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Seasonal Variations of Arsenic and Other Trace Elements in Bay Mussels (*Mytilus edulis*)

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Arsenic is considered hazardous as both an acute and chronic poison; it is believed to combine with sulfhydryl enzymes and interfere with cellular metabolism (DREISBACH 1974). It is also a known carcinogen (IARC 1979; MARTELL 1981) and is listed by the U.S. EPA as a priority pollutant.

Arsenic in the environment has both natural and anthropogenic origins. BENNETT (1981) estimated global quantities of anthropogenic and natural releases of As at 24.1^6 kg y^{-1} and 8.1^6 kg y^{-1}, respectively. CRECELIUS et al. (1975) described an input of As by a copper smelter into Puget Sound (Tacoma, WA) and also found that sewage treatment plants, river run-off and seawater were additional sources. Mining operations have also contributed to environmental arsenic concentrations (KLUMP & PETERSON 1979).

Arsenic is rarely included in studies of trace metal uptake by organisms, probably because the methods for its determination require more complex procedures than those used in flame atomic absorption spectrometry. FUKAI & MEINKE (1962) used neutron activation analysis combined with radiochemical separation to determine arsenic, vanadium, molybdenum, tungsten, rhenium and gold in various marine organisms. KARBE et al. (1977) used instrumental neutron activation analysis (INAA) to identify and measure many elements, including As, in separate populations of *Mytilus edulis* at different times of the year.

The purposes of this study were to investigate seasonal variations of arsenic in a population of bay mussels *(Mytilus edulis)* and to compare results with variations of several other trace elements more commonly measured in environmental studies. Seasonal variations of manganese, nickel, copper, zinc, and cadmium were investigated previously (LA TOUCHE & MIX 1981), but arsenic and its relationship with those metals is now reported for the first time.

MATERIALS AND METHODS

Sample Preparation. Mussels were collected at regular intervals from an uncontaminated site on Yaquina Bay (Newport, OR) during September 1980-September 1981. Preparation consisted of shucking (removing from the shell), homogenizing and wet

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digestion as described by LA TOUCHE et al. (1981).

Arsenic. For As determination, 0.5-mL aliquots of the digest solution were double contained (LA TOUCHE et al 1981) and activated for 1 h in a rotating rack position in the OSU TRIGA reactor. The power level employed was 1 MW which provided a thermal neutron flux of approximately 3×10^{12} n cm^{-2} s^{-1}.

After a delay of 18 h to permit decay of short-lived radionuclides, As was retained on aluminum oxide (Al_2O_3) as described by GLADNEY & OWENS (1976). Disposable polypropylene columns (Bio-Rad econo-columns) were used to make a bed of Al_2O_3 (J. T. Baker Chemicals, Reagent, Brockmann activity grade I) approximately 36 mm in length by 8 mm diameter in the lower part of the column. The upper part of the column consisted of a reservoir volume of 11 mL. The washing sequence used by GLADNEY & OWENS (1976) was satisfactory for eliminating most of the ^{24}Na from the column and allowed detection and counting with a relatively low Compton background. Arsenic-76 was not eluted from the column but was counted *in situ*. An As standard was also retained in a column and was used to calculate As levels. The accuracy of the method was determined by similar treatment of a sample of NBS oyster tissue (NBS Standard Reference Material 1566).

Samples and standards were counted for 1000 s with a 2048 channel analyzer (Nuclear Data Corp. ND-600) interfaced with a 15% Ge(Li) detector.

Cadmium, Copper, Manganese, Nickel and Zinc. Flame atomic absorption spectrometry was used to determine concentrations of Cd, Cu, Mn, Ni and Zn, the digest solution was aspirated directly into the flame.

Data reduction and statistical treatments were accomplished with a Hewlett-Packard HP-85 computer.

RESULTS AND DISCUSSION

Table 1 summarizes the data obtained in successive analyses of the mussel samples from Yaquina Bay. In general, the choice of variables determined was the same as those employed by LA TOUCHE & MIX (1981). The reproductive state of mussels was found previously to have a significant effect on trace metal tissue burdens and hence, the gonad index (GI) was also routinely determined. All parameters listed in Table 1 were included in a product-moment correlation matrix to identify significant relationships; highly correlated variables are shown in Table 2. It is evident that gonadal burdens of Mn, Cu, Zn and As are related to each other, and to the gonad index and average gonad weight.

Table 1. Tissue burdens of manganese, nickel, copper, zinc, cadmium and arsenic in gonadal (G) and somatic (S) tissues of *M. edulis* (dry weight). Burden is the total content of an element in μg, within a specific tissue compartment (i.e., gonadal or somatic). GI-gonad index, AGW - average gonad weight, ASW - average somatic weight.

	Day No.	AGW (g)	ASW (g)	GI mg g^{-1}	Mn G	Mn S	Ni G	Ni S	Cu G	Cu S	Zn G	Zn S	Cd G	Cd S	As G	As S
9/04/80	1	0.13	0.44	298	0.64	3.0	0.34	2.6	0.81	4.2	6.8	84	0.18	2.3	1.5	5.5
10/09/80	35	0.10	0.56	169	0.36	3.1	0.39	4.4	0.36	5.7	4.2	110	0.28	6.5	1.2	7.4
11/18/80	75	0.16	0.62	241	0.51	3.5	0.34	3.6	0.46	5.1	6.2	116	0.34	7.4	1.6	6.1
12/17/80	104	0.17	0.62	269	0.60	4.1	0.36	5.5	0.60	6.5	7.0	133	0.34	6.3	1.6	6.5
1/15/81	133	0.12	0.52	238	0.60	4.7	0.73	5.8	0.53	4.4	5.5	93	0.19	3.7	1.3	5.3
2/17/81	166	0.08	0.49	170	0.38	5.6	0.69	8.1	0.32	4.7	4.5	96	0.19	3.4	1.2	6.0
4/07/81	215	0.19	0.63	314	0.70	4.5	1.10	4.2	0.87	4.4	7.6	122	0.23	3.7	2.8	9.5
5/21/81	259	0.11	0.58	193	0.44	3.9	0.18	2.1	0.42	3.4	5.8	97	0.15	3.2	1.4	9.3
6/10/81	279	0.16	0.57	277	0.74	6.3	0.35	3.4	0.66	4.0	8.2	94	0.19	3.8	2.4	8.6
7/08/81	307	0.25	0.62	399	0.80	3.9	0.43	1.1	0.93	6.6	7.5	18	0.20	2.6	2.4	7.1
9/01/81	361	0.15	0.65	230	0.42	3.8	0.32	3.1	0.48	3.8	4.4	85	0.24	4.8	1.7	9.8

Table 2. Product-moment correlation matrix showing r-values for the relationships between gonadal burdens of elements, mean gonad weights and gonad index. Abbreviations as in Table 1.

	G.I.	AGW	Mn G	Cu G	Zn G	As G
G.I.	1.00					
AGW	0.91	1.00				
Mn G	0.92	0.79	1.00			
Cu G	0.96	0.81	0.91	1.00		
Zn G	0.79	0.70	0.91	0.80	1.00	
As G	0.76	0.78	0.79	0.79	0.78	1.00

The metal burdens varied in relation to season and reproductive state of the mussels. There were two periods of gametogenesis and subsequent spawnings in the mussel population, during April and July of 1981. Gonadal burdens of Mn, Cu, Zn and As showed peaks on both of these occasions. Nickel reached a maximum gonadal burden in April, but no July peak was noted. Trace element burdens did not, in general, show variations that were strongly correlated with somatic tissue weights. Arsenic was exceptional, in that it was positively correlated with the average somatic tissue weight ($r = 0.62$). It is noted that when somatic tissues are considered as a whole, gut contents may influence results and possibly obscure relationships since they represent a transient body of material, containing variable quantities of elements, that is external to the animal tissue.

If tissue concentrations of the elements are considered, the data indicate that As in mussel tissues was not controlled similarly to other elements investigated. Arsenic gonadal concentrations were not greatly different from somatic concentrations, and in fact gonadal concentrations were slightly higher in some samples. For the one year period of this study, gonadal As concentrations ranged from 9 to 15 $\mu g\ g^{-1}$ and somatic tissues from 10 to 16 $\mu g\ g^{-1}$. The mean concentrations for the entire year were 11.9 ± 2.2 and $12.8 \pm 2.2\ \mu g\ g^{-1}$, respectively. There was a positive correlation between concentration values ($r = 0.62$) but the correlation between gonadal and somatic arsenic burdens was not as great ($r = 0.48$). Somatic concentrations of other elements investigated in this study and previously (LA TOUCHE & MIX 1981) were always considerably higher than gonadal concentrations.

Arsenic concentration values in *M. edulis* generally have been reported on the basis of total soft tissues. KARBE et al. (1977) found an As range of 7 to 14 $\mu g\ g^{-1}$ (dry wt.) at one of their collection sites in the North Sea. LUNDE (1970) reported a value of 8.0 ppm (wet wt.) which would be approximately equivalent to 40 $\mu g\ g^{-1}$ (dry wt.). LEATHERLAND & BURTON (1974) reported As levels of 9.5 and 15 ppm (dry wt.) in the whole soft tissues of *M. edilus* sampled near Southampton (U.K.). NAS (1977) has summarized many reported values for the As concentration in seafoods; they ranged as high as 128 ppm (shrimp, dry wt.).

If the mussels analyzed in the present study were considered on the basis of total soft tissue, without separation into somatic and gonadal tissues, then the total tissue burden of arsenic would be correlated positively with average total weight ($r = 0.60$). Concentration values were not correlated with average total weight ($r = 0.03$). Total soft tissue concentration over the year ranged from 10 to 15.5 $\mu g\ g^{-1}$ (dry wt.).

In monitoring As levels in mussels, separation of gonadal and somatic tissues appears to be unnecessary, but in order to state this unequivocally it would be necessary to conduct a study in which there was controlled administration of As at a high but sublethal level. The results of such a study would provide information about tissue distribution of As in mussels exposed to unusually high levels of this toxic element. At the same time, possible excretion routes could be determined by analysis of gut contents and byssal threads.

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