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MERCURY AND SELENIUM IN BLUE MARLIN, *MAKAIRA NIGRICANS*, FROM THE HAWAIIAN ISLANDS

In a previous study, nine species of pelagic and inshore fish caught in Hawaiian waters were analyzed for total and organic mercury (Rivers et al. 1972). In all but one species the organic mercury was >80% of the total, a finding consistent with other mercury values reported (Kamps et al. 1972; Westöö 1973). In muscle and liver tissues of blue marlin, *Makaira nigricans* Lacépède, however, only a small portion of the total mercury was found to be organic mercury. Additional studies on marlin landed during fishing tournaments in 1972 (Schultz et al. 1976) and 1973 (Schultz and Crear 1976) revealed low levels of organic mercury in six other tissues. These studies also showed that the difference between total and organic mercury was indeed inorganic mercury. G. Westöö (National Swedish Food Administration, Stockholm. Pers. commun., 1972) had previously identified the organic fraction as methyl mercury.

An assessment of mercury is complicated by the presence of selenium. Selenium has been shown to reduce the toxicity of mercuric chloride and methyl mercury in laboratory animals when given as selenite, selenomethionine, or as selenium present in tuna (Parízek et al. 1971; Ganther and Sunde 1974). The presence of selenium in tuna, a principal food item of marlin (Naughton[1]), indicates that it should also be present in marlin.

For this report, nine tissues from blue marlin were analyzed for selenium, total mercury, and organic mercury.

Materials and Methods

Samples of muscle, liver, kidney, spleen, pyloric caecum, stomach, gill, gonad, and blood were collected from 46 marlin landed during a fishing tournament in Kailua-Kona, Hawaii, during August 1974. The tissues were ground with Dry Ice[2] in a blender and stored in acid-washed plastic vials.

The organic extraction was carried out as described by Rivers et al. (1972), i.e., a benzene extraction of the methyl mercury was reextracted with cysteine, oxidized with permanganate, and reduced to elemental mercury with stannous ion prior to being volatilized into the flameless atomic absorption apparatus. Total mercury digestions were performed (Rivers et al. 1972) but with 10 ml of concentrated nitric acid instead of 30 ml. All analyses were made with a Perkin-Elmer 303 atomic absorption spectrophotometer equipped with a vapor chamber (Manning 1970).

Selenium was determined by a fluorometric technique (Watkinson 1966), as modified by S. Nishigake (Tokyo Metropolitan Research Laboratory of Public Health, Tokyo, Japan. Pers. commun., 1975), i.e., following sample digestion with nitric and perchloric acids, the selenium was complexed with 2,3-diaminonaphthalene and this fluorescent compound then extracted into cyclohexane. All analyses were made using a Turner Model 110 fluorometer equipped with a primary filter at 369 nm and a secondary filter at 522 nm.

[1]Naughton, J. J. 1973. To all billfishermen. (Summary report of 15th Hawaiian International Billfish Tournament, 27-31 August 1973), 9 p. Southwest Fisheries Center Honolulu Laboratory, National Marine Fisheries Service, NOAA, Honolulu, HI 96812.

[2]Reference to trade names does not imply endorsement by the National Marine Fisheries Service, NOAA.

Results

A summary of mercury and selenium concentrations in the marlin is given in Table 1. Average total mercury and selenium values were greatest in kidney (26.33 mg/kg Hg, 23.42 mg/kg Se) and least in blood (0.18 mg/kg Hg, 1.29 mg/kg Se) and gill (0.32 mg/kg Hg, 1.29 mg/kg Se). Average methyl mercury was highest in muscle (0.40) mg/kg) and lowest in blood (0.04 mg/kg) and gill (0.06 mg/kg). The percentage of organic to total mercury ranged from 1% in kidney to 27% in gonad. The molar ratio of mercury to selenium ranged from 0.06 in blood to 0.62 in muscle. (Molar ratio is computed here using sample average statistics of combined male and female data.)

An analysis of variance revealed significant differences ($P<0.05$) in total mercury between males and females for all tissues except gill and blood. A similar pattern was found for selenium. The organic mercury levels were not statistically different ($P>0.05$) between the sexes. In earlier studies on marlin caught from the same area during fishing tournaments in 1971, 1972, and 1973, mercury concentrations in both sexes were found to be similar.

Table 2 presents correlation coefficients for body weight and tissues. In most cases, the relationships are positive and highly significant. Figures 1-6 illustrate the dependence of mercury and selenium on weight and on each other.

Discussion

The data clearly demonstrate that methyl mercury concentrations are low relative to total mercury in blue marlin. Westöö (pers. commun.) and Nishigaki (pers. commun.) confirmed this low percentage in our samples based on subsamples sent to them. Nishigaki has also confirmed our selenium results.

In a study of 37 Pacific blue marlin (50-238 kg, average 109 kg) from Japanese waters, Nishigaki (pers. commun.) found total mercury levels ranging from 0.02 to 13.0 mg/kg (average 2.83 mg/kg) and methyl mercury ranging from 0.02 to 1.28 mg/kg (average 0.57 mg/kg). Selenium values for 11 marlin ranged from 0.52 to 1.99 mg/kg, averaging 0.97 mg/kg. These values are similar to our findings for mercury and selenium in marlin from Hawaiian waters.

TABLE 1.—Summary of mercury and selenium data in 46 blue marlin from the Hawaiian Islands by sex.[1]

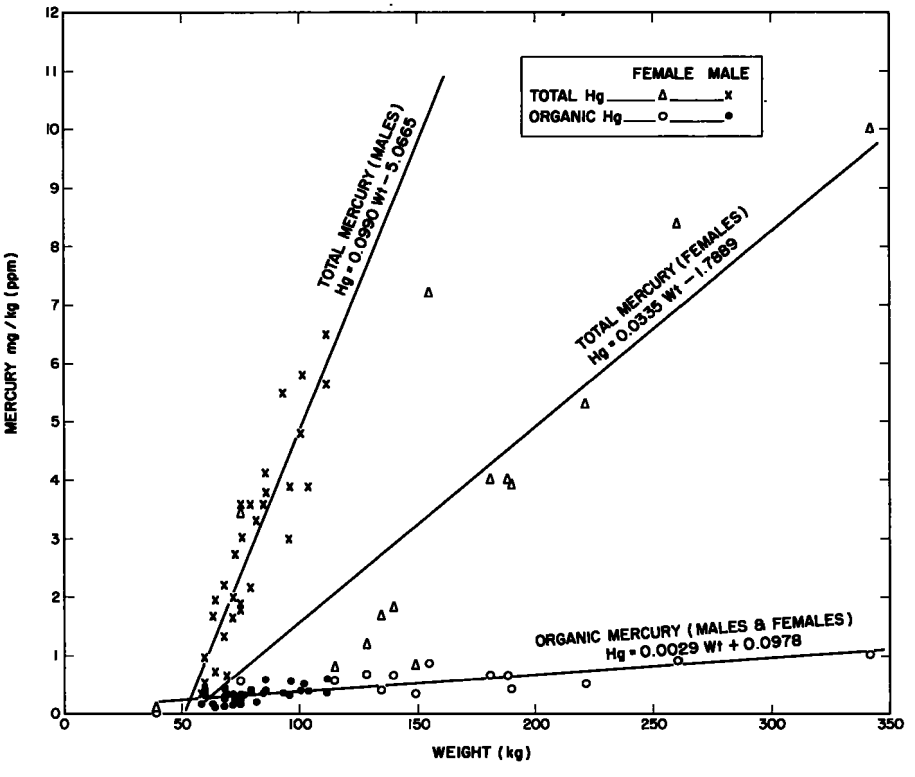
	Total Hg (mg/kg)				Organic Hg (mg/kg)				% organic Hg of total Hg	Se (mg/kg)				Hg/Se molar ratio
	Mean			Range	Mean			Range		Mean			Range	
Tissue	M & F	M	F	M & F	M & F	M	F	M & F	M & F	M & F	M	F	M & F	M & F
Muscle	3.12	2.83	3.76	0.09-10.00	0.40	0.32	0.58	0.02-1.02	13	1.98	1.88	2.21	0.63-5.32	0.62
Liver	11.58	12.53	9.46	0.13-39.20	0.26	0.21	0.38	0.09-0.76	2	17.47	20.36	11.06	2.50-61.12	0.26
Kidney	26.33	26.25	26.53	0.18-77.00	0.22	0.16	0.35	0.04-0.86	1	23.42	25.33	19.06	2.63-56.25	0.44
Spleen	6.93	6.34	8.21	0.08-17.60	0.18	0.12	0.30	0.02-0.66	3	9.31	9.12	9.73	0.63-24.25	0.29
Stomach	1.27	1.33	1.16	0.06-3.00	0.12	0.08	0.21	0.03-0.47	9	2.91	3.16	2.39	1.35-4.03	0.17
Pyloric caecum	1.83	1.74	2.03	0.17-4.50	0.30	0.22	0.49	0.08-0.98	16	4.92	5.10	4.52	2.28-10.10	0.15
Gill	0.32	0.26	0.44	0.08-0.96	0.06	0.03	0.11	<0.01-0.34	19	1.29	1.31	1.26	0.71-2.21	0.10
Gonad	0.40	0.30	0.68	0.03-2.15	0.11	0.06	0.25	0.03-0.65	27	2.14	1.97	2.60	1.24-3.80	0.07
Blood	0.18	0.18	0.18	0.02-0.53	0.04	0.04	0.05	<0.01-0.11	22	1.29	1.33	1.19	0.72-2.30	0.06

[1]Weights of 32 males ranged from 58 to 112 kg (average 80); 14 females weighed 39, 75, and 115-342 kg (average 166). Average for all samples was 106 kg.

TABLE 2.—Correlation coefficient of mercury, selenium, and weight in 46 blue marlin from the Hawaiian Islands by sex.

	Total Hg/wt			Organic Hg/wt	Organic/ total Hg	Se/wt			Total Hg/Se	Organic Hg/Se
Tissue	M & F	M	F	M & F	M & F	M & F	M	F	M & F	M & F
Muscle	0.69**	0.90**	0.83**	0.79**	0.72**	0.68**	0.88**	0.85**	0.93**	0.61**
Liver	0.23	0.76**	0.69**	0.76**	0.13	0.00	0.68**	0.38	0.80**	−0.08
Kidney	0.49**	0.83**	0.79**	0.87**	0.42**	0.32*	0.79**	0.73**	0.91**	0.30*
Spleen	0.61**	0.88**	0.75**	0.84**	0.51**	0.45**	0.72**	0.61*	0.87**	0.41**
Stomach	0.38*	0.77**	0.82**	0.81**	0.35*	−0.27	0.18	0.15	0.32*	−0.33*
Pyloric caecum	0.59**	0.83**	0.82**	0.86**	0.59**	−0.11	0.32	−0.10	0.25	−0.14
Gill	0.86**	0.70**	0.90**	0.88**	0.77**	0.04	0.08	0.16	0.21	−0.14
Gonad	0.85**	0.75**	0.95**	0.82**	0.76**	0.15	−0.10	−0.53	0.10	0.25
Blood	0.28	0.32	0.57*	0.36*	0.44**	−0.04	−0.17	0.49	0.44**	0.09

*$P<0.05$.
**$P<0.01$.


FEMALE MALE
TOTAL Hg
ORGANIC Hg
TOTAL MERCURY (MALES)
Hg = 0.0990 Wt - 5.0665
TOTAL MERCURY (FEMALES)
Hg = 0.0335 Wt - 1.7889
ORGANIC MERCURY (MALES & FEMALES)
Hg = 0.0029 Wt + 0.0978
MERCURY mg/kg (ppm)
WEIGHT (kg)

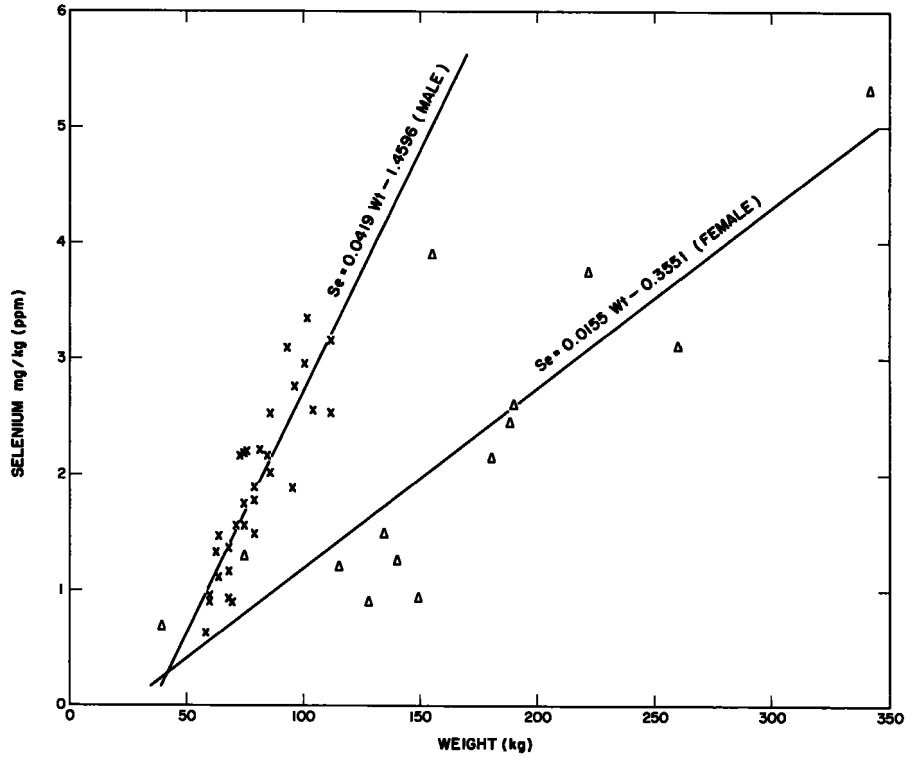

Se = 0.0419 Wt - 1.4596 (MALE)
Se = 0.0155 Wt - 0.3551 (FEMALE)
SELENIUM mg/kg (ppm)
WEIGHT (kg)

FIGURE 1.—The relationship of total and organic mercury in muscle tissue of 46 blue marlin from the Hawaiian Islands to fish weight.

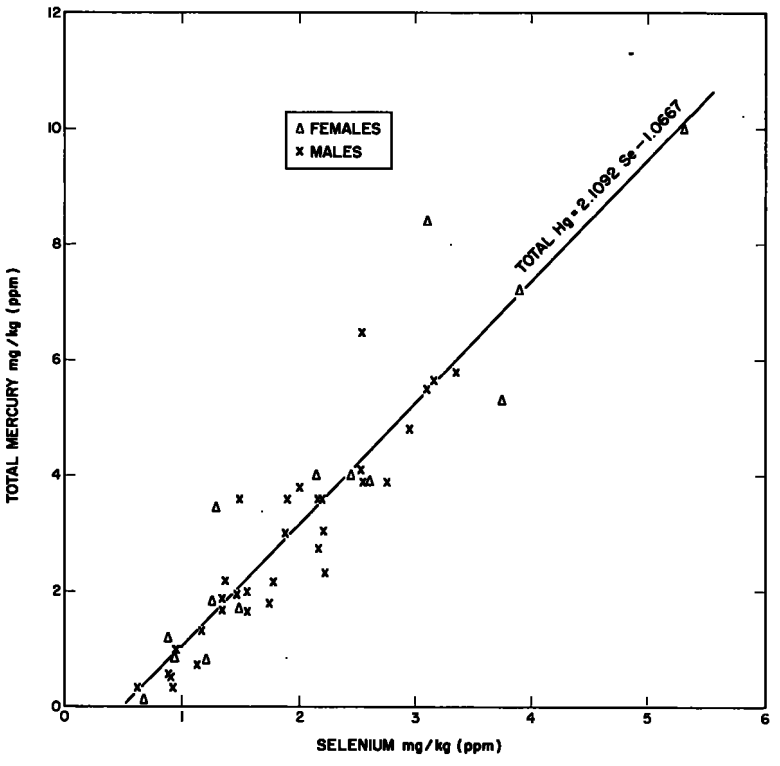


FIGURE 3.—Relationship between total mercury and selenium in muscle tissue of 46 blue marlin from the Hawaiian Islands.

FIGURE 2.—Relationship between selenium in muscle tissue and weight of 46 blue marlin from the Hawaiian Islands.

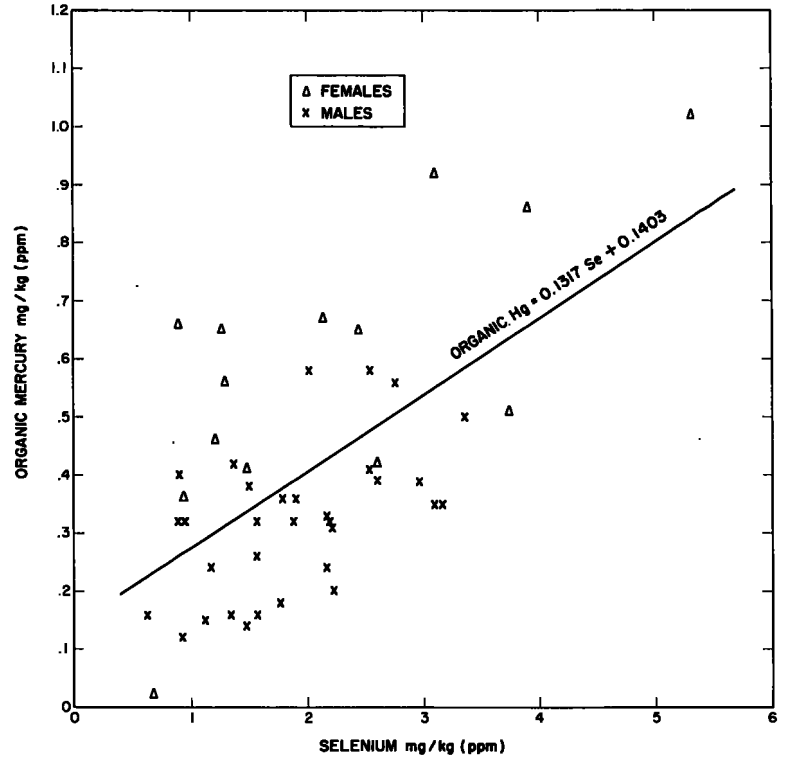


FIGURE 4.—Relationship between organic mercury and selenium in muscle tissue of 46 blue marlin from the Hawaiian Islands.

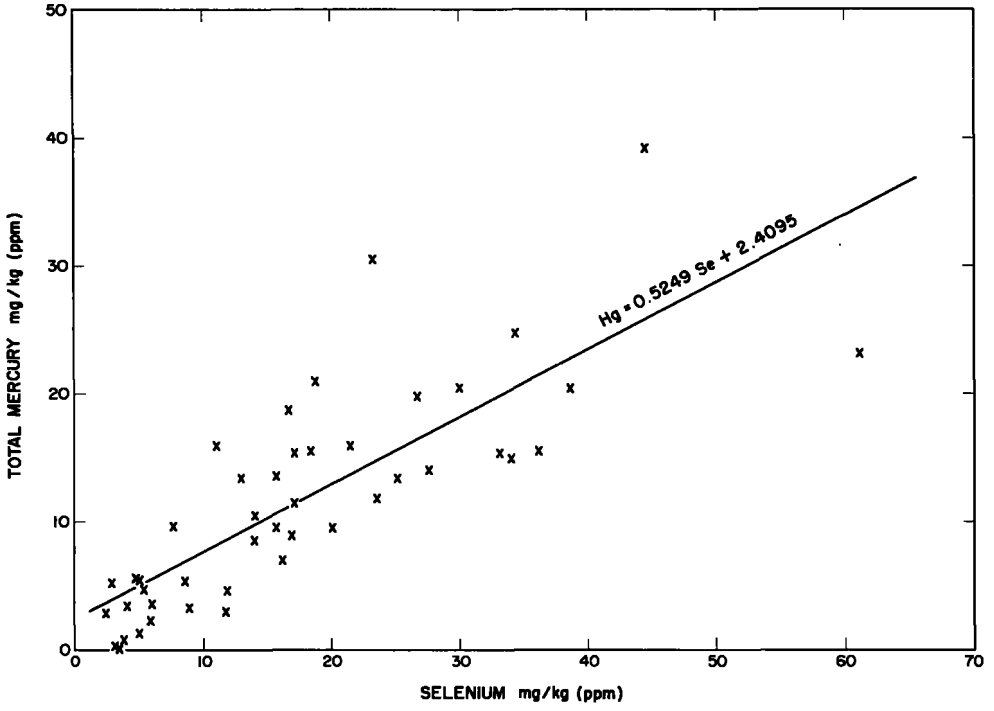


FIGURE 5.—Relationship between total mercury and selenium in liver of 46 blue marlin from the Hawaiian Islands.

Concentration through the food chain is apparently the reason for the elevated levels of mercury found in the marlin. Stomach contents examined in 76 blue marlin captured in 1973 showed that the most common food items were tuna, mostly *Katsuwonus pelamis* (38% occurrence); mackerel scad, *Decapterus pinnulatus* (36%); squid (21%); spiny puffer, Diodontidae (19%); and dolphin, Coryphaenidae (12%) according to Naughton (see footnote 1).

Mercury levels were reported for yellowfin tuna, *Thunnus albacares*, 0.54 mg/kg; skipjack tuna, *K. pelamis*, 0.38 mg/kg; and for dolphin, *Coryphaena hippurus*, 0.25 mg/kg; by Rivers et al. (1972). These are pelagic species and as such, are exposed to the same amount of mercury in their physical environment; yet all have mercury levels nearly an order of magnitude less than that of the marlin. In addition, their mercury content was essentially all methyl mercury.

If most of the mercury entered the marlin via the food chain as methyl mercury it would seem that demethylation to inorganic mercury had occurred. Conversion of methyl mercury to inorganic mercury has been shown to occur in bluegill (Burrows and Krenkel 1973) and in rats (Norseth and Clarkson 1970).

It is indicated in Figure 1 that the mercury is accumulated with size but at different rates for males and females. This observation contrasts with previous year's results in which no sex-related concentration disparities were found (Shultz and Crear 1976; Shultz et al. 1976). The reason for this year's anomaly is unclear and not enough information is available to determine if we are dealing with more than one population.

Selenium levels in the marlin are presented in Table 1 and show an increase with weight and age (Figure 2). The high correlation of mercury and selenium with weight (Table 2), and the observation that selenium modifies the activity of mercury in experimental animals, indicate that they are highly correlated with each other, as is seen in Figures 3-6. The precise nature of the mercury-selenium interaction is not known, although a number of suggestions have been advanced. Parízek et al. (1971) demonstrated with rats that the protective effect of selenite against mercuric chloride was not related to an increase in mercury excretion but to a decrease, resulting in a change

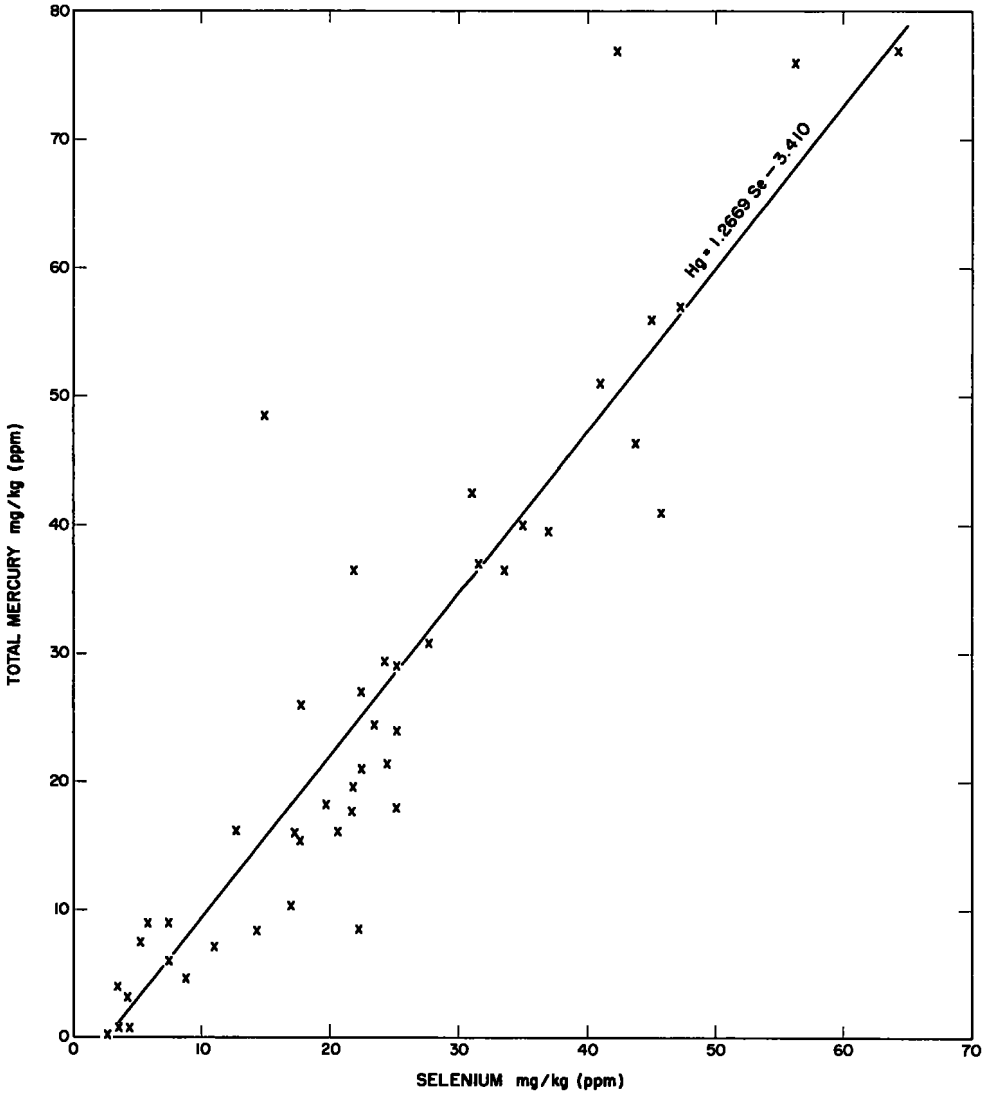


FIGURE 6.—Relationship between total mercury and selenium in kidney of 46 blue marlin from the Hawaiian Islands.

in organ distribution of mercury. The kidneys and intestines lost mercury while the testes gained mercury relative to the controls. In addition, mercury in the macromolecular fraction of blood plasma increased after addition of selenite. Burk et al. (1974) found a similar increase of mercury in plasma protein when mercuric chloride was administered simultaneously with selenite. This was not the case when mercuric chloride or selenite was injected alone. Their experiments using dialysis of rat plasma protein indicated that selenium and mercury are bound in a 1:1 molar ratio to a single protein, with selenium attached to the protein through a sulfhydryl group and mercury attached to the selenium. They also observed a time lag after injection of selenite before detection of protein binding during which the selenite was apparently metabolized to another form. Lunde (1970) has found selenium to be associated also with proteins in marine organisms.

The molar ratio of average total mercury to average selenium in muscle is 0.62. Subtracting the methyl mercury to obtain inorganic mercury (Schultz and Crear 1976), the ratio reduces to 0.54.

Ganther et al. (1972) reported that the mercury to selenium molar ratio for high-mercury tuna (can tuna) (average 2.87 mg/kg) approaches 0.5. They also noted that the mercury and selenium increments between low-mercury tuna (0.32 mg/kg) and high-mercury tuna were about in a 1:1 molar ratio, implying they are accumulated together.

The total mercury-selenium relationships observed in marine mammals and man are similar to those found in tuna. Koeman et al. (1973) found a 1:1 molar ratio in the livers of seals, *Phoca vitulina*, porpoises, *Phocoena phocoena*, and dolphins, *Tursiop truncatus*, *Delphinus delphis*, *Lagenorhynchus obscurus*, and *Sotalia guianensis*. Regression analyses of their data give an average slope of 2.7 ± 0.2 or 1.1 ± 0.1 on a molar basis for mercury-selenium interactions ($r = 0.932$). Interestingly, they found that only 2 to 14% of mercury in the liver and 2 to 13% in the brain was recovered as methyl mercury. Post-mortem studies on humans exposed to high inorganic mercury (from a mercury mine) showed a 1:1 molar ratio of mercury to selenium ($r = 0.998$) in tissues which had accumulated high amounts of mercury, i.e., thyroid, pituitary, kidney, and brain (Kosta et al. 1975). They noted, however, that this ratio did not exist for a nonexposed group in which mercury and selenium levels were insignificant. Elevated mercury levels were apparently responsible for increasing the selenium concentrations such that, in many cases, the molar ratio of mercury to selenium increments over normal levels approached 1:1 (selenium was low in the mine environment: 1 mg/kg versus 100 mg/kg Hg—in contrast to the relative enrichment of selenium in the diet of tuna and marine mammals). The levels of methyl mercury in organs of the exposed group were low, implying that no significant in vivo methylation occurs in man.

Because selenium is high in the marlin (average 1.98 mg/kg in muscle, 17.47 mg/kg in liver, 23.42 mg/kg in kidney), the possibility of selenium toxicity should not be discounted. Aptly, though, mercury has been shown to mitigate the toxicity of selenium in rats and chicks (Parízek et al. 1971; Hill 1974).

In an earlier study, it was indicated that cooking did not remove either methyl or total mercury from marlin fillets (Schultz and Crear 1976). Higgs et al. (1972) have found that baking does not remove selenium from flounder or chicken although some loss was reported from boiling two vegetables. It does appear then that mercury (muscle average 3.12 mg/kg) and selenium (muscle average 1.98 mg/kg) concentrations in raw fillet are representative of that in cooked fish.

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RECENT RECORDS OF *CALLINECTES DANAE* AND *CALLINECTES MARGINATUS* (DECAPODA: PORTUNIDAE) FROM NORTH CAROLINA WITH ENVIRONMENTAL NOTES

Temperature and latitudinal distributions of the genus *Callinectes* are best known for *C. sapidus* Rathbun (Williams 1974; Norse 1977). The northern limits of *C. danae* Smith and *C. marginatus* A. Milne Edwards are listed as Bermuda and southern Florida, with one specimen of *C. marginatus* from North Carolina regarded as a temporary range extension (Williams 1974). We report the taking of two specimens of *C. danae* and six specimens of *C. marginatus* by 12.2-m (40-ft) otter trawl in and near the Cape Fear River estuary, N.C. All specimens have been deposited at the Institute of Marine Sciences, University of North Carolina, Morehead City, N.C. Measurements listed are of carapace width in millimeters including lateral spines.

Two specimens of *C. danae* (UNC 2766, ♂ 115; ♂ 113), 1 *C. marginatus* (UNC 2765, ♂ 97), 6 *C. ornatus* Ordway, and 7 *C. similis* Williams were captured by trawl in the Intracoastal Waterway on 19 September 1977, just south of the Carolina Beach Inlet, on a sand-shell bottom 4 m deep in water of 36‰ surface salinity and 26°C. Four *C. marginatus* (UNC 2763, ♀ 92; ♂ 103; ♂ 62; ♂ 81) were also caught at this location on 14 September 1977, along with 30 *C. ornatus*, 35 *C. similis*, and 10 *C. sapidus*. Bottom salinity was 20‰, and bottom temperature was 26.5°C. Several other small specimens of *C. marginatus* (40-60 mm) were observed, but not retained in this trawl. A sixth specimen of *C. marginatus* (UNC 2764, ♀ 91), 1 *C. ornatus*, 30 *C. similis*, and 20 *C. sapidus* were collected in the intake canal of the Carolina Power and Light Company generating plant in the Cape Fear River estuary west of buoy 19 on 11 October 1977. Bottom type was silty-sand at depth of 4 m. Surface salinity was 31‰ and surface water temperature was 17°C.

The present record of *C. danae* represents a northward range extension of 1,000 km, from Biscayne Bay, Fla., to the Cape Fear River. Williams (1974) noted that it occurs in a wide range of salinities and habitats. However, Norse (1977) believed *C. danae* prefers lower salinities, from studies in the Caribbean.

The six specimens of *C. marginatus* bring the total recorded in North Carolina and north of southern Florida to seven. Shallow environments over a wide range of substrates are preferred in a salinity range of 19-32‰ and temperature range of 22°-30°C (Williams 1974). Norse (1974) has inferred a preference for higher salinities by *C. marginatus*; note, we obtained four of the six specimens at 20‰ and a fifth was captured inside the Cape Fear estuary where salinities fluctuate widely.

Callinectes danae, *C. marginatus*, and *C. ornatus*, with the exception of two specimens of the latter from Charleston, S.C., are now recorded from Florida, North Carolina, and Bermuda. Another species which occurs in Florida and Bermuda, *C. exasperatus* Gerstaecker, has yet to be taken in