

[CL]

Express Letter

Pre- and post-bomb radiocarbon in fish otoliths

John M. Kalish¹

MAF Fisheries Greta Point, P.O. Box 297, Wellington, New Zealand

Received December 9, 1992; revision accepted January 4, 1993

ABSTRACT

Measurements of radiocarbon in seawater dissolved inorganic carbon (DIC), or suitable proxies such as hermatypic corals, are a valuable source of information on carbon flux and ocean circulation. However, knowledge of the global distribution of both pre- and post-bomb radiocarbon is limited due to the sources of these data. Suitable hermatypic corals are restricted to shallow tropical and subtropical waters and oceanographic collections of seawater are prohibitively expensive. What is needed is a proxy for ocean radiocarbon that can be collected at most latitudes and depths, and which can be reliably aged. Here I report accelerator mass spectrometry analyses of radiocarbon from selected regions of fish otoliths and show that such measurements are suitable for determining both pre- and post-bomb radiocarbon in all oceans and at most depths. Radiocarbon data obtained from otoliths can extend our knowledge of carbon flux in the oceans and atmosphere and help to develop further understanding of the fate of atmospheric CO₂ and ocean circulation. The data presented here represent the first pre- and post-bomb time series of radiocarbon levels from temperate waters. Furthermore, I demonstrate that the dramatic increase in radiocarbon in the atmosphere and oceans, attributable to the atmospheric testing of thermonuclear bombs during the 1950's and 1960's, provides a chemical mark on fish otoliths that is suitable for the validation of age in fishes.

1. Introduction

Measurements of cosmogenically produced and anthropogenic radiocarbon in the atmosphere and ocean are invaluable in determining the flux of carbon through the biosphere and ocean radiocarbon can also serve as a tracer to investigate ocean circulation. Retrospective determinations of ¹⁴C can help to understand climate change, and analyses of ¹⁴C in dated tree rings and bands of hermatypic corals have proven to be good proxies for past ¹⁴C levels [1–6]. Further impetus to investigating historical radiocarbon levels derives from two major anthropogenic alterations to atmosphere and ocean ¹⁴C. The rate of fossil fuel

CO₂ input to the ocean, the major reservoir of inorganic carbon, has been estimated by determining changes in ocean radiocarbon inventories [7]. The ability to quantify these rates is a by-product of the dilution of cosmogenically produced radiocarbon by ¹⁴C-free CO₂ released into the atmosphere from the burning of fossil fuels and the incorporation of this CO₂ into the ocean as dissolved inorganic carbon (DIC). Although the gradual dilution of cosmogenically produced radiocarbon has been obscured by atmospheric tests of thermonuclear bombs in the 1950's and 1960's, great benefits can be obtained from these events through the monitoring of the flux of bomb-derived ¹⁴C in the atmosphere and ocean.

Historical records of ocean ¹⁴C are typically obtained from hermatypic corals; however, the major limitation of corals as recorders of these data is that suitable corals are restricted to the upper 50 m of tropical and subtropical oceans.

¹ Present address: Division of Botany and Zoology, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia.

Improved estimates of the input of bomb ^{14}C to the ocean would result from more widespread estimates of both pre- and post-bomb ^{14}C . Molluscan shells can provide an alternative to corals [5,8], but suitable material is often limited in distribution and difficult to date. What is needed is a proxy for ocean ^{14}C that can be collected at most latitudes and depths, and which can be reliably aged.

Teleost fish possess three pairs of otoliths within the paired membranous labyrinths and they act, in concert with sensory maculae, as both gravity and auditory receptors. The sagitta, usually the largest otolith, is composed of aragonite and typically less than 1% organic material. In many fish species, the dominant features in sagittae are alternating opaque and translucent zones, which together comprise annual increments. The quantification and measurement of annual increments in otoliths is a major source of information on the age and growth of fishes [9]. Further resolution on the age and growth of fish is possible in many species due to the ability to resolve daily increments—bipartite structures composed of an organic matrix-dominant and an aragonite-dominant zone [9]. The suitability of annual and daily increments in otoliths for the age determi-

nation of fishes is based on the finding that, under normal circumstances, otolith aragonite is not resorbed after deposition, thus providing a record of the fish's age and growth [10]. Because otolith aragonite is not resorbed during the life of the fish, it also retains a chemical record that can be related to both the biology of the fish and the physical and chemical properties of its environment. Several studies have investigated trace elements [11–14], stable isotopes [15–17], and radioisotopes [18–20] in fish otoliths in relation to a range of biological and environmental hypotheses. Results from research on the growth and composition of otoliths suggest that it would be possible to extract data on both pre- and post-bomb ^{14}C from these structures. In this study, I report accelerator mass spectrometry analyses of ^{14}C from selected regions of otoliths from fish of known age to determine if such measurements are suitable for estimating levels of pre- and post-bomb ^{14}C .

2. Experimental method

Sagittal otolith pairs from specimens of a marine teleost, *Pagrus auratus*, were selected from archives at the Ministry of Agriculture and Fish-

TABLE 1

Otolith data from *Pagrus auratus* collected off the east coast of North Island, New Zealand. Values of $\Delta^{14}\text{C}$ are reported with ± 1 standard deviation

Date spawned	Collect. date	Fish age (yrs)	Otolith wt. (mg)	$\delta^{13}\text{C}$ (‰,PDB)	$\Delta^{14}\text{C}$ (‰)
1918	1972	54	948	-2.5	-48.4 ± 6.4
1928	1972	44	704	-2.0	-39.6 ± 6.9
1932	1972	40	538	-2.6	-58.5 ± 6.4
1943	1992	49	810	-3.0	-55.0 ± 7.2
1943	1992	49	810	-3.1	-51.1 ± 6.6
1950	1992	42	675	-2.6	-65.9 ± 6.2
1955	1992	37	689	-4.1	-50.6 ± 6.7
1960	1972	12	246	-2.5	-33.9 ± 6.8
1962	1972	10	213	-3.0	-18.6 ± 7.0
1963	1972	9	255	-2.0	-11.3 ± 7.0
1964	1972	8	210	-2.0	27.8 ± 7.6
1966	1972	6	142	-2.2	55.3 ± 8.2
1969	1973	4	88	-2.3	64.9 ± 11.6
1969	1973	4	88	-2.1	75.6 ± 11.9
1972	1992	20	353	-2.7	94.0 ± 8.5
1980	1992	12	398	-2.3	98.4 ± 8.8
1985	1992	7	189	-2.3	96.5 ± 9.8
1990	1992	2	94	-3.1	81.7 ± 10.5
1990	1992	2	94	-2.9	76.5 ± 10.4

eries, Wellington, New Zealand. Throughout its life *P. auratus* lives in shallow coastal waters and, on the basis of capture-mark-recapture studies, the majority of fish make net movements of less than 50 km. An additional reason for selecting *P. auratus* was because of the extensive research on the age and growth of the species [21]. Individuals for this study were collected from the east coast of the North Island, New Zealand, between East Cape and Hawke Bay (39°S, 179°E), where coastal waters are greatly influenced by adjacent oceanic waters and there appears to be no significant upwelling.

Otolith-based ages were determined from right sagittae using procedures that have been validated for this species by a capture-mark-recapture experiment [21]. Right sagittae were sectioned through the core along the transverse plane and otoliths were baked at 280°C for about 5 min. This increased contrast between the opaque and translucent zones of annual increments. The number of annual increments was counted by viewing baked sections with a binocular microscope at 50× magnification. Otoliths were considered acceptable for ^{14}C analysis only if there was agreement on the fish's age among three

otolith readers. It was assumed that there were no errors in the estimation of age. The date when a fish was spawned was determined on the basis of the fish age at capture. The range of dates spawned encompassed the early industrial period and the post-bomb decrease in ocean ^{14}C (Table 1).

Otolith aragonite deposited during the first year of life was isolated from the left sagitta of each fish. This material would have been deposited during the year when a fish was spawned because the majority of *P. auratus* spawn between November and February. Sample weights ranged from 25 to 30 mg. Otolith carbonate was converted to CO_2 by reaction with 100% phosphoric acid and a sample of the CO_2 was analyzed by mass spectrometry to determine $\delta^{13}\text{C}$. The remainder was graphitized and ^{14}C was determined by accelerator mass spectrometry (AMS) at the Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand [22]. Radiocarbon values are reported as $\Delta^{14}\text{C}$, which is the age- and fractionation-corrected permil deviation from the activity of nineteenth century wood [23]. Determinations were made via the NBS oxalic acid standard in conjunction with the ANU su-

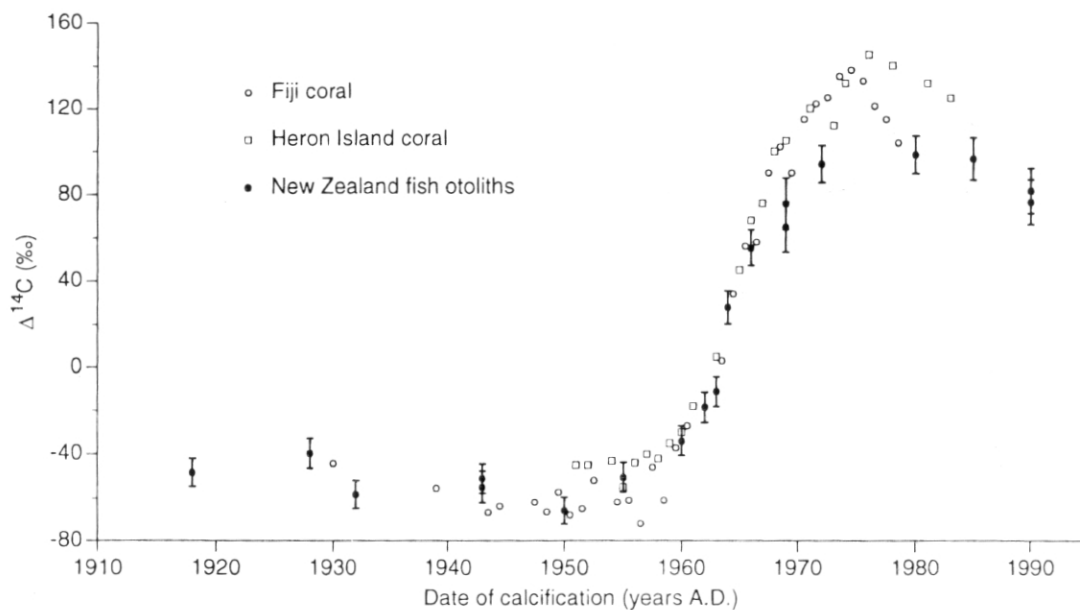


Fig. 1. $\Delta^{14}\text{C}$ (± 1 sd) of *Pagrus auratus* otolith aragonite from New Zealand over the time period 1918 to 1990. $\Delta^{14}\text{C}$ measurements from hermatypic corals sampled in Fiji and Heron Island, Australia are presented for comparison [5,8].

crose standard. Reported errors are 1 standard deviation, and include both counting errors and laboratory random errors.

3. Results and discussion

Otolith $\Delta^{14}\text{C}$ values plotted against date of calcification (spawning) result in a curve similar to those derived from corals (Fig. 1). The near pre-anthropogenic (1918) $\Delta^{14}\text{C}$ value of $-48.4 \pm 6.8\text{‰}$ was not significantly different from the mean of pre-1920 values (-55.5‰) measured in lower latitudes of the southern hemisphere as reported in Toggweiler et al. [5]. (The record from the Galapagos was not included due to the effect of upwelling.) There was a net decrease in otolith $\Delta^{14}\text{C}$ between 1918 and 1950 to a minimum value of $-65.9 \pm 6.6\text{‰}$; however, these data provide only weak evidence for a Sues effect (S_e , the decline in atmospheric $\Delta^{14}\text{C}$ levels between 1900 and 1950) due to their variability. Based on linear regression, the estimated S_e between 1918 and 1950 in the ocean off New Zealand was approximately -16‰ . This value is higher than the S_e measured at tropical southern hemisphere locations [5], but it is within the range of values determined from corals at sites near Bermuda (-25‰) [4] and Florida (-11.5‰) [3]. The effect of the atmospheric detonation of thermonuclear bombs on ocean ^{14}C is shown by the steep rise in $\Delta^{14}\text{C}$ that begins in about 1955. The increase in bomb ^{14}C measured in otoliths mimics trends determined in hermatypic corals from Fiji [5] and Heron Island, Australia [8] until about 1966. After 1966 the rate of increase in bomb ^{14}C is greater for the southern hemisphere corals than for otoliths and the peak coral $\Delta^{14}\text{C}$ is greater by at least 40‰ . After 1980 there is a gradual decrease in otolith $\Delta^{14}\text{C}$, indicating ocean mixing and the loss of ^{14}C from seawater DIC to other pools; however, this decrease is more gradual than that determined in the corals from Heron Island and Fiji. This may result from several factors, including the ocean transport of bomb ^{14}C from lower to higher latitudes, more rapid loss of DIC to other carbon pools in the tropics, or a greater rate of dilution of bomb ^{14}C by deeper water in the tropics. Finally, a direct indication that otolith $\Delta^{14}\text{C}$ values are a good proxy for ocean $\Delta^{14}\text{C}$ is provided by comparing

TABLE 2

Measurements of $\Delta^{14}\text{C}$ made on South Pacific surface water samples from latitudes comparable to collection locations for *Pagrus auratus* otoliths. * The $\Delta^{14}\text{C}$ value from Jan. 1954 to Mar. 1958 is the mean of eight measurements

Lat.	Long.	Collect. date	$\Delta^{14}\text{C}$ (‰)	Ref.
41.1°S	178.0°E	Jan. 1954– Mar. 1958	-47 *	[25]
42.7°S	96.0°W	Nov. 1957	-40	[24]
44.9°S	166.0°W	Mar. 1974	80	[7]
38.6°S	170.1°W	Mar. 1974	110	[7]

surface water measurements of $\Delta^{14}\text{C}$ near 39°S in the Pacific [7,24,25] (Table 2) with otolith-based data (Table 1).

The similarity of $\Delta^{14}\text{C}$ measured in fish otoliths to the $\Delta^{14}\text{C}$ of seawater DIC would be expected based on our understanding of the sources of otolith carbon [10]. Also, evidence from studies of stable carbon in fish otoliths suggests that about 70% of otolith carbon is derived directly from seawater DIC and that it is incorporated via branchial pathways [17,26]. The remaining 30% of otolith carbon would be derived from metabolic sources, specifically ingested food. *Pagrus auratus* is omnivorous, consuming a range of benthic and pelagic invertebrates as well as fishes. Because the majority of these dietary items would have $\Delta^{14}\text{C}$ levels similar to those measured in seawater [27,28], these alternative sources of ^{14}C would not be expected to alter $\Delta^{14}\text{C}$ values measured in otoliths. However, significant effects due to diet, on otolith $\Delta^{14}\text{C}$, might be expected in fish that consumed detritivores; in deep-sea species that consumed prey that ingested material derived from surface waters; in fishes, such as tuna, that might forage at fronts associated with upwelled waters; and in other similar circumstances.

The presence of teleost fishes in all marine environments provides a rich source of data on ocean ^{14}C that will make it feasible to model more accurately the global flux of carbon and understand the fate of atmospheric CO_2 , the principal greenhouse gas. Furthermore, the longevity of many fish species [18–20], combined with our ability to accurately determine the age of some species, makes it possible to extend the ocean $\Delta^{14}\text{C}$ record to pre-bomb periods in a wide

range of environments. The existence of otolith archives at fisheries laboratories throughout the world ensures the accessibility of this data source.

Additional benefits to be derived from the measurement of ^{14}C in fish otoliths relate to the determination and validation of fish age. Age is among the most important parameters for determining the production of fish populations. Fish ages are generally determined through the interpretation of periodic features on calcified structures such as otoliths, scales, spines or vertebrae [9]; however, despite the great emphasis on age estimation, it is infrequent that a method of age determination is proven to be accurate [29]. The lack of age validation studies can be attributed to the high cost and logistical difficulty of mark-recapture studies. The application of the bomb ^{14}C chronometer and AMS to the validation of fish ages provides an alternative to traditional validation studies and, in many cases, provides a method for age validation where standard techniques are not suitable. The method is based on the occurrence of an anthropogenic chemical marker in otoliths, specifically the sharp increase in $\Delta^{14}\text{C}$ in the 1950's and 1960's that should be evident in the otoliths of fish species that inhabit at least the upper 200 m of the water column. The rationale is similar to that employed in age determination studies of molluscs using the bomb ^{14}C chronometer [8,30]; however, as in the present study, only the earliest formed portions of the otoliths need be analyzed. An age 'calibration curve' based on otolith $\Delta^{14}\text{C}$ in fish of known age, such as *P. auratus*, could be produced for an ocean region and $\Delta^{14}\text{C}$ determinations from other species could be applied to the relationship. Alternatively, more reliable results would be obtained by producing a sigmoid $\Delta^{14}\text{C}$ versus presumed annual increment curve and, ultimately, assigning ages to the fish. In many cases age validation via the measurement of ^{14}C would be more effective than mark-recapture methods. Mark-recapture studies only provide direct evidence of the frequency of annual increment formation between the time of marking and recapture, whereas determination of ^{14}C levels in fish otoliths can be used to determine the absolute age of a fish (if samples are available with presumed birth dates in the range of about 1958 to 1970). In those instances where the fish are not

long-lived (< 30 yrs) it should be feasible to utilize the historical otolith collections held at many fisheries laboratories. Furthermore, estimation of age using the bomb chronometer eliminates the stress related to capture and tagging, which can greatly affect fish growth and bias results.

In conclusion, measurements of ^{14}C in fish otoliths can provide both pre- and post-bomb estimates of ocean ^{14}C in a broad spectrum of environments and can serve as an adjunct to data from hermatypic corals in shallow tropical and subtropical seas. These data can be applied to studies of carbon flux in the atmosphere and oceans, and make it feasible to investigate ocean circulation in most regions on time scales ranging from years to decades. Fish biologists can also benefit from AMS analyses of otolith ^{14}C due to the utility of these data for the validation of fish age.

Acknowledgements

I thank L. Paul for access to the otolith archives and R. Sparks and J. McKee for sample processing. AMS analyses were carried out by the Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand under contract to MAF Fisheries.

References

- 1 H.E. Suess, The radiocarbon record in tree rings of the last 8000 years, *Radiocarbon* 22, 200-209, 1980.
- 2 M. Stuiver and P.M. Quay, Atmospheric ^{14}C changes resulting from fossil fuel CO_2 release and cosmic ray flux variability, *Earth Planet. Sci. Lett.* 53, 349-362, 1981.
- 3 E.M. Druffel and T.W. Linick, Radiocarbon in annual coral rings of Florida, *Geophys. Res. Lett.* 5, 913-916, 1978.
- 4 Y. Nozaki, D.M. Rye, K.K. Turekian and R.E. Dodge, A 200-year record of carbon-13 and carbon-14 variations in Bermuda coral, *Geophys. Res. Lett.* 5, 825-828, 1978.
- 5 J.R. Toggweiler, K. Dixon and W.S. Broecker, The Peru upwelling and the ventilation of the South Pacific thermocline, *J. Geophys. Res.* 96, 20467-20496, 1991.
- 6 E.R.M. Druffel, Bomb radiocarbon in the Pacific: Annual and seasonal timescale variations, *J. Mar. Res.* 45, 667-698, 1987.
- 7 W.S. Broecker, T.-H. Peng, G. Ostlund and M. Stuiver, The distribution of bomb radiocarbon in the ocean, *J. Geophys. Res.* 90, 6953-6970, 1985.
- 8 N.H. Landman, E.R.M. Druffel, J.K. Cochran, D.J. Donahue and A.J.T. Jull, Bomb-produced radiocarbon in the

- shell of the chambered nautilus: rate of growth and age at maturity, *Earth Planet. Sci. Lett.* 89, 28–34, 1988.
- 9 R.C. Summerfelt and G.E. Hall, eds., *Age and Growth of Fish*, 544 pp., Iowa State University Press, Ames, Iowa, 1987.
 - 10 K. Simkiss, Calcium metabolism of fish in relation to ageing, in: *Ageing of Fish*, T.B. Bagenal, ed., pp. 1–12, Unwin, London, 1974.
 - 11 J.S. Edmonds, M.J. Moran, N. Caputi and M. Morita, Trace element analysis of fish sagittae as an aid to stock identification: pink snapper (*Chrysophrys auratus*) in Western Australian waters, *Can. J. Fish. Aquat. Sci.* 46, 50–54, 1989.
 - 12 J.M. Kalish, Otolith microchemistry: Validation of the effects of physiology, age and environment on otolith composition, *J. Exp. Mar. Biol. Ecol.* 132, 151–178, 1989.
 - 13 D.W. Townsend, R.L. Radtke, M.A. Morrison and S.D. Folsom, Recruitment implications of larval herring overwintering distributions in the Gulf of Maine inferred using a new otolith technique, *Mar. Ecol. Prog. Ser.* 55, 1–13, 1989.
 - 14 J.M. Kalish, Determinants of otolith chemistry: seasonal variation in the composition of blood plasma, endolymph and otoliths of bearded rock cod *Pseudophycis barbatus*, *Mar. Ecol. Prog. Ser.* 74, 137–159, 1991.
 - 15 I. Devereux, Temperature measurements from oxygen isotope ratios of fish otoliths, *Science* 155, 1684–1685, 1967.
 - 16 S.A. Mulcahy, J.S. Killingley, C.F. Phleger and W.H. Berger, Isotopic composition of otoliths from a benthopelagic fish, *Coryphaenoides acrolepis*, Macrouridae: Gadiformes, *Oceanol. Acta* 2, 423–427, 1979.
 - 17 J.M. Kalish, ^{13}C and ^{18}O isotopic disequilibria in fish otoliths: metabolic and kinetic effects, *Mar. Ecol. Prog. Ser.* 75, 191–203, 1991.
 - 18 J.T. Bennett, G.W. Boehlert and K.K. Turekian, Confirmation of longevity in *Sebastes diploproa* (Pisces: Scorpaenidae) using $^{210}\text{Pb}/^{226}\text{Ra}$ measurements in otoliths, *Mar. Biol.* 71, 209–215, 1982.
 - 19 S.E. Campana, K.C.T. Zwanenburg and J.N. Smith, $^{210}\text{Pb}/^{226}\text{Ra}$ determination of longevity in redfish, *Can. J. Fish. Aquat. Sci.* 47, 163–165, 1990.
 - 20 G.E. Fenton, S.A. Short and D.A. Ritz, Age determination of orange roughy, *Hoplostethus atlanticus* (Pisces: Trachichthyidae) using $^{210}\text{Pb}/^{226}\text{Ra}$ disequilibria, *Mar. Biol.* 109, 197–202, 1991.
 - 21 R.I.C.C. Francis, L.J. Paul and K.P. Mulligan, Ageing of adult snapper (*Pagrus auratus*) from otolith annual ring counts: validation using tagging and oxytetracycline injection, *Aust. J. Mar. Freshwater Res.* 43, in press, 1992.
 - 22 G. Wallace, R.J. Sparks, D.C. Lowe and K.P. Pohl, The New Zealand accelerator mass spectrometry facility, *Nucl. Instrum. Meth.* B29, 124–128, 1987.
 - 23 M. Stuiver and H.A. Polach, Reporting of ^{14}C data, *Radiocarbon* 19, 355–363, 1977.
 - 24 G.S. Bien, N.W. Rakestraw and H.E. Suess, Radiocarbon concentration in Pacific Ocean water, *Tellus* 12, 436–443, 1960.
 - 25 T.A. Rafter and B.J. O'Brien, Exchange rates between the atmosphere and the ocean as shown by recent C-14 measurements in the South Pacific, in: *Nobel Symposium 12, Radiocarbon Variations and Absolute Chronology*, I.U. Olsson, ed., pp. 355–377, Wiley, New York, 1970.
 - 26 J.M. Kalish, Oxygen and carbon stable isotopes in the otoliths of wild and laboratory-reared Australian salmon (*Arripis trutta*), *Mar. Biol.* 110, 37–47, 1991.
 - 27 W.G. Pearcy and M. Stuiver, Vertical transport of carbon-14 into deep-sea food webs, *Deep-Sea Res.* 30, 427–440, 1983.
 - 28 P.M. Williams, E.R.M. Druffel and K.L. Smith, Dietary carbon sources for deep-sea organisms as inferred from their organic radiocarbon activities, *Deep-Sea Res.* 34, 253–266, 1987.
 - 29 R.J. Beamish and G.A. McFarlane, The forgotten requirement for age validation in fisheries biology, *Trans. Am. Fish. Soc.* 112, 735–743, 1983.
 - 30 K.K. Turekian, J.K. Cochran, Y. Nozaki, I. Thompson and D.S. Jones, Determination of shell deposition rates of *Arctica islandica* from the New York Bight using natural ^{228}Ra and ^{228}Th and bomb-produced ^{14}C , *Limnol. Oceanogr.* 27, 737–741, 1982.