	1.214± 0.249	4.45 ± 1.05
	CRM 17	9	155.9± 2.19	0.178±0.002	5	15.18 ± 2.57	67.5 ±10.8
	TRM 521	2	244.0±33.0	0.278±0.038	2	5.33 ± 0.923	15.4 ± 4.65
	TRM 425	3	202.7± 8.09	0.231±0.009	3	4.30 ± 0.801	14.3 ± 2.45
	TRM 100	8	199.5± 3.49	0.227±0.004	5	2.29 ± 0.182	7.74 ± 0.547
Elliptio dilatatus	CRM 66	2	222.0± 6.52	0.253±0.007			
	CRM 47	10	206.2± 5.16	0.235±0.006	2	0.39 ± 0.42	0.99 ± 1.75
	TRM 425	1	218	0.248	1	4.16	12.9
Elliptio crassidens	CRM 47	10	260.9± 5.00	0.297±0.006			
	TRM 521	15	211.4± 3.66	0.241±0.004	10	24.9 ± 2.39	36.5 ± 3.78
	TRM 425	7	196.4± 6.40	0.224±0.007	7	7.00 ± 0.742	24.6 ± 2.78
	TRM 100	5	228.2±15.5	0.260±0.018	5	3.96 ± 1.52	12.5 ± 5.05
Pleurobema cordatum	CRM 47	10	201.0± 5.63	0.229±0.006	2	0.185± 0.184	0.525± 0.620
	TRM 425	11	237.3± 6.60	0.270±0.007	2	4.24 ± 3.21	13.8 ±10.1
Fusconaia subrotunda	CRM 47	9	184.3± 2.18	0.210±0.002			
Amblema costata	CRM 47	2	184.5± 0.707	0.210±0.001			
	TRM 425	3	201.7±10.4	0.230±0.012	2	12.6 ± 0.089	22.2 ± 1.28
Megalonaias gigantea	TRM 425	3	188.7± 2.97	0.215±0.003			
Cyclonaias tuberculata	CRM 47	2	213.5± 3.54	0.243±0.004	2	0.714± 0.621	1.25 ± 0.952
	TRM 521	10	242.6± 5.51	0.276±0.006	7	4.81 ± 0.488	12.3 ± 1.42
	TRM 425	4	203.8±10.4	0.232±0.012	4	5.70 ± 0.737	18.9 ± 2.07
	TRM 100	5	208.8± 6.43	0.238±0.007	4	3.13 ± 0.341	10.2 ± 1.16
Lampsilinae							
Plagiola lineolata	TRM 425	3	199.7± 4.06	0.227±0.005			
Actinonaias carinata gibba	CRM 47	7	185.7± 5.55	0.211±0.006			
Ligumea recta latissima	CRM 47	6	182.2± 3.28	0.208±0.004			
	TRM 425	1	191	0.218			
Lampsilis ovata	CRM 66	7	231.1± 7.33	0.263±0.008	2	0.790± 0.045	1.15 ± 0.039
	CRM 47	6	224.0±11.2	0.255±0.013	2	0.392± 0.397	1.32 ± 1.47
Proptera alata	Grassy Creek	4	220.5±11.3	0.251±0.013			
	TRM 521	1	248	0.282			
	TRM 425	1	190	0.216			

[1] White Oak Creek flows into the Clinch River at CRM 20.8 at a distance of 2.5 miles below Oak Ridge National Laboratory; CRM = Clinch River mile; TRM = Tennessee River mile.

[2] All averages ± one standard error of the mean.

[3] Calcium was not determined for all specimens (see text).

[4] Grassy Creek joins the Clinch River at CRM 14.5.

analyzed were aged by the annual ring method (Haskin, 1954). The age frequency of the clams analyzed for strontium-90 is shown in Table 2. None of the clams used in determining the behavior of strontium-90 was living prior to 1943.

Chemical analyses for strontium and calcium were made by flame photometry. The strontium determinations were further checked for accuracy by spectrophotometry; in a total of 13 samples the same strontium concentration was found in nine. The extreme difference between the two methods was five per cent. In a further test of flame photometry, two analyses of each of 16 samples were run at different times. The standard deviation within determinations was 3.1 micrograms of strontium per gram and the coefficient of variation was 1.2 per cent. Thus, the chemical analyses of these shells were apparently completed with a high degree of accuracy and precision. An important consideration in these analyses was that mass spectrometer-produced calcium was used for the standards. This calcium is virtually pure calcium-40 and, therefore, free from strontium contamination. A radiochemical separation was used to obtain strontium-90 and counting was done in a low-background counter (Wyatt and Smith, 1958). The strontium determined by flame photometry is the total strontium present in the shell which also includes the strontium-90 and is referred to in this paper as strontium. Most chemical data in this paper are averages for each species of clam from the different collecting sites. The results of individual analyses will be included in a future report which will be available from the author. Estimates of the average river discharge at the respective collecting stations were obtained from the U. S. Geological Survey (Cragwall and Mathews, 1961).

Table 2. Age distribution of clams analyzed for strontium-90.

Age (years)[1]	Clinch River Mile (CRM): 66 and 47	Clinch River Mile (CRM): 4.7 to 17	Tennessee River Mile (TRM): 521	Tennessee River Mile (TRM): 425	Tennessee River Mile (TRM): 100
1 to 3	1	1	1		
3 to 6	3	2	4	2	1
6 to 9	5	5	3	1	3
10 to 12		3	5	6	9
13 to 16	3	1	6	9	1
17				1	

[1] Includes end points of intervals.

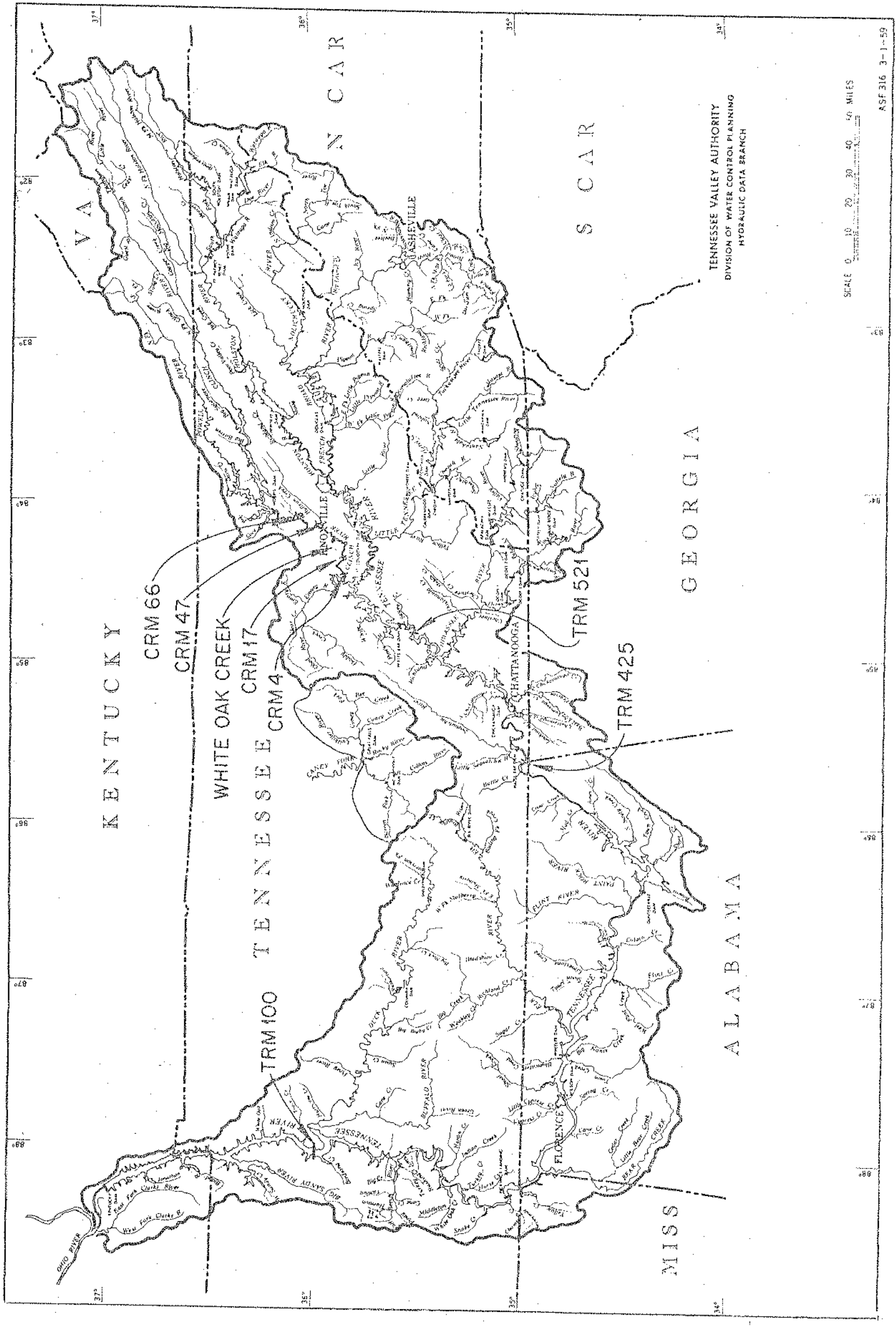

Figure 1. Tennessee River drainage showing the location of White Oak Creek and clam collection sites.

CALCIUM IN CLAM SHELLS

The aragonite shell of clams is relatively pure calcium carbonate which should yield 400 milligrams of calcium per gram. The initial analyses of the ashed shells showed the calcium concentration to be as expected; consequently, in subsequent analyses only one shell in ten was analyzed for calcium. The following species were analyzed for calcium (number of individuals): Anodonta corpulenta (1), Quadrula pustulosa (2), Elliptio dilatatus (3), E. crassidens (10), Pleurobema cordatum (2), Fusconaia subrotunda (1), Megalonaias gigantea (1), Actinonaias carinata gibba (1), Ligumea recta latissima (1), and Lampsilis ovata (1). The average calcium concentration (± one standard error of the mean) was 400.9 ± 1.38 milligrams per gram of shell. These deviations from the expected value are within the limits of variability of the analytical technique. The average calcium concentration (± one standard error of the mean) based on 64 determinations of marine pelecyods analyzed by Thompson and Chow (1955) was 391.8 ± 1.18 milligrams per gram of shell (ash weight). These results amply demonstrate the constancy of calcium in both fresh-water and marine clams. The difference between the means is statistically significant (calculated $t = 4.29$, with 85 degrees of freedom). The difference may be due to the inclusion of greater amounts of other cations within the shells of clams living in marine environments. Odum (1957) showed there was about six times as much strontium in calcareous materials of marine origin as there was in similar fresh-water samples. Marine clam shells also contain small amounts of magnesium, silica, aluminum, iron, and manganese (Vinogradov, 1953).

STRONTIUM IN CLAM SHELLS

The average strontium concentration of 16 species of clams collected in the Tennessee River system ranged from 382 micrograms per gram (Anodonta corpulenta) to 156 micrograms per gram (Quadrula pustulosa) (Table 1). The highest strontium concentration in A. corpulenta was 518 micrograms per gram and the lowest in Q. pustulosa was 146 micrograms per gram. These values, which differ by a factor of 3.5, also represent the extreme range for all strontium determinations. These two species were obtained in the Clinch River downstream from White Oak Creek. Since the clams were collected in adjacent areas of the river, it is reasonable to assume they were in similar chemical environments. The strontium to calcium atom ratio in water of the Tennessee River system from which clams were collected is relatively constant. Therefore, differences in strontium content of all species must be due to factors other than environment.

When clams were selected for strontium analysis it was assumed, as in marine species (Thompson and Chow, 1955), strontium concentration was independent of age. The data and subsequent analyses showed that in fresh-water clams the strontium content is at least partially age dependent. For Elliptio crassidens collected from Tennessee River mile (TRM) 521, the strontium content of five clams three to six years old was 212, 201, 207, 201, and 202 micrograms per gram. The strontium content of ten clams 10 to 15 years old was 200, 219, 254, 197, 211, 209, 202, 216, 223, and 217 micrograms per gram. The difference between the means is not statistically significant (calculated $t = 1.35$, with 13 degrees of freedom). However, four A. corpulenta two and three years old had strontium contents of 232, 263, 294, and 383 micrograms per gram, while individuals 11 and 13 years old had strontium contents of 441 and 518 micrograms per gram, respectively. Since it was not possible to obtain a complete age series of any one species, four E. crassidens shells were sectioned and each annual increment of growth was separated and analyzed. The strontium concentration in the nacreous layers deposited when the clam is one to six years old is one-half to two-thirds as much as in the layers deposited in years seven to nine (Nelson, in press). These differences could not be detected unless one analyzed clams representing different year classes or sectioned the shell. The nacre deposited in the first several years is a small portion of a thick-shelled clam (E. crassidens) ten or more years old, and consequently does not materially affect the results of analyses of whole shells of this species. Anodonta corpulenta has a thin shell in which the nacreous layers deposited in the first two to three years comprise at least one-half the shell of an individual four years old. The comparison of strontium analyses of two-and-three year-old A. corpulenta with 11 and 13-year-old individuals showed there was less strontium deposited in the young clams than in the older clams. These results were completely unexpected since previous workers had claimed a homogeneous distribution of strontium within clam shells (Thompson and Chow, 1955; Odum, 1957). Because of these results, an anticipated statistical analysis of variance comparing the strontium content of clams at different collecting sites was not completed. However, with the data available from selected species it is possible to discuss some factors which apparently affect strontium deposition in fresh-water clams.

Swan (1956) postulated an inverse relationship between growth rate and strontium deposition, but the average growth rate observed for A. corpulenta (CRM 4.7 to 14.5) was 8.7 ± 1.1 (± one standard error of the mean) grams per year and that for Q. pustulosa (CRM 17) was 2.1 ± 0.11 grams per year based on seven and nine observations, respectively. He calculated $t = 2.14$, which is significant at the 95 per cent level with 14 degrees of freedom. The average strontium content of A. corpulena was 382.3 ± 40.8 (± one standard error of the mean) micrograms per gram and the strontium of Q. pustulosa was 155.9 ± 2.19 micrograms per gram. The difference is highly significant (calculated $t = 6.34$, with 14 degrees of freedom). Data on the seven individual A. corpulenta suggest that the variability in strontium content in that species is associated with age (Table 3). With the exception of one seven-year-old clam the strontium content increased with age. Also, the growth rate of older clams appears to be more rapid than that of younger clams. These data are only suggestive. However, with Pleurobema cordatum (Table 4) collected from CRM 47 and TRM 425 there does not appear to be an effect of age on strontium content or growth rate. There are significant differences between

Table 3. Age, growth rate, and strontium content of seven Anodonta corpulenta collected from Clinch River mile 4.7 to 14.5.

Age (years)	Growth rate (grams per year)	Strontium content (micrograms per gram)
2	3.6	232
4	6.6	387
4	9.0	426
7	9.8	238
7	12.4	431
11	11.2	441
13	8.3	518

Table 4. Age, growth rate, and strontium content of *Pleurobema cordatum* collected from Clinch River mile 47 (CRM 47) and Tennessee River mile 425 (TRM 425).

Age (years)		Growth rate (grams per year)		Strontium content (micrograms per gram)	
CRM 47	TRM 425	CRM 47	TRM 425	CRM 47	TRM 425
6	9	4.1	9.8	198	217
9	10	3.7	6.5	187	256
11	14	3.2	5.5	180	220
12	16	3.2	4.7	189	205
12	17	3.5	5.0	235	281
14	18	3.3	5.8	187	237
14	18	3.8	6.0	190	221
14	20	2.7	5.6	219	232
20	20	2.6	4.9	213	238
23	23	3.6	5.8	212	245
	24		4.9		258
Average		3.37	5.86	201	237.3
Standard error		0.149	0.427	5.63	6.60

the growth rate of the two populations (calculated t = 3.16, with 19 degrees of freedom) as well as strontium contents (calculated t = 4.14, with 19 degrees of freedom).

Strontium deposition is also governed by other factors in addition to growth rate. *Elliptio dilatatus* (CRM 47) (Table 5) and *E. crassidens* (TRM 521) had the same strontium concentrations but significantly different growth rates (calculated t = 10.7, with 16 degrees of freedom). In connection with strontium deposition in the biosphere, Odum (1957) discussed what he called "isolation of the depositional surface" as a function of both circulatory system and separation of the calcification surface from the external environment. The circulatory system of clams may be considered relatively constant, leaving in effect surface-volume relationships as another factor affecting strontium deposition in clams. The increase in strontium content with age in the nacreous layers of *E. crassidens* shells may be related to a decreasing surface-volume relationship. A young clam would have a greater surface in proportion to its volume and consequently ionic exchange between the depositional tissues and the external environment would be more rapid. Since there is discrimination against strontium relative to calcium in shell deposition, the tissues surrounding the site of deposition become relatively enriched with strontium. In a clam with a high surface to volume relationship, there would be a greater opportunity for the strontium excluded from the crystal deposition to escape to the environment. The slowly growing *E. dilatatus* also has an elongated, flattened shell. This combination should produce a low strontium content, but the shells analyzed contained as much strontium as faster-growing species. These data suggest there are inherent species differences associated with the nonhomogeneous distribution of strontium in clam shells.

Table 5. Age, growth rate, and strontium content of *Elliptio crassidens* collected from Tennessee River mile 521 (TRM 521) and *E. dilatatus* from Clinch River mile 47(CRM 47).

Age (years)		Growth rate (grams per year)		Strontium content (micrograms per gram)	
CRM 47	TRM 425	CRM 47	TRM 425	CRM 47	TRM 425
6	3	2.1	6.9	181	202
7	5	1.5	7.5	213	201
8	5	1.4	5.5	198	207
8	5	1.6	5.8	202	201
9	6	1.1	6.0	225	212
9	9	1.3	4.8	198	216
9	10	1.0	4.7	231	209
9	12	1.5	3.6	185	202
10		1.6		212	
11		1.0		217	
Average		1.41	5.60	206.2	206.2
Standard error		0.106	0.442	5.16	2.02

STRONTIUM TO CALCIUM ATOM RATIOS IN CLAM SHELLS

The results of this study may be compared with those of Odum (1957) only on the basis of strontium to calcium atom ratios (Table 6). It is apparent that the strontium content of clams from the Clinch and Tennessee Rivers results in much lower strontium to calcium atom ratios. Since apparently the calcium content of fresh-water clams is relatively constant, the discrepancy must be related to: (1) differences in species of clams analyzed, (2) differences in growth rate, (3) differences in the strontium to calcium atom ratio in the environment which would in turn affect the ratio in the clam shells, (4) analytical errors in the chemical determination of strontium, and (5) sampling error.

Table 6. Comparison of the frequency of strontium to calcium atom ratios for clam shells from this study with those reported by Odum (1957).

Strontium to[1] calcium atom ratio x 10^{-3}	This study		Odum (1957)	
	Number of occurrences	Per cent total	Number of occurrences	Per cent total
.00 to .25	142	70.0	3	7.7
.26 to .50	60	29.6	8	20.5
.51 to .75	1	0.5	9	23.1
.76 to 1.0			9	23.1
Greater than 1.0			10	25.6

[1] Includes end points of intervals.

A species comparison with Odum's work was possible only for *Quadrula metanevra*. The strontium to calcium atom ratios from four analyses of Clinch-Tennessee River specimens were 0.184, 0.183, 0.188, and 0.185 (all x 10^{-3}) and in one analysis by Odum the ratio was 0.46 x 10^{-3}. Odum's specimen came from the Cumberland River near Nashville, Tennessee, so the difference may be due to growth rate or the environmental strontium to calcium atom ratio. A number of Odum's analyses were on *Anodonta*, specific identification not given. *Anodonta corpulenta* accounted for the seven highest (0.443, 0.504, 0.487, 0.496, 0.592, 0.438, and 0.409, all x 10^{-3}) strontium to calcium atom ratios in this study. Most of the remaining clams analyzed by Odum were *Musculium* spp., "old genus *Unio*" and *Unio* spp.; consequently species differences may be important. It is impossible to compare the effect of growth rate because Odum gives no data on growth. But if the abundance and diversity of clams are an indication of the suitability of the habitat, the Tennessee River must be considered a favorable environment for clam growth.

The strontium to calcium atom ratio in Clinch River water is 1.4 x 10^{-3} (Carrigan, 1961) which is a relatively high ratio when compared with other rivers in the eastern United States. The strontium to calcium atom ratios in a number of those rivers have been calculated from data (Durum et al., 1960):

Mississippi River, Baton Rouge, Louisiana	0.96×10^{-3}
Atchafalaya River, Krotz Springs, Louisiana	1.2×10^{-3}
St. Lawrence River, Levis, P.Q., Canada	1.4×10^{-3}
Mobile River, 41 Mi. N. Mobile, Alabama	2.4×10^{-3}
Hudson River, Green Island, New York	1.5×10^{-3}
Susquehanna River, Conowingo, Maryland	0.74×10^{-3}
Apalachicola River, Blountstown, Florida	0.74×10^{-3}

Most of the clams analyzed by Odum came from eastern United States. Therefore, if the environmental strontium to calcium atom ratio is a major factor in freshwater streams, a much higher ratio could be expected in clams from the Tennessee River system rather than the comparatively low ratios observed.

Because 25 per cent of Odum's analyses result in ratios greater than 1 x 10^{-3}, errors in strontium determination may be one reason for the discrepancy. The two ratios for freshwater clams reported by Thompson and Chow (1955) are 1.02 x 10^{-3} and 0.90 x 10^{-3}, which are in general agreement with those reported by Odum. The determination of strontium in the presence of large amounts of calcium, as in the case with clam shells, presents analytical difficulties. Preparation of standard solutions is a major problem. Neither Thompson and Chow (1955) nor Odum (1950) reported strontium contamination of the reagent calcium compounds used in preparation of their standards. Strontium contamination of reagent grade calcium compounds is surprisingly high and is of the same order of magnitude as the concentration of strontium in clam shells (Table 7). Therefore, it is possible that errors in their determinations of Sr in freshwater clams could account for the high strontium to calcium ratios.

Table 7. Strontium contamination of reagent grade calcium compounds.

Compound	Micrograms of strontium per gram of calcium	Manufacturer and lot number	
Calcium citrate	285	Baker	81844
Calcium phosphate, dibasic	500	B and A	N 220
Calcium chloride	1615	B and A	L 098
Calcium nitrate	139.5	Mallinckrodt	EXP
Calcium oxide	345	Baker	27427
Calcium sulfate	877	Baker	91405
Calcium carbonate	174	Baker	7069
Calcium hydroxide	346	Mallinckrodt	GKH

STRONTIUM-90 TO STRONTIUM ATOM RATIOS

The specific activity of strontium-90 (atoms of strontium-90 divided by atoms of strontium) was used to determine if clams might be quantitative biological indicators of strontium-90 in the Tennessee River system. In aquatic organisms the accumulation of a radionuclide is directly proportional to the specific activity of the isotope in its environment. Application of the commonly used strontium-90 to calcium relationship would be questionable, if not meaningless, because of the demonstrated differences in stable strontium content of the shells and the equally demonstrated constancy of calcium.

The strontium-90 to strontium atom ratios in clams from the Clinch River upstream from White Oak Creek which are subject only to fallout levels of strontium-90 were compared with the ratios in clams collected in the Clinch River downstream from White Oak Creek and at three locations in the Tennessee River (Figure 1). Ratios observed and the ratios expected from dilution of Clinch River water in Tennessee River water are shown in Table 8. The expected ratios were calculated by dividing the average observed ratio of clams in the Clinch River downstream from White Oak Creek by the appropriate dilution factors (Cragwall and Mathews, 1961). There is an excellent agreement between expected and observed atom ratios considering that this represents a tracer experiment over almost 500 river miles. The accrual of fallout strontium-90 to river water is dependent largely on run-off (Morgan and Stansbury, 1961). Therefore, higher values than the fallout strontium-90 to strontium atom ratio may be attributed to Laboratory releases of strontium-90.

The contribution of Laboratory releases of strontium-90 to the Clinch and Tennessee Rivers may be compared with that from fallout through use of the strontium-90 to strontium atom ratios in clams collected upstream from White Oak Creek and the atom ratio in clams collected downstream from White Oak Creek (Table 8). Each of the downstream ratios can be divided by the upstream ratio to determine the relative abundance of strontium-90 from each source. Thus, the Laboratory contributed 78 atoms of strontium-90 for each atom of fallout strontium-90 in the Clinch River. This ratio then decreased at downstream locations in proportion to the dilution of Clinch River water.

These data suggest that clams may be used as indicators of the behavior of strontium-90 in streams. Since there is no significant loss of strontium-90 from the Tennessee River water, strontium and strontium-90 in the water are in equilibrium with other components of the system such as organisms and bottom sediments.

Table 8. Observed and expected strontium-90 to stable strontium atom ratios (x 10^{-11}) in clams as a function of the dilution of Clinch River water.

Collection site	Dilution factor for Clinch River water	Expected on the basis of dilution	Number analyzed	Observed average	Atoms of fallout strontium-90: laboratory released strontium-90
CRM 47[1] (upstream from White Oak Creek)			12	1.67±0.50[2]	
CRM 17 to 4.7 (downstream from White Oak Creek)	1	130.8[3]	12	130.8±22.7	1:78
TRM 521[1]	5.6	23.4	19	25.74±3.36	1:15
TRM 425	7.05	18.6	19	19.78±1.71	1:12
TRM 100	12.3	10.6	14	10.14±1.81	1:6

[1] CRM = Clinch River mile; TRM = Tennessee River mile; the Clinch River joins the Tennessee River at TRM 568 (river miles measured from mouth of the river).

[2] All averages ± one standard error of the mean.

[3] Strontium-90 to strontium atom ratio in clams from the Clinch River downstream from White Oak Creek is the basis for the atom ratios expected because of dilution.

DISCUSSION

The specific activity of strontium-90 in clam shells was used to describe the behavior of strontium-90 released to the Tennessee River system. For the purposes of this analysis the strontium-90 released by the laboratory was considered as a tracer, although, in the strict sense, the release was not the typical tracer experiment. A typical tracer experiment consists of introducing a known amount of an isotope into a closed system. Thereafter, certain conditions must pertain: (1) stable and radioactive isotopes of the same element are completely mixed; (2) the supply of atoms is sufficient to meet the requirements of all metabolically active sites; and (3) metabolic discrimination between stable and radioactive isotopes does not occur, or else corrections can be made for such discrimination. Rate processes and equilibrium conditions are determined by counting radioactivity in components of the system at selected intervals. Results may be interpreted directly from radioactivity associated with each phase of the system.

Rivers are open systems with a continual flux of water containing dissolved and suspended solids. There are short-term variations in discharge and chemical quality of the water. Because of this a classical tracer experiment requiring a constant specific activity could be conducted only with considerable effort. Therefore, determining metabolic rate processes or equilibrium conditions for aquatic organisms is not feasible in a river.

Nevertheless, the releases of low-level radioactive wastes to a river can be used to determine the behavior of nuclides in the environment. In such a study, samples are taken at suitable locations downstream from the waste outfall. A control sampling location is established immediately upstream from the release point. The control point is required to evaluate the level of fallout from nuclear weapons tests or other industrial releases of the nuclide under consideration. Additional control points should be established on each major tributary where releases of nuclides occur.

The index point is the first sampling location downstream from the release site and is located sufficiently far downstream so that the radioactive wastes are completely dispersed with the river water. Ideally, the index point is located at the first reach of the river where complete mixing occurs. If this point is too far from the release site, it is possible that transient phenomena involving a nuclide could be overlooked. Data from other downstream sampling stations are interpreted using the index point as the base.

Upon release of wastes to the environment a specific activity is established for each radioactive nuclide in the waste. The specific activity in the water can change either by the release of different amounts of the radionuclide or by differences in the quantity of the stable element. Irrespective of these variations, a mass of water is tagged whenever radionuclides are released in the waste effluent. Concentrations of many radioactive nuclides are so low (strontium-90 for example) it is difficult to quantify the small releases in water. However, radioactivity and stable element concentrations at all sampling stations are measured in an organism which concentrates the nuclide. The organisms sampled at each location must be of the same age or, as in the case of clams, of a similar age distribution. The water mass flows through the index point and the organisms take up stable and radioactive isotopes of an element in the same proportion as they occur in the water.

This same water mass passes downstream and mixes with other masses preceding and following it (Parker, 1958). Thus, there are errors associated with the start and end of a water flow. These errors can be reduced to a minimum by sampling organisms or tissues, such as clam shell, which accumulate a nuclide over long periods. Two factors which affect the specific activity of a water mass are: (1) dilution of the contaminated water by uncontaminated water, and (2) changes in the concentrations of the stable isotopes by the confluence of streams having different concentrations of the element. In either case, specific activity in the water can be corrected for dilution and for differences in the concentration of the stable element. Therefore, the significant aspects of a tagged water mass are not altered as the water flows by distant sampling locations.

Nuclide behavior is determined by comparing the specific activity in samples collected from downstream locations with samples from the index point. The magnitude of nuclide uptake is of no consequence as long as it is possible to determine the specific activity. If predicted and observed specific activities are equal, there is no isotope loss from the water. Therefore, the living and nonliving components of the stream ecosystem are in equilibrium with the element. If the observed specific activity is less than expected, uptake in some phase of the system is suggested.

Strontium-90 and clams shells are a particularly suitable combination for an analysis of this nature. There are 10^9 to 10^{10} times as many atoms of stable strontium as strontium-90 in the clam shells (Table 8). No metabolic discrimination between the isotopes of strontium is expected and the same proportion of stable and radioactive atoms occurs in the water. Therefore, variations in the amount of strontium-90 released by the laboratory do not appreciably affect the total quantity of strontium. The clams analyzed live as long as 30 years and thus are best used as long-term indicators of strontium-90. Other mollusks, such as Sphaeriidae and Physidae, live one to two years and could be used as shorter-term indicators. Young Sphaeriidae develop in the gills of the parent and should be useful for periods as short as two or three months.

Most tissues, unlike clam shell, continually exchange atoms with their environment. A tissue containing an element for which there is a rapid exchange with the environment is suitable for an analysis of the type discussed here. It is feasible to introduce organisms at specific locations in a river and then coordinate sampling time with water flow rate. Another possibility is sampling during a period when the environmental specific activity is constant. The period of time in which this type of sampling is satisfactory is directly dependent upon the biological half-life of the element in the organism or tissue. Hence, the criterion of five biological half-lives in which the sampled material reaches 31/32 of its equilibrium concentration can be used as the minimum time for a constant environmental specific activity. Somewhat longer periods of constant specific activity are desirable because of the mixing of water masses.

The possibility of using low-level environmental discharges of radioactive wastes as tracers to determine the behavior of elements in the environment is dependent upon: (1) an organism or substrate which concentrates a specific nuclide so that suitable radioassays are obtained, (2) knowledge of river discharges required to compute dilution factors, and (3) quantitative chemical analyses for the element studied. In most cases river flow rates and biological half-lives for the element are also necessary.

There are exciting possibilities in using tracers of this nature to determine the fate and behavior of elements in surface water streams. Questions regarding the behavior of elements in natural surface waters of different quality may be answered with such studies. Elements required for biological production in water are of particular interest and a knowledge of the behavior of these elements is requisite to an understanding of biological productivity.

SUMMARY

The shells of a number of species of clams from the Clinch and Tennessee Rivers were analyzed for calcium, strontium, and strontium-90 to determine: (1) the content of these elements and this isotope of strontium as a function of species and location in the river, and (2) whether they could be used as biological indicators of strontium-90 in the water. The calcium content of the shells was relatively constant and constituted 40 per cent of the shell ash weight as would be expected with calcium carbonate. The average strontium content of shells of different species of clams ranged from 156 to 382 micrograms per gram. The differences in strontium content are due to inherent differences between species rather than to the strontium to calcium ratio in the environment.

Two factors which appear to affect strontium deposition in clam shells are growth rate and surface to volume relationships. The strontium content of clam shells increases with growth rate and with a reduced surface to volume ratio. These factors do not explain the strontium content of all species, and the inherent species differences may be related to the nonhomogeneous distribution of strontium within the clam shells.

Probable reasons for the lower strontium to calcium ratios obtained in this study compared to the ratios reported by others are differences in species and populations analyzed, environmental ratios, and errors in strontium determination. However, this is not an unequivocal explanation.

The low-level releases of strontium-90 by the Laboratory were used as a tracer to determine the behavior of strontium-90 released to the Tennessee River system. There was a very good agreement between the strontium-90 to stable strontium atom ratios observed and expected in clam shells on the basis of dilution of Clinch River water by Tennessee River water. This agreement suggests that clams may be used as samplers of strontium-90 and that strontium-90 released to the Clinch River is in equilibrium with the living and nonliving components of the river system. Concentrations of strontium-90 in the Tennessee River will be directly related to dilution of the contaminated water by noncontaminated water.

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