HEAVY METALS IN THE NORTHERN FUR SEAL, *CALLORHINUS URSINUS*, AND HARBOR SEAL, *PHOCA VITULINA RICHARDI*

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ABSTRACT

Samples of liver, muscle, and kidney from fur seal, *Callorhinus ursinus*, and liver from harbor seal, *Phoca vitulina richardi*, were analyzed for total mercury. Liver and kidney of fur seals were analyzed for lead, cadmium, and arsenic. Fur seals were from the Pribilof Islands, Alaska, and from off the Washington coast. Harbor seals were from the waters of southern California, Oregon, Washington, and the Bering Sea. All of the samples, including a fetus taken 3 mo before birth, contained mercury, lead, and cadmium. Arsenic was not detected. Mercury was highest in liver, followed by kidney, then muscle. The maximum concentration of mercury in liver was about 700 ppm in a southern California harbor seal and 170 ppm in a fur seal taken off the Washington coast. Concentrations of cadmium and lead were highest in the kidney (maximums of 1.8 ppm lead and 15.6 ppm cadmium) of fur seals. Concentrations of mercury did not correlate with age in muscle or kidney ($P > 0.05$) but did correlate significantly with age in liver ($P < 0.01$). Concentrations of cadmium and lead in liver and kidney did not correlate with age ($P > 0.05$). In samples of liver collected from harbor seals, the highest concentrations of mercury were from southern California seals.

Heavy metals are persistent contaminants that ultimately end up in the oceans. Little is known of the sublethal effects of these contaminants on living marine resources, but some heavy metals are known to be harmful. One ppb (part per billion) of four commonly used organomercurial fungicides reduced the photosynthetic rate of a marine diatom (Harriss, White, and MacFarlane, 1970). Skerfving, Hansson, and Lindsten (1970) reported chromosome breakage in humans who ate fish containing 1-7 ppm (parts per million) methylmercury.

Heavy metals are added to the sea by land erosion, volcanic activity, and man. A committee of experts selected mercury, lead, cadmium, and arsenic as the four inorganic pollutants most threatening to the marine environment (Food and Agriculture Organization of the United Nations, 1971). The same elements were selected for this study. Average levels of the four most critical heavy metals in the ocean are about 0.00003 ppm (mg/l) mercury, 0.08 ppm cadmium, 0.00003 ppm lead, and 0.003 ppm arsenic (U.S. Senate, 1970). Williams and Weiss (1973) found 0.00027 ppm mercury at 10-m depth and 0.000029-0.000096 ppm from 100- to 4,080-m depth in water samples taken 430 km southeast of San Diego, Calif.

Amounts of contaminants in seals provide us with data at this time in a marine species near the top of the food web in the ocean. Up to 172 ppm mercury in liver of northern fur seals, *Callorhinus ursinus* (Anas, 1970a); 66 ppm in liver of gray seals, *Halichoerus grypus* (Jones, Jones, and Stewart, 1972); and 24 ppm mercury in liver of short-finned pilot whales, *Globicephala scammoni* (Hall, Gilmartin, and Mattsson, 1971) have been reported. Buhler[2] reported 60 ppm cadmium in the kidney, 6 ppm cadmium in the liver, and 225 ppm mercury in the liver of California sea lions, *Zalophus californianus*. This report documents the amounts of mercury, lead, cadmium, and arsenic in northern fur seals and of mercury in harbor seals, *Phoca vitulina richardi*.

Northern fur seals are a migratory species that breed each summer mainly on the Pribilof Islands, Alaska, and on the Commander Islands

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and Robben Island, USSR. Small breeding colonies are found in the Kurile Islands, Japan, and on San Miguel Island, Calif. During winter and spring, fur seals are pelagic and migrate as far south as southern California and Japan. Fur seals feed principally on fishes and squids in offshore areas.

Harbor seals are a nonmigratory species found in the northern hemisphere in both the Pacific and Atlantic Oceans. Those collected for this study (subspecies *richardi*) are found from Mexico to the Bering Sea. Harbor seals feed principally on fishes, squids, and octopuses near coastlines.

METHODS

The liver and kidneys were selected as the principal tissues for this study because heavy metals tend to accumulate in these organs (DuBois and Geiling, 1959; Curry, 1969). Samples of muscle were collected from fur seals but not from harbor seals.

Collection of Samples

In general, the sampling was conducted as follows: From a seal liver weighing about 1.8 kg, a kidney weighing about 0.5 kg, or muscle from the shoulder area, a sample of about 75 g was placed in a new unwashed glass bottle or polyethylene bag and stored at −23°C. Analyses were made about 5 mo after initial sampling.

Samples included liver and muscle from 3-mo-old pups and 2- and 3-yr-old male fur seals from the Pribilof Islands; liver, muscle, and kidney from fur seals (mostly adult females) from Washington; and liver from harbor seals from California, Oregon, Washington, and the Bering Sea. Tissues from fur seals taken on the Pribilof Islands were kept in polyethylene bags; all other tissues were kept in new glass bottles.

Analyses of Samples

For the analysis of mercury, four replicate 20-mg samples were taken from a piece of tissue in the sample bottle and analyzed. The mean of these four replicates was taken as representative of the particular tissue for that analysis. The analytical procedure for mercury involves introduction of the weighed sample into a tubular furnace from which the products of combustion and vaporized mercury are drawn. After scrubbing and filtering to remove interfering components, the mercury vapor is passed through a cell and read by atomic absorption spectrophotometry.[3]

For lead, cadmium, and arsenic analyses, a separate 2-g sample was taken for each metal. The lead analysis was carried out by digesting the sample in a 5:2 nitric-sulfuric acid mixture followed by dry ashing in a muffle furnace at 550°C until all organic material was removed. Following dissolution in 5 ml of hydrochloric acid, lead content was determined by the double extraction, mixed color dithizone method (Committee on Chemical Procedures of the Occupational Health Section, American Public Health Association, 1955).

For cadmium, the sample was wet ashed in a 2:1 nitric-perchloric acid mixture, and the resultant solution diluted to a known volume with water. The cadmium was extracted into methyl isobutyl ketone (MIBK) by means of chelation with sodium diethyldithiocarbamate (NDDC) and measured by atomic absorption (Berman, 1967).

For arsenic, the sample was wet ashed in an 8:4:1 nitric-perchloric-sulfuric acid mixture to oxidize organic matter and release organically bound arsenic. Following digestion, the sample was diluted to 25 ml volume with water and arsenic determined by the silver diethyldithiocarbamate method (American Public Health Association, 1971).

Detection limits of the analyses were 1 ppb for mercury, 0.1 ppm for lead, 0.01 ppm for cadmium, and 0.2 ppm for arsenic. Recoveries were over 90% for mercury and cadmium where mercury was added as elemental mercury dissolved in nitric acid and cadmium was added as cadmium sulfate. Lead and arsenic recoveries were over 95% with lead added as lead nitrate and arsenic added as arsenic trioxide.

All of the tissue samples were analyzed by Environmental Health Laboratories Inc.,

[3] Hermann, W. J., Jr., J. W. Butler, and R. G. Smith. 1968. A dynamic system for the rapid microdetermination of mercury in undigested biological materials. Presented at Applied Seminar on Laboratory Diagnosis of Diseases Caused by Toxic Agents, Washington, D.C., Nov. 8-9, 1968. Wayne State Univ., Detroit, Mich., Dep. Med., 14 p., 1 fig. (Processed.)

Farmington, Mich.[4] A sample of paper lid liners from the glass bottles was analyzed by the use of neutron activation by Battelle Pacific Northwest Laboratories, Richland, Wash., to determine amounts of mercury, lead, cadmium, and arsenic.

Age Determinations

Ages were assigned to fur seals by counting layers of dentine in sectioned upper canine teeth (Scheffer, 1950; Fiscus, Baines, and Wilke, 1964). Errors in assigning ages to fur seals are small in young seals but increase sharply in animals older than 7 yr (Anas, 1970b). Most errors in older animals, however, are only of a magnitude of ± 2 yr. Although canine teeth of harbor seals have layers of dentine, it is not known if these layers accurately portray age. Ages were not assigned to harbor seals, but body lengths were taken.

RESULTS

Heavy Metals in Fur Seal Tissues

Amounts of total mercury were higher in liver than in muscle or kidney of fur seals (Table 1). Mercury in liver ranged from 0.4 ppm in a fetus taken 3 mo before birth (the liver of the 11-yr-old mother had 86 ppm), to 0.1-0.3 ppm in 10 pups, 3-19 ppm in 30 young males, 7-78 ppm in two young females, and 19-172 ppm in 36 adult females. For muscle, 0.1 ppm was found in five pups, 0.1-0.4 ppm in 29 young males, and 0.2-0.4 ppm in 10 adult females. Mercury in kidney ranged from 0.2 ppm in a fetus (the mother had 1 ppm), to 0.7 ppm in a young male, and 0.6-1.6 ppm in eight females, 1 to 20 yr old.

A wide range of mercury was found only in the liver, so variability due to sampling is more important for liver than for muscle or kidney. The 95% confidence limits of within-sample variability for the 20-mg samples of liver were ± 11% of the mean values. The average variability between seals within ages was 55 times greater than the variability within the 20-mg samples. Thus, to increase accuracy, larger samples of seals are more important than additional 20-mg samples from each piece of liver.

Methylmercury was not determined in this study. However, in samples of liver from California sea lions, about 2% of the total mercury was methylmercury (Buhler, see Footnote 2).

On the average, amounts of lead and cadmium were higher in kidney than in liver (Table 2). Arsenic was not detected in any of the samples. Lead in liver ranged from 0.8 ppm in a fetus (the mother also had 0.8 ppm), to 0.2 ppm in a young male, and 0.4-0.8 ppm in eight females. Lead in kidney ranged from 0.3 ppm in a fetus (0.8 ppm in the mother), to 1.8 ppm in a young male, and 0.8-1.2 ppm in eight females. Cadmium in liver ranged from 0.5 ppm in a fetus (4.6 ppm in the mother), to 0.6 ppm in a young

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

TABLE 1. — Parts per million mercury on a wet weight basis in liver, muscle, and kidney of fur seals taken off Washington and on the Pribilof Islands, 1970-71.

Age (years)	Sex	Area	Year collected	Number of seals	Tissue	Mercury
0.3 (Pups)	Mixed	Pribilof Islands	1970	10	Liver	0.1–0.3
			1970	5	Muscle	0.1
2-3	Male	Pribilof Islands	1970	29	Liver	3.0–19.0
			1970	29	Muscle	0.1–0.4
5-19	Female	Washington Coast	1970	29	Liver	19.0–172.0
			1970	10	Muscle	0.2–0.4
Fetus	Male	Washington Coast	1971	1	Liver	0.4
			1971	1	Kidney	0.2
1	Male	Washington Coast	1971	1	Liver	3.7
			1971	1	Kidney	0.7
1-20	Female	Washington Coast	1971	8	Liver	7.1–132.0
			1971	8	Kidney	0.6–1.6

TABLE 2. — Parts per million cadmium and lead on a wet weight basis in kidney and liver of fur seals taken off Washington, 1971.[1]

Age (years) of specimens	Sex of specimens	Kidney		Liver	
		Cadmium	Lead	Cadmium	Lead
Fetus	M	0.1	0.3	0.5	0.8
1	M	1.7	1.8	0.6	0.2
1	F	6.9	0.8	0.9	0.6
3	F	4.3	0.8	2.2	0.6
6	F	15.6	1.2	2.6	0.6
8	F	0.2	0.9	1.2	0.5
11	F	6.2	0.8	4.6	0.8
15	F	9.6	0.9	1.1	0.4
16	F	1.0	1.0	1.7	0.5
20	F	6.8	0.8	1.7	0.7

[1] Arsenic was not found above the limit of detection of 0.2 ppm (mg/kg) in either kidney or liver in any of the samples.

male, and 0.9-4.6 ppm in eight females. Cadmium in kidney ranged from 0.1 ppm in a fetus (6.2 ppm in the mother), to 1.7 ppm in a young male, and 0.2-15.6 ppm in eight females.

Lid liners from new glass bottles had 1.1 ppm mercury and 0.4 ppm arsenic. Lead and cadmium were not detected. The tissues and lid liners were never in direct contact, but some transfer of mercury from the lid liners and glass bottles could have occurred. However, the maximum contribution from the lid liners would have been 0.004 ppm mercury, so the data were not adjusted.

Heavy Metal — Age Comparisons in Fur Seals

Regression equations were computed for samples from fur seals collected in 1970 and 1971 to determine if mercury in liver, muscle, and kidney and if lead and cadmium in liver and kidney were correlated with age. Significant correlations for mercury have been reported for fur seal liver (Anas, 1970a) and whole fishes (Bache, Gutenmann, and Lisk, 1971). Untransformed data were used here because log transformations did not significantly improve the correlations. Fetuses and pups were not included in the calculations. Only liver tissues were collected both in 1970 and 1971. The correlation coefficients in the two years for mercury in liver were common ($P > 0.05$), so the data were pooled. Mercury in liver had a significant positive correlation with age ($P < 0.001$, $r = +0.84$). The data indicate that mercury accumulates in liver. Mercury in muscle and kidney did not correlate with age ($P > 0.05$, $r = +0.05$ and $+0.51$, respectively). Also, lead and cadmium in liver and kidney did not correlate with age ($P > 0.05$, $r = +0.19$ and -0.45 for lead and $r = +0.17$ and $+0.04$ for cadmium in liver and kidney, respectively). Sample sizes were 67 for mercury in liver, 39 for mercury in muscle, and 9 for cadmium and lead in liver and kidney.

Mercury in Harbor Seal Livers

Harbor seals are nonmigratory, so levels of contaminants in this species are useful for locating geographical concentrations of contaminants, provided that the food species do not migrate long distances. Studies suggest that the principal food species of harbor seals do not migrate far (Scheffer and Sperry, 1931; Spalding, 1964; Kenyon, 1965). The highest levels of mercury were found in harbor seals from San Miguel Island (Table 3). One harbor seal from San Miguel Island had 700 ppm mercury in the liver. The amount of mercury in this sample is so much higher than the amounts found in the other seals that the possibility of contamination of the sample should be considered. However, as far as is known, this sample was treated no differently than the other samples. The sample size is small and the ages are not known, but the concentrations of

TABLE 3. — Parts per million mercury on a wet weight basis in liver of harbor seals taken in the eastern Pacific Ocean, 1970-71.

Location	Date collected	Sex	Length (cm)	Mercury
San Miguel Is., Calif.	2 June 1971	F	161	700
	2 June 1971	F	153	81
	4 June 1971	M	176	124
	5 June 1971	F	156	171
Columbia R., Oregon	May 1971	M	—	0.3
	do	M	112	3.2
	do	F	126	68
Washington Coast	2 Sept. 1971	F	84	1.3
Puget Sound, Washington	24 Nov. 1970	M	—	60
	21 June 1971	M	95	12
Pribilof Is., Alaska	17 Aug. 1971	M	135	0.6
	do	F	140	3.2
	do	M	175	8.9

mercury in San Miguel Island seals appear to differ significantly from those from the Pribilof Islands. Except for the one seal with 700 ppm mercury, the amounts of mercury found in harbor seals from all areas studied are within the range of those found in livers of fur seals.

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