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Correlations Between Lead, Cadmium, Copper, Zinc, and Iron Concentrations in Frozen Tuna Fish

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The presence of metallic pollutants in marine ecosystems has promoted wide research plans in order to evaluate pollution levels in marine organisms. However, little is known concerning environmental and physiological processes that regulate the concentration of trace metals in marine organisms. Even though the toxicity of lead and cadmium is well established, copper, zinc and iron are considered as essential elements for mammals. However, in high concentrations they may cause poisoning or changes in the organoleptic qualities of food, owing mainly to their role as catalysts in many degradation processes.

Little is known about heavy metals, other than mercury, concentrations in fresh and frozen tuna fish, but some results have been reported (Vinogradov 1953, Evans *et al.* 1975). Establier (1970) determined the concentration of Cu, Zn, Fe and Mn in several organs of *Thunnus thynnus* and found that the liver and pancreas are rich in Cu, Zn and Fe, and contain relatively large amounts of Mn, and also that exceptionally large concentrations of Fe and Zn are found in spleen.

MATERIALS AND METHODS

The fifty samples analyzed were obtained at the entrance of a canning factory in Santa Cruz de Tenerife (Canary Islands) and were caught in the South African Fishing Bank. Three replica 20-30 gr homogenized samples of muscle from the mid-dorsal region of each fish were IR-dried and then ashed at 450 ± 10°C until white ashes were obtained, which were then treated with 15 ml hot concentrated hydrochloric acid, filtered and made up to 100 ml with deionized water in a volumetric flask. Determinations were carried out by flame atomic-absorption spectrophotometry using deuterium arc background correction for Cd, Pb and Zn. Results were treated by applying the Statistical Package for the Social Sciences (Nie *et al.* 1975) compiled and linked in the software of a Digital VAX/VMS 11/780 (V3.2) computer.

RESULTS AND DISCUSSION

Since *Thunnus thynnus*, *Katsuwomus pelamis*, *Thunnus albacares* and *Thunnus alalunga* are under the generic denomination of "canned tuna", we have not distinguished between them either analytically or statistically.

The mean concentrations of lead, cadmium, copper, zinc and iron together with their frequency distribution statistical parameters are summarized in table 1. In general, these values indicate that the manufacturers are not faced with heavy metal contamination problems. Of the metals for which the Spanish Food Directorate has set tolerances (Pb, Cd and Cu: 3, 1 and 20 ppm, respectively) there is no indication of any health hazard in the specimens analyzed.

Table 1. Statistical parameters of the frequency distribution of Pb, Cd, Cu, Zn and Fe concentrations in tuna fish

Statistics	Element(ppm, wet basis)				
	Pb	Cd	Cu	Zn	Fe
Mean	0.347	0.259	1.011	8.034	4.845
Median	0.405	0.250	0.685	7.685	4.025
Mode	0.000	0.200	0.500	7.730	3.000
Minimum	0.000	0.020	0.340	5.530	2.000
Maximum	1.070	0.420	6.960	17.560	11.400
Mean std. error	0.035	0.011	0.149	0.270	0.331
Standard deviation	0.248	0.078	1.054	1.910	2.344
Kurtosis	0.264	0.934	21.257	11.790	1.140
Skewness	0.231	0.040	4.207	2.721	1.140

The mean values for the metals found in this study fall within the ranges of concentration reported by Vinogradov (1953); values for zinc are lesser and for copper are higher than those reported by Mershina *et al.* (1963) for Asiatic ocean fishes, and lead and zinc are lesser, cadmium higher and copper of the same order than values reported by Uthe and Bligh (1971) for Canadian freshwater fishes.

Statistical analysis was undertaken in order to investigate whether or not a relation existed between each of the heavy metal concentrations in tuna fish, in order to establish whether there were correlations significative enough within the population studied to establish positive metabolic or pollution relations between these heavy metals or not.

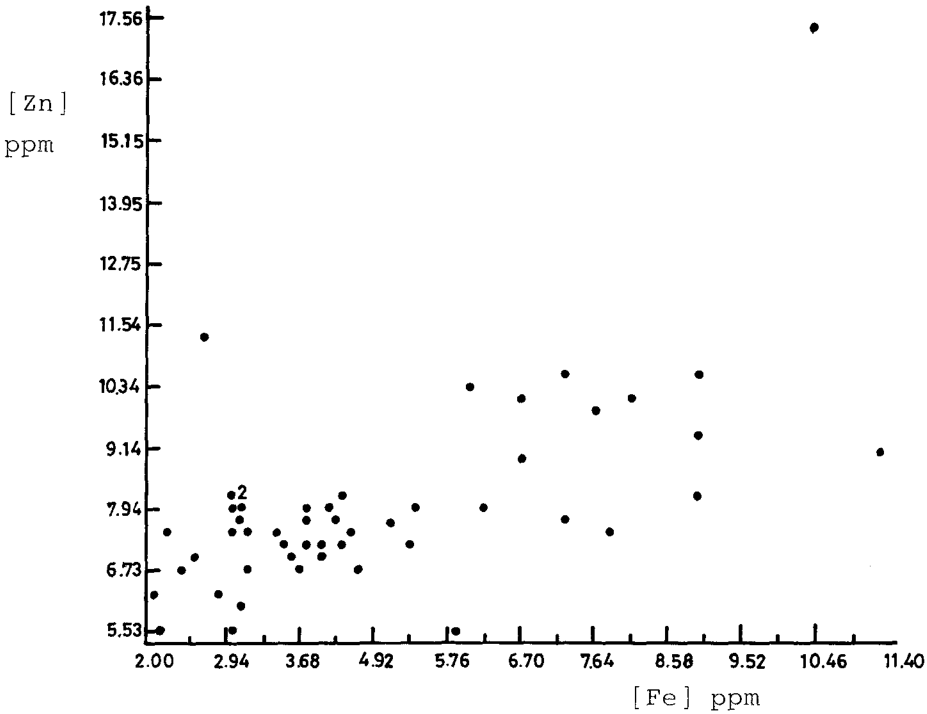

Figure 1. Computer plot of the data [Zn] *versus* [Fe]

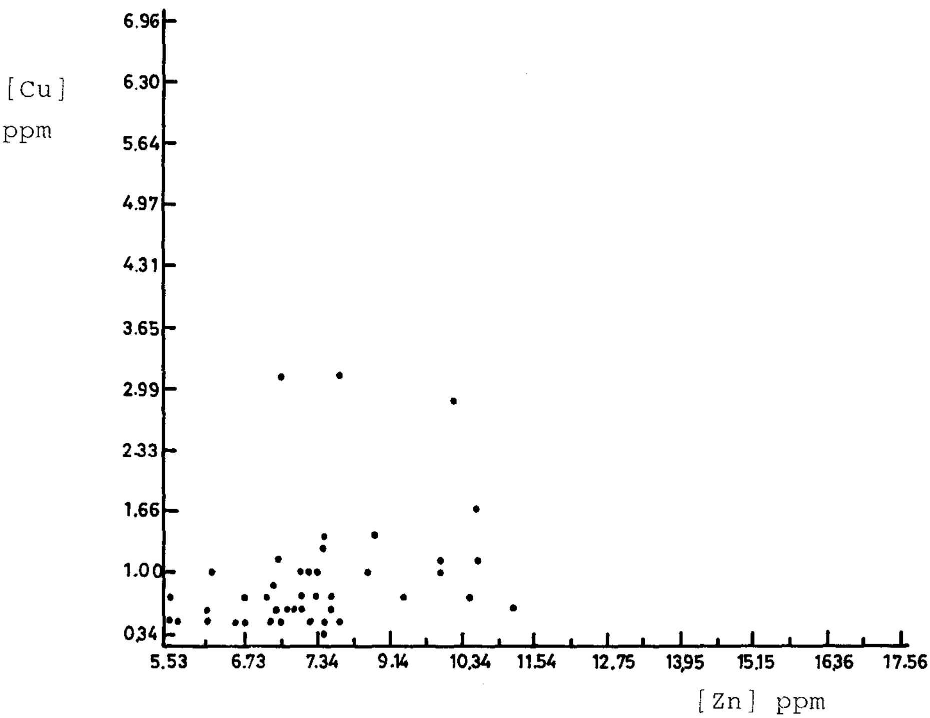

Figure 2. Computer plot of the data [Cu] *versus* [Zn]

Figures 1 and 2 show, as an example, the computer plots for the data in the systems [Zn] *vs* [Fe] and [Cu] *vs* [Zn], and Table 2 summarizes the results of the scattergrams of simple regression for between-metal correlations, whose significance values indicate the intimate relation of each other pair, even though correlation coefficients are not very high.

Table 2. Equations of the regression lines for the inter-metal correlations in tuna fish.

Equation*	Correlation	Significance
[Pb] = -1.057 + 1.855[Cu]	0.459	0.0007
[Fe] = -0.474 + 1.261[Cu]	0.585	0.0001
[Zn] = 5.490 + 2.525[Cu]	0.719	0.0000
[Zn] = 5.540 + 0.512[Fe]	0.628	0.0000

* Concentrations in ppm (wet basis)

Besides, in Table 2, one can see how the concentrations of iron, zinc and lead are related to that of copper, and zinc concentration to those of iron and copper. Based on these facts analysis of multiple regression was carried out in order to determine if the concentration of copper

Table 3. Results of the multiple regression analysis of the data

Variable	Multiple R	R^2	RSQ Change	Simple R	B	β
[Cu]						
versus [Fe]	0.05847	0.3419	0.3419	0.5847	0.0466	0.34367
versus [Pb]	0.6737	0.4538	0.1119	0.4587	0.4551	0.38698
versus [Zn]	0.7128	0.5081	0.0543	0.4598	0.0634	0.28196
				constant	-0.1155	
[Zn]						
versus [Fe]	0.7193	0.5174	0.5174	0.7193	0.9993	0.55076
versus [Cu]	0.8000	0.6310	0.1226	0.6275	0.3170	0.38863
				constant	-5.4880	

could be explained in terms of the concentrations of iron, lead and zinc, and that of zinc in terms of the concentration of copper and iron. Results are shown in Table 3, from which the following equations may be deduced

$$[Cu] = -0.1155 + 0.0466[Fe] + 0.4551[Pb] + 0.0634[Zn]$$

$$[Zn] = 5.4880 + 0.9993[Cu] + 0.3170[Fe]$$

However, further studies are clearly needed to explain these simple and multiple intermetallic correlations from metabollic as well as pollution standpoints.

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REFERENCES

Establier R (1970) Copper, iron, manganese and zinc levels in several organs of *Thunnus thynnus*. Inv Pesq 34:399-408

Evans WH, Read JL, Lucas MB (1978) Evaluation of a method for the determination of total Cd, Pb and Ni in foodstuffs using measurements by flame atomic-absorption spectrophotometry. Analyst 103:580-594

Mershina KM, Khalina NM, Krasnitskaya AI (1962) Trace elements in far-eastern fish, crustaceans and mollusks Mykroelementy v Vost Sibiri i na dal'n Vost, Inform Byul Koordinats Komis po Mikroelementam dlya Sibiri i Dal'n Vost (1):35-43; Chem Abstr (1963) 59:13270

Nie N, Hull CH, Jenkins JC, Steinbrenner K, Bent DH (1975) Statistical package for the social sciences. 2nd Ed. McGraw-Hill, New York

Uthe, JF, Bligh EG (1971) preliminary survey of heavy metal contamination in Canadian freshwater fish. J Fish Res Board Can 28:786-788

Vinogradov AP (1953) The elementary composition of Marine organisms. Sears Foundation for Marine Research, Yale University, Memoir II

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