Reports

Nickel-63 in Marine and Terrestrial Biota, Soil, and Sediment

Abstract. *A previously unreported radionuclide, nickel-63 (half-life, 92 years), produced in the testing of nuclear devices, was measured in biological and environmental samples from areas of the Pacific Ocean and the eastern seaboard of the United States. The concentrations of nickel-63 are low (maximum of 163 disintegrations per minute per gram of dry weight), but this radionuclide may be a useful tracer of oceanic processes because of its long half-life and long residence time in the ocean.*

A review of the concentrations of radionuclides measured in biota of the Pacific Proving Ground during testing of thermonuclear devices indicated that the production of measurable quantities of the radionuclide ^{63}Ni was probable. The large amounts of ^{55}Fe, ^{65}Zn, ^{57}Co, ^{58}Co, and ^{60}Co reported by Lowman (*1*) resulted largely from nuclear interactions in the structural material used in and around the device. We concluded that stable nickel in these materials would yield ^{63}Ni through the (n,γ) activation process. The cross section for this reaction is large (15 barns).

Detection of ^{63}Ni by other than specific radiochemical separation and liquid scintillation counting is doubtful. The radionuclide decays by the emission of a beta particle (100 percent) whose maximum energy is only 67 kev (*2*), an energy intermediate between those of ^{3}H and ^{14}C. Compared to other radionuclides produced in weapons testing, the radiological hazard from ^{63}Ni is much less and therefore was of little concern in the evaluation of the effects of radioactivity on biota. The specificity of the required analysis and the lesser hazard probably account for the fact that measurements of the concentrations of ^{63}Ni in the environment have not been made until now. However, the use of radioisotopes, both artificial and natural, as tracers of oceanic currents and water mixing (*3*) prompted us to look for ^{63}Ni since (i) the residence time of nickel in the ocean is 1.8×10^4 years; (ii) nickel is a constituent of ferromanganese minerals, comprising some 0.4 percent (by weight) (*4*); and (iii) ^{63}Ni has a radioactive half-life of 92 years and is thus a more useful long-term tracer than other radionuclides of the transition elements which have been found in the oceans but which have half-lives of a few years or less.

We separated nickel from biological and environmental samples and other elements by precipitation and solvent extraction. Before dissolution of the samples in concentrated nitric and perchloric acids, 6 mg of stable nickel were added to each sample to serve as both a carrier and a yield determinant. Nickel was concentrated from the digest by precipitation of nickel 1,2-cycloheptanedione dioxime from acid solution (*5*). The precipitate was collected by filtration, removed from the filter by dissolution in 8*M* HNO_3, and oxidized with perchloric acid to destroy the organic matter; the nickel was concentrated again by a second precipitation with heptoxime. After dissolution and oxidation of the second precipitate, $Ni(OH)_2$ was precipitated by the addition of NaOH. The precipitate was dissolved in 6*N* HCl, and the resultant solution was extracted with 10 ml of a solution of 10 percent Alamine-336 in xylene. The phases were separated by centrifugation, the organic layer was decanted, and the nickel was again precipitated as the hydroxide. The hydroxide precipitate was prepared for liquid scintillation counting (Packard Instrument liquid scintillation spectrometer model 3375) by dissolution in 0.5

Table 1. Concentration of nickel-63 in environmental samples. Errors given are the 95 percent confidence levels (2 σ) of the count rate measurements.

Location	Sample	Date of collection	Concentration of nickel-63 (disintegrations per minute per gram of dry weight)
	Eniwetok Atoll		
Belle Islet	Soil	May 1954	8.2 ± 0.2
Belle Islet	Clam kidney*	August 1964	158.0 ± 2.6
Belle Islet	Clam kidney*	August 1964	67.8 ± 1.6
Elugelab Islet	Crater sediment	August 1964	9.6 ± 0.2
Engebi Islet	Soil	August 1958	7.5 ± .2
Aaraanbiru Islet	Clam kidney†	September 1958	41.2 ± .6
Engebi Islet	Clam kidney‡	August 1964	11.4 ± .6
	Bikini Atoll		
Bokonejien Islet	Crater sediment	May 1967	80.0 ± 1.0
Namu Islet	Soil	August 1964	9.8 ± 0.2
Bokororyuru Islet	Clam kidney‡	August 1964	163.0 ± 3.5
	Rongelap Atoll		
Kabelle Islet	Soil (0–0.6 cm)	September 1961	3.1 ± 0.2
Kabelle Islet	Soil (0.6–1.3 cm)	September 1961	0.5 ± .06
	Christmas Island		
	Clam kidney‡	April 1962	.91 ± .14
	Penrhyn Atoll		
	Clam kidney*	April 1962	.42 ± .14
	Northeast Pacific Ocean		
	Chaetognaths§	February 1964	.93 ± .80
44°38′N,125°20′W	Chaetognaths	February 1964	2.3 ± 1.0
44°38′N,125°20′W	Chaetognaths	April 1964	4.0 ± 3.0
44°38′N,125°20′W	Chaetognaths	June 1964	4.5 ± 2.4
47°39′N,173°05′W	Squid‖	October 1965	0.19 ± 0.08
50°30′N,167°00′W	Squid‖	August 1966	.13 ± .08
30°N,140°W	Squid¶	July 1965	.38 ± .24
	Aleutian Islands		
Amchitka Island	Lichen#	October 1965	.18 ± .04
Amchitka Island	Lichen	October 1965	.35 ± .04
	Eastern seaboard		
	Composite shellfish	August 1963	.02 ± .002

* *Tridacna crocea.* † *Tridacna* sp. ‡ *Tridacna gigas.* § *Sagitta elegans.* ‖ *Onychoteuthis* sp. ¶ *Stenoteuthis bartrami.* # Principally *Cladonia pacificia.*

Table 2. Specific activities of nickel-63 in clam kidneys.

Sample	Location	Nickel-63 (disintegrations per minute)	Stable nickel (mg)	Specific activity of nickel-63 (disintegrations per minute per milligram)
Tridacna sp.	Eniwetok Atoll	305 ± 3	12.4	24 ± 0.2
Tridacna gigas	Bikini Atoll	1050 ± 11	3.8	276 ± 3
Tridacna gigas	Christmas Island	7 ± 0.4	8.7	0.8 ± 0.05
Tridacna crocea	Penrhyn Atoll	3 ± 0.7	4.0	0.8 ± 0.17

ml of 6*N* CH_3COOH, 2 ml of Bio-Solv (Beckman Instruments), and 15 ml of a solution containing 5 g of 2,5-diphenyloxazole (PPO) and 0.5 g of 1,4-bis-[2-(4-methyl-5-phenyloxazolyl)]-benzene (POPOP) per liter of toluene. We measured the yield by wet-ashing the liquid scintillation solution with HNO_3 and $HClO_4$, reprecipitating the nickel as the heptoxime complex, and weighing the dried product. Decontamination factors of $> 10^4$ were observed for the radioisotopes ^{90}Sr-Y, ^{55}Fe, ^{137}Cs, ^{207}Bi, ^{106}Ru-Rh, ^{147}Pm, ^{60}Co, ^{125}Sb, ^{144}Ce, ^{95}Zr-Nb, ^{110m}Ag, ^{226}Ra plus daughters, and ^{65}Zn. The clean separations obtained suggest that the activity in the low-activity samples is indeed ^{63}Ni.

Figure 1 shows the relative activity plotted against lower level settings derived from the liquid scintillation counting of a ^{63}Ni standard and a ^{59}Ni spike, along with the spectrum obtained from the analysis of a clam kidney that was collected at Bikini Atoll. Clearly, the activity separated from this tissue was ^{63}Ni. The concentrations of ^{63}Ni in these samples are listed in Table 1.

Generally, the liquid scintillation counter was set to record 10,000 sample counts or to count for 500 minutes. Background was counted for 500 minutes, and the average rate for the ^{63}Ni settings was 15.8 ± 0.4 count min^{-1}. The detection limit at this background counting rate and at an average overall efficiency of 59 percent for ^{63}Ni detection was 1.4 ± 1.0 disintegrations per minute per sample at the 95 percent confidence level (*6*). The values listed in Table 1 are adjusted to unit dry weight and therefore are numerically smaller than the detection limit. However, sample sizes exceeded 10 g, except for the chaetognaths, and the values for all samples were above the calculated detection limit.

The ^{63}Ni concentrations in marine species ranged from a low of approximately 0.02 disintegration per minute per gram of dry weight for shellfish taken on the eastern seaboard of the United States to a high of 163 disintegrations per minute per gram of dry weight for a clam kidney taken on the western rim of Bikini Atoll. Nicholls *et al.* (*7*) reported high concentrations of stable nickel in chaetognaths, which prompted us to analyze this organism for ^{63}Ni. The concentrations were very low, approaching the limit of detection. This suggests a low concentration of ^{63}Ni in surface waters in this area and indicates the absence of appreciable amounts of ^{63}Ni in Columbia River water, which is used upstream as a coolant for the nuclear reactors at the Hanford complex. This observation is consistent with Kirby's (*8*) radiochemical procedure for the isolation of ^{65}Ni from Columbia River water (8 to 12 liters) collected near the reactors. This procedure makes possible the measurement of a concentration of 10^{-8} μc of ^{65}Ni per milliliter. Because of its low specific activity, the activity of ^{63}Ni is expected to be much lower than this. In addition, there are large dilutions in the Columbia River and ocean waters; thus the river is an unimportant source of ^{63}Ni for the marine environment.

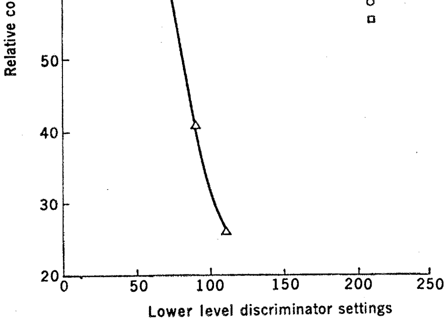

Fig. 1. Relative activity and discriminator settings for ^{59}Ni (△) and ^{63}Ni (○) spike solutions, plus the activity isolated from *Tridacna gigas* clam kidney collected from Bikini Atoll (□). Instrument settings were 20 percent gain and 4 percent window.

Folsom and Young supplied us with the squid specimen (*Stenoteuthis bartrami*) for which they reported values for the concentrations of ^{60}Co and ^{110m}Ag of 4100 and 1500 pc per kilogram of wet weight, respectively (*9*). Using a ratio of wet weight to dry weight of 4 for this specimen, we calculated that the ^{63}Ni concentration is approximately two orders of magnitude lower than the reported ^{60}Co concentration present at the time of catch, 1965. The average concentration of ^{63}Ni for lichens from the Aleutians is lower by only a factor of 2 than the ^{60}Co concentrations of lichens reported by Hanson *et al.* (*10*) for Anaktuvak Pass, Alaska; however, the comparison of results from insular species in the Aleutians to those of similar continental species may be invalid.

Some specimens contained sufficient stable nickel to permit comparison of the specific activities of ^{63}Ni, an indication of the variations that occur between similar organisms. Table 2 shows the results of the measurements of ^{63}Ni specific activity in clam kidneys collected at test sites and from islands some distance away.

The high specific activity in the clam kidney from Bikini Atoll is due, in part, to the fact that this specimen was taken at Bokororyuru Islet on the western edge of the atoll. Wind-driven surface currents move the lagoon waters toward the southwest and, as a consequence, Bokororyuru Islet receives waterborne radionuclides in addition to local fallout at the time of testing. The presence of ^{63}Ni in association with short-lived ^{57}Co (*11*) in the specimens taken from Christmas Island and Penrhyn Atoll in April 1962, prior to the United States tests of that year, suggests that the source of ^{63}Ni in these specimens was the Soviet tests of 1961. The evidence is not conclusive, however, since the age of the clams was not determined and it is probable that they were accumulating ^{63}Ni over a period of time. Bikini and Eniwetok atolls lie in the path of the North Equatorial Current which moves water toward the Asian continent.

Von Arx (*12*) has described the circulation and refreshment times of both Bikini and Rongelap atolls and has found that the exchange of lagoon water with seawater resulted in winter months from tide and wave action and in summer months from tides and the North Equatorial Current. The surface movement of waterborne radioactivity from Bikini and Eniwetok atolls would therefore be westward toward the Philippine Islands, with the possibility of some movement back toward the east in the Equatorial Countercurrent and possibly eastward at shallow depth in the Cromwell Current (*13*). Both Christmas Island and Penrhyn Atoll lie in the path of the westward-moving South Equatorial Current and consequently would be unlikely recipients of waterborne radioactivity emanating from Bikini and Eniwetok lagoons.

Nickel-58 comprises some 68 percent of stable nickel, and we have considered the possibility of the production of ^{59}Ni (half-life, 80,000 years) both by (n,γ) interactions with stable nickel, (p,n) reactions with stable cobalt, and (p,α) reactions with ^{56}Fe (92 percent abundance). Based on abundances, cross sections, and decay constants, we calculated an activity ratio of ^{63}Ni to ^{59}Ni of approximately 600 for the (n,γ) production of ^{59}Ni. Nickel-59 decays by electron capture and is determined by measuring the 6.9-kev x-ray which results from the de-excitation of its daughter, ^{59}Co. A 3000-minute count of the most radioactive clam kidney from Eniwetok Atoll in an anticoincidence shielded x-ray counter gave a positive indication of ^{59}Ni (at a counting error of 1 S.D.), with an upper limit of some 0.1 disintegration per minute per gram of dry weight. No ^{59}Ni was detected in 1000-minute counts of soil samples obtained from either atoll. It is probable, therefore, that no large amounts of ^{59}Ni were produced, and that the presence of small amounts of ^{59}Ni precludes its usefulness as a tracer in oceanic processes.

A realistic assessment of the total ^{63}Ni present at Bikini and Eniwetok atolls is not possible from the data presented here, although knowledge of such an inventory and of the rate at which it is injected into the North Equatorial Current would help one to determine its usefulness as a downstream tracer for these waters. However, the giant clam *Tridacna* sp. appears to be an excellent indicator organism, which could be used to delineate the downstream penetration of ^{63}Ni.

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Automatic Determination of Crystal Structure

Abstract. *Several crystallographic computer programs have been organized into one large automatic program for solving crystal structures. The emphasis of this organization has been to produce a noninteractive system, that is, to have all decisions made by the computer. Input data are the raw intensity data, cell constants, space group, chemical formula, and other miscellaneous items. The output is a stereo picture of the contents in a unit cell. The program, operating in a noninteractive mode, has successfully solved compounds of unknown structure; in addition, for a test compound of completely unknown composition, this program deduced the correct structure with an average error in bond distance of 0.05 angstrom and an average error in bond angle of 7°.*

It is generally recognized that there is a very important unsolved problem in crystallography—the phase problem. By this we mean that diffraction experiments do not permit one to obtain the structure factor and yield only its magnitude $|F|$. The great number of crystal structures that have been solved indicates that the problem is not insurmountable. For the most part these structures have been solved by the Patterson technique (*1*). More recently the symbolic addition procedure (*2*) is becoming the method of choice, especially for organic compounds with no heavy atom. This latter technique can be reduced to a formalism in which one starts with phases for a small number of reflections and generates relations between these and a large enough set of other reflections so that a Fourier map based on these phases permits a trial model to be obtained. If, in carrying out the symbolic addition, the program is unable to clearly distinguish the best starting combination of phases, one can calculate all possible E-maps (usually a small number) and attempt to obtain a correct trial model from one of these.

It is of interest to discover if one can use such a structure-solving capability together with other crystallographic programs to obtain a completely automatic structure-solver. In this connection we desire a noninteractive system which may be used by the noncrystallographer, rather than an interactive one for the professional crystallographer similar to those already described (*3*). Based on our experience so far, the answer is clearly yes.

We have constructed an automatic structure-solving program consisting, in the main, of standard crystallographic programs as subroutines. These subroutines have been integrated together with decision-making subroutines so as to eliminate the decisions which were previously reserved by the crystallographer for himself. The user supplies raw data, space group, and other miscellaneous items; the program produces a stereo plot of the best trial model.

At present, the algorithms for the solution of the structure are relatively unsophisticated; it is anticipated that they can be made more clever as additional experience is gained. For greater flexibility, it is possible to interrupt the program in order to overrule decisions made by it. This has usually proved to be unnecessary; in fact the "hands off" policy may sometimes be the best approach. The structure of $PaOCl_2$ (*4*) was easily solved by this program after