

Concentrations of Elements in a Marine Food Chain Cultured in Sewage Wastewater

A. Keith Furr¹, Thomas F. Parkinson¹, John Ryther², Carl A. Bache³,
Walter H. Gutenmann³, Irene S. Pakkala³ and Donald J. Lisk³

¹*Office of Occupational Health and Safety, and Nuclear Reactor Laboratory, respectively, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061;* ²*Woods Hole Oceanographic Institute, Woods Hole, MA 02543;* ³*Toxic Chemicals Laboratory, Cornell University, Ithaca, NY 14853*

Considering the earth's given land area and ever increasing population, much research is presently underway to utilize and cultivate fresh water and marine species as an additional source of protein (BARDACH et al. 1972). One of the main obstacles to this endeavor is water pollution with the probability of absorption, concentration and biological magnification of toxic constituents. Of special significance in this regard are current attempts to utilize domestic wastewater as a basic source of nutrients for growing aquatic organisms (ALLEN and CARPENTER 1974; D'ITRI 1975; RYTHER et al. 1972). The effluent from conventional secondary sewage treatment is particularly appropriate for this purpose since it contains in dissolved form most of the nutrients (N, P, etc.) originally present in untreated wastewater while most of the toxic trace contaminants, both organic and inorganic, are usually adsorbed or otherwise bound to the particulate fraction and carried down in the sludge during the secondary sewage treatment process (CHEN et al. 1974). This is not true of all trace contaminants, however, as some are highly soluble and remain in the effluent fraction at significant concentrations. Furthermore, even those that may be present at very low, even undetectable levels in the sewage effluent may subsequently become concentrated in the cultivated organisms and their concentrations further amplified by passage up the food chain (WOODWELL et al. 1967).

It is essential to learn which elements and organic constituents in treated sewage effluent are absorbed by aquatic species and whether the magnitude of absorption may constitute a hazard to consumers. In the work reported, an aquatic food chain including seaweed, clams, oysters, lobsters, and flounder has been cultured in secondary sewage effluent from the Wareham, Massachusetts treatment plant. The aquatic organisms were then analyzed for 44 elements by neutron activation, flameless atomic absorption, anodic stripping voltammetry and other methods. Element concentrations in the sewage sludge (collected from the final clarification stage) was also analyzed and is reported to demonstrate the probable origin of the elements found in the cultured organisms.

EXPERIMENTAL

The new Wareham, Massachusetts waste treatment facility is a conventional activated sludge, secondary treatment plant. At the time of this study, the entire Town of Wareham was not yet serviced and the plant was operating at less than (220,000 gallons per day) full capacity. Treatment therefore included extended aeration of the wastewater. Following final clarification, greater than 95% of suspended solids and BOD are removed from the effluent. Prior to chlorination, approximately 8,000 gallons per day of the final effluent was trucked daily to the Woods Hole Oceanographic Institution's aquaculture facility during the three month period in which the organisms were cultured. Organisms exposed to seawater alone served as controls.

The organisms cultured and studied were four seaweeds (Agardhiella tenera (At), Chondrus crispus (Cc), Gracilaria foliifera (Gf), and Hypnea musciformis (Hm), and hardshell clams or quahogs (Mercenaria mercenaria), American oysters (Crassostrea virginica), American lobster (Homarus americanus) and winter flounder (Pseudopleuronectes americanus). The rearing procedure is described by RYTHER et al. (1975).

The trophic relationships of the organisms grown in the aquaculture system is not representative of the classical "food chain" of primary producers - herbivores - carnivores. Thus the lobsters and flounder did not feed upon the principal herbivores of the system, the bivalve molluscs, but upon small invertebrates that in turn, fed upon solid wastes of the shellfish that settled directly out of the raceways. Nevertheless, three or more distinct trophic levels are represented in the samples.

A sample of sewage sludge was obtained from the clarifier at the Wareham plant for analysis. The entire seaweed plant material and the edible flesh of the shellfish and flounder were analyzed. The plant material was first thoroughly rinsed with distilled water. The samples were then subdivided, mixed and freeze-dried. Subsamples were analyzed for 34 elements using nondestructive neutron activation analysis as previously described (FURR et al. 1975).

Arsenic, boron, cadmium, chromium, copper, lead, mercury, nickel, selenium and zinc were determined by other methods. The determination of cadmium, copper, lead and zinc was performed by dry ashing the samples up to 475° C followed by analysis by conventional anodic stripping voltammetry using a Princeton Applied Research Corp. Model 174 Polarographic analyzer (GREWELING 1966).

Following dry ashing, nickel and chromium were determined by furnace atomic absorption using a Perkin Elmer Model 303 spectrophotometer equipped with an HGA-2000 graphite furnace. Arsenic analysis was performed by dry ashing (EVANS and BANDEMER 1954), distillation of arsine and determination using the silver diethyldithiocarbamate spectrophotometric procedure (FISHER SCIENTIFIC CO. 1960). The determination of boron was accomplished by the curcumin

spectrophotometric method (GREWELING 1966).

Mercury was determined by flameless atomic absorption following combustion of the dry sample using an oxygen flask (BACHE et al. 1973). The determination of selenium was accomplished by a modification of the method of OLSON (1969) employing wet digestion of the sample and measurement of the fluorescence of piasselenol resulting from reaction of selenium with 2,3-diaminonaphthalene.

RESULTS AND DISCUSSION

The elemental concentrations in ppm (dry weight) in the sludge are listed in Table 1. In Table 2 are given the concentrations of specific elements which were found most consistently at higher concentrations in the aquatic plants cultured on the sewage wastewater as compared to the corresponding control plant species. Similarly, in Table 3 are given the concentrations of those elements which were usually higher in the shellfish and flounder raised in the sewage wastewater as compared to the corresponding control fish. The data indicate that appreciable concentration increases for a number of elements may occur in marine organisms exposed to sewage wastewater as compared to the corresponding controls. The accumulations of cadmium, copper, lead, nickel and zinc by clams, oysters, lobsters and/or fin fish has been reported by other investigators (ISHIO et al. 1973; EISLER et al. 1972; BRYAN 1971; SHUSTER and pringle 1969; RAY 1978; CRESPO et al. 1979; FRIEDRICK and FILICE 1976; REICHERT et al. 1979) in studies involving fish exposed to experimental concentrations of these metal ions or naturally polluted water.

Alga, snails, mosquito larva and fish have also been shown to accumulate high levels of cadmium, copper, lead and zinc when 1% sewage sludge was added to their culture medium (YOUNG and LANGILLE 1958). The accumulation of elements by aquatic species may be considerable with concentration factors over those in seawater (COULSON et al. 1935) reaching values of 200,000 for zinc in oysters and 2,040,000 for cerium in algae (PRINGLE et al. 1968; MCKEE and WOLF 1971; BENDER et al. 1970). The form of the element in water is probably a factor affecting its extent of absorption. The presence of metals in water as soluble complexes with organic constituents in sewage is possible (DOUDOROFF and KATZ 1953). The absorption of metals by aquatic organisms and the factors affecting their toxicity to them have been comprehensively reviewed (KLEIN et al. 1974).

This study of the culture of aquatic organisms in wastewater indicates that the accumulation of elemental pollutants by various species may be considerable. Since a major portion of copper, cadmium, chromium, nickel and zinc in municipal wastewater is believed to derive from domestic uses (HALL 1974), monitoring metal concentrations in wastewater from domestic as well as industrial sources prior to reuse is recommended.

TABLE 1.
Elemental concentration (ppm, dry weight) in the sludge.

Element	Concentration	Element	Concentration
Al	5347	Mo	7.5
As	2.9	Na	5367
Au	1.0	Ni	11.6
B	5.0	Pb	205
Ba	1558	Rb	18
Br	114	Sb	7.7
Ca	6553	Sc	0.5
Cd	18	Se	5.5
Ce	31	Sm	5.2
Cl	3150	Sn	120
Co	6.1	Sr	319
Cr	57	Ta	0.1
Cs	0.6	Th	3.5
Cu	1877	Ti	915
Dy	1.6	U	1.6
Eu	0.4	V	14
Fe	13420	W	3.5
Hf	1.2	Yb	0.9
Hg	64	Zn	611
I	63		
K	7720		
La	6.6		
Lu	0.1		
Mg	4740		
Mn	92		

TABLE 2.
Elemental concentrations (ppm, dry weight) in aquatic plants.

Element	Seaweed (At)		Seaweed (Cc)		Seaweed (Gf)		Seaweed (Hm)	
	Con- trol	COSW ^a	Con- trol	COSW	Con- trol	COSW	Con- trol	COSW
Br	519	788	645	1137	324	464	425	593
Co	2.2	4.6	3.6	5.6	1.5	3.3	2.8	3.0
Cu	6.6	138	8.2	55	1.5	102	4.4	223
I	58	158	310	371	97	188	71	150
Zn	34	188	62	383	19	106	25	39

^acultured on sewage wastewater

TABLE 3.
Elemental concentrations (ppm, dry weight) in shellfish and flounder.

Element	Clam		Oyster		Lobster		Flounder	
	Con-trol	COSW ^a	Con-trol	COSW	Con-trol	COSW	Con-trol	COSW
Cd	0.4	0.7	1.5	4.4	0.09	0.5	0.02	0.1
Cu	9.7	37	81	517	136	155	1.7	0.4
Fe	159	276	166	1740	50	202	83	127
I	2.3	6.4	2.7	6.0	6.3	8.9	0.6	0.9
Mn	14	73	7.3	17	12	7.1	3.9	5.2
Ni	3.4	6.5	1.7	3.2	1.4	5.7	0.5	0.5
Pb	0.5	1.9	0.31	2.0	0.2	1.5	0.5	2.3
Se	0.9	1.0	1.0	1.6	2.2	3.1	1.3	0.8
Zn	115	377	1948	3856	135	207	73	109

^a cultured on sewage wastewater

REFERENCES

- ALLEN, R., and L. CARPENTER: Proceedings of the Conference of Wastewater Use in the Production of Food and Fiber. EPA 660/2-74-041. 1974.
- BACHE, C. A., W. H. GUTENMANN, L. E. ST. JOHN, JR., R. D. SWEET, H. H. HATFIELD, and D. J. LISK: J. Agr. Food Chem. 21, 607 (1973).
- BARDACH, J. E., J. H. RYTHER, and W. E. MCLARNEY: Aquaculture. The Farming and Husbandry of Freshwater and Marine Organisms. Wiley-Interscience, New York 1972.
- BENDER, M. E., W. R. MATSON, and R. A. JORDAN: Environ. Sci. Technol. 4, 520 (1970).
- BRYAN, G. W.: Proc. Roy. Soc. Lond. B. 177, 389 (1971).
- CHEN, K. Y., C. S. YOUNG, T. K. JAN and N. ROHATGI: J. Water Poll. Contr. Fed. 46, 2663 (1974).
- COULSON, E. J., R. E. REMINGTON, and K. M. LYNCH: J. Nutr. 10, 255 (1935).
- CRESPO, S., R. FLOS, J. BALASCH and G. ALONSO: Comp. Biochem. Physiol. 63C, 261 (1978).
- D'ITRI, F. M., Ed.: Proceedings of the International Conference on the Renovation and Recycling of Wastewater Through Aquatic and Terrestrial Systems. Bellagio, Italy 1975.
- DOUDOROFF, P., and M. KATZ: Industrial Wastes 25, 802 (1953).
- EISLER, R., G. E. ZAROOGIAN, and R. J. HENNEKEY: J. Fisheries Res. Bd. Can. 29, 1367 (1972).
- EVANS, R. J. and S. L. BANDEMER: Anal. Chem. 26, 595 (1954).
- FISHER SCIENTIFIC CO.: Tech. Data Bull. TD-142 (1960).
- FRIEDRICH, A. R. and F. P. FILICE: Bull. Environm. Contam. Toxicol. 16, 750 (1976).
- FURR, A. K., G. S. STOEWSAND, C. A. BACHE, W. H. GUTENMANN, and D. J. Lisk: Arch. Env. Health 30, 244 (1975).

- GAJAN, R. J. and D. LARRY: J. Assoc. Offic. Anal. Chem. 55, 727 (1972).
- GREWELING, H. T.: The Chemical Analysis of Plant Tissue. Mimeo No. 6622, Agronomy Dept., Cornell University, Ithaca, NY 14853. (1966).
- HALL, E. T.: J. Assoc. Off. Anal. Chem. 57, 1068 (1974).
- ISHIO, S., N. OHBA, Y. TANAKA, and S. TADOKORO. Bull. Japanese Soc. Scientific Fisheries 39, 705 (1973).
- KLEIN, L. A., M. LANG, N. NASH, and S. L. KIRSCHNER: J. Water Poll. Contr. Fed. 46, 2653 (1974).
- MCKEE, J. E. and H. W. WOLF: Water Quality Criteria. 2nd ed., Publ. No. 3-A. The Resources Agency of California, State Water Resources Control Board. 1971.
- OLSON, O. E.: J. Assoc. Off. Anal. Chem. 52, 627 (1969).
- PRINGLE, B. H., D. E. HISSONG, E. L. KATZ, and S. T. MULAWKA: Proc. Amer. Soc. Civil Engineers 1968.
- RAY, S.: Bull. Environ. Contam. Toxicol. 19, 631 (1978).
- REICHERT, W. L., D. A. FEDERIGHI, and D. C. MALINS: Comp. Biochem. Physiol. 63C, 229 (1979).
- RYTHER, J. H., W. M. DUNSTAN, K. R. TENORE, and J. E. HUGUENIN: Bioscience 22, 144 (1972).
- RYTHER, J. H., J. C. GOLDMAN, C. E. GIFFORD, J. E. HUGUENIN, A. S. WING, J. P. CLARNER, L. D. WILLIAMS, and B. E. LAPOINTE: Aquaculture 5, 163 (1975).
- SHUSTER, C. N., JR., and B. H. PRINGLE: Proc. Natl. Shellfisheries Assoc. 59, 91 (1969).
- WOODWELL, G. M., C. F. WURSTER, and P. A. ISAACSON: Science 156, 821 (1967).
- YOUNG, E.G., and W. M. LANGILLE: Can. J. Botany 36, 301 (1958).