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Distribution of Metals in Some Fishes from Santa Cruz de Tenerife, Canary Islands

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As a part of a monitoring program of the coastal ecosystem of the City of Santa Cruz de Tenerife (Díaz *et al.* 1990; 1992), the present study was conducted to determine the means and ranges of some important trace metals in fishes of economic importance in these islands. In addition, a study of the binary and multiple intermetallic relationship and between metal concentrations and fish size were undertaken to contribute to the knowledge of the behavior of these metals in the fishes studied.

MATERIALS AND METHODS

One-hundred-sixty-one fish from several species were collected during the years 1984-85 by fish-trap at three locations along the coast of Santa Cruz de Tenerife City. The sampling locations were chosen near city outfalls and the harbour, in order to evaluate these potential sources of contamination on our coastal waters (Díaz *et al.* 1992). Fork-length and weight were recorded and individuals immediately frozen to -20ºC in polyethylene bags until analyzed. After thawing, two replicate 8g samples of homogenized mid-dorsal muscle tissue were IR-dried and then ashed at 450±100ºC in an electric furnace, until white ash was obtained. Samples were then treated with 10mL hot diluted hydrochloric acid (5M), filtered and made up to 25mL with Milli-Q water in a measuring flask. Determinations of Pb, Cd, Fe, Ni, Cu and Zn were carried out by flame atomic-absorption spectrophotometry using deuterium arc background correction. Another two 3g replicate samples were mineralized with concentrated HNO_3/H_2SO_4 at 45ºC in closed vessels and mercury determined by the cold vapour technique. The material used in sample processing was cleaned with Acationox (2%), treated with HNO_3 (1M) for 4 hr, and repeatedly rinsed with distilled and Milli-Q

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Table 1. Mean±standard deviation of metal determination in NBS-SRM-1577a:1) our results of 10 replicate analysis, and 2) certified values.

	Cd	Pb	Fe	Cu	Zn	Hg	Ni
1)	0.134±0.004	0.44±0.16	198±10	155±6	120±2	<0.002	-
2)	0.135±0.015	0.44±0.06	198±20	158±7	123±8	0.004±0.002	-

water. All reagents were ultrapure quality. Table 1 shows the analytical accuracy and precision that were periodically checked by analyzing samples of NBS SRM-1577a bovine liver. Only the fish species with N>10 were included in statistical analysis, because N≤10 were not likely to be statistically representative. Simple and multiple correlation studies were carried out by applying the Statistical Package for the Social Sciences (Nie *et al.* 1975).

RESULTS AND DISCUSSION

The mean concentrations and ranges for Hg, Pb, Cd, Fe, Ni, Cu and Zn in the fish analyzed, as well as mean averages of fork-length are summarized in Table 2.

In general, the mean metal concentrations in fishes sampled in this study indicate that consumers are not faced with heavy metal contamination problems for the metals which the 1990 Spanish Food Directorate has set tolerance levels (Hg, Cd, Pb and Cu of 1, 1, 3 and 20 ppm). There is no indication of any health hazard in the individuals analyzed, with the exception of Pb in one individual each of *A. luridus, C. limbatus, P. acarne* and *S. cretensis,* which surpass the maximum concentration legislated.

Qualitatively it can be seen that the ranges for the metals determined were not uniform in these species, but among them the wide range of lead concentration in *P. acarne* seems exceptional due to the high lead value (9.99 ppm) in one individual; deleting this value provides results similar to those found for other species.

A comparison of metal levels for these species with those from other seas is only possible for some metals, especially Hg, but one must keep in mind that many bibliographical data are given for only one specimen or for a composite sample. However, it can be seen that our data for Hg, Fe, Cu and Zn for *P. acarne* are of the same order as values reported for specimens coming from the Aegean (Grimanis *et al.* 1980), Ligurian (Caviglia & Cugurra 1978) and Adriatic (Stegnar *et al.* 1978) seas. However, our data for Hg in *Litognatus mormirus, Sparus*

Table 2. Mean (X), standard deviation (SD), minimum (m), and maximum (M) of metal concentrations (ppm, wet weight) and fork-lengh (cm) in fish from Santa Cruz de Tenerife.

Species		L	Hg	Pb	Cd	Fe	Ni	Cu	Zn	N*
Abudefduf	X =	9.7	0.28	1.57	0.08	7.47	0.68	1.40	5.43	19
luridus	SD=	1.4	2.01	0.87	0.04	3.44	0.17	0.75	2.01	
	m =	6	0.09	0.71	0.04	3.87	0.47	0.44	2.59	
	M =	12	0.81	4.30	0.17	16	0.98	3.37	8.68	
Chromis		10.1	0.19	2.00	0.19	6.45	0.86	2.31	4.75	17
limbatus		1.5	0.23	1.20	0.08	2.75	0.18	1.38	2.04	
		8.8	0.06	0.95	0.12	2.10	0.63	0.75	1.78	
		12	1.02	4.67	0.35	12.4	1.10	6.60	10.0	
Monacanthus		13.1	0.25	1.07	0.06	11.9	0.72	1.23	5.86	11
hispidus		1.4	0.21	0.25	0.02	6.10	0.31	0.51	1.34	
		12	0.10	0.74	0.04	3.11	0.42	0.66	3.25	
		16	0.90	1.59	0.11	24.3	1.48	2.23	7.91	
Pagellus		15.9	0.28	1.81	0.12	7.76	0.72	1.5	5.10	16
acarne		4.4	0.13	2.23	0.05	3.76	0.32	0.9	2.17	
		8.6	0.13	0.60	0.06	3.30	0.27	0.5	3.08	
		22	0.55	9.99	0.26	19.7	1.31	3.6	10.9	
Pagellus		12.9	0.23	0.75	0.09	9.36	0.47	0.6	4.78	12
erythrinus		1.8	0.07	0.11	0.02	6.07	0.15	0.1	0.95	
		8.6	0.09	0.54	0.04	3.22	0.54	0.4	3.45	
		15	0.32	0.91	0.13	23.5	0.91	0.9	6.29	
Pseudocaranx		18.4	0.24	1.37	0.13	8.55	0.74	2.1	6.00	15
dentex		8.5	0.10	0.40	0.02	7.30	0.32	1.1	2.82	
		9.5	0.10	1.00	0.10	2.70	0.68	0.7	2.80	
		33	0.42	2.02	0.15	27.9	0.81	4.3	12.7	
Sarpa		13.7	0.22	0.92	0.07	6.54	0.70	1.2	6.17	13
salpa		1.3	0.18	0.46	0.02	2.15	0.17	0.8	1.35	
		11	0.18	0.41	0.04	3.44	0.28	0.6	2.94	
		15	0.22	0.64	0.09	6.34	0.72	0.9	5.29	
Sparisoma		11.8	0.23	1.43	0.77	9.41	0.71	1.6	5.26	17
cretensis		3.5	0.11	0.76	0.03	4.31	0.22	1.1	5.26	
		8	0.10	0.40	0.04	3.26	0.37	0.4	2.45	
		20	0.48	4.54	0.14	17.2	1.03	4.5	9.37	
Trachinotus		25.4	0.33	0.83	0.06	6.28	0.56	1.0	4.51	12
ovatus		7.4	0.21	0.43	0.02	1.97	0.08	0.2	1.31	
		16	0.09	0.51	0.03	3.92	0.40	0.6	3.18	
		35	0.73	1.70	0.08	9.71	0.66	1.5	7.40	

Table 3. Parameters of the logarithmic relationships between metal concentration and fork length (log [ppm] = a log L(cm) + b). a= slope; b= intercept; R^2= square of correlation coefficient (* $P<0.05$).

Species		Hg	Cd	Pb	Zn	Cu	Fe	Ni
Pagellus	a =	0.910	-0.767	-0.491	-0.676	-1.085	-0.045	-0.344
acarne	b =	-1.677	-0.067	0.712	-1.467	1.395	0.907	0.236
N=16	R^2=	0.409*	0.351*	0.058	0.329*	0.280*	0.001	0.027
Sarpa		-0.789	-0.432	0.599	-0.364	0.203	-1.374	0.487
salpa		0.138	-0.701	0.742	-1.193	-0.225	2.356	-0.717
N=13		0.013	0.029	0.035	0.026	0.001	0.218	0.043
Chromis		1.387	-1.631	0.288	0.346	1.188	-0.233	0.118
limbatus		-2.226	0.871	-0.034	0.292	1.498	1.008	0.196
N=17		0.101	0.440	0.007	0.012	0.086	0.005	0.004
Abudefduf		-0.757	-3.772	-1.200	-1.470	-2.081	-0.987	1.866
luridus		0.109	2.625	1.339	2.161	2.148	1.809	1.700
N=19		0.034	0.511*	0.170	0.366*	0.344*	0.119	0.507*
Sparisoma		0.773	-0.946	-0.989	-1.372	-0.563	0.929	0.298
cretensis		-1.449	-0.139	1.182	2.157	0.743	1.915	0.159
N=17		0.190	0.423	0.691*	0.904*	0.059	0.220	0.052
Pseudocaranx		0.732	0.031	-0.327	-0.805	-0.641	-0.548	-0.110
dentex		-1.549	-0.903	0.499	1.721	1.059	1.500	-0.002
N=15		0.529*	0.030	0.274	0.712*	0.291*	0.144	0.685
Thrachinotus		1.278	-0.276	0.874	-0.212	0.529	0.547	-0.059
ovatus		-2.477	-0.860	-1.335	0.930	-0.727	0.026	-0.180
N=12		0.352*	0.050	0.310	0.050	0.413*	0.247	0.011
Monacanthus		2.350	2.005	-0.404	-1.301	-0.403	-2.000	-0.485
hispidus		-3.304	-3.462	1.584	2.184	0.507	3.241	0.372
N=11		0.150	0.222	0.319	0.281	0.011	0.120	0.018
Pagellus		0.170	-0.861	-0.121	-0.421	-0.369	-2.608	-0.935
erythrinus		-0.847	-0.096	0.007	1.143	0.198	3.817	0.696
N=12		0.004	0.070	0.006	0.039	0.016	0.158	0.071

pagrus, *Sarpa salpa* and *Spondylosoma cantharus* were higher than values reported by Caviglia and Cugurra (1978) for specimens from the Ligurian Sea.

Statistical analysis of the data was undertaken to investigate the relations between heavy metal concentrations and fish size, with the purpose of ascertaining whether there might be correlations strong enough to establish fish size limits with safe heavy metal concentrations. Although not presented here, results of a comparison of simple correlations of heavy metal concentrations on length and on weight showed that there was little to choose between the two where both were significant. Therefore, length was chosen as the basic measure since it is less likely to be subject to major day-to-day fluctuations, as weight is highly influenced by feeding. Computation was carried out on both untransformed data and on logarithmic transformed variables. Only correlations using logarithmic transformed variables have been included in Table 3 since they were more significant than those when untransformed data were used. From this table, and in spite of the poor significance of most correlations, it can be seen that for most of the species studied Hg concentration increased with length (a positive). Correlation coefficients for *A. luridus* were negative for every metal, except for Ni, thus for this species heavy metal concentrations decreased as length increased. Correlation coefficients, except for Cd and Fe, were all positive in *C. limbatus*. For the other species, positive and negative correlation coefficients values were found although the latter predominate. It can be also seen in Table 3 that the positive correlation between a metal concentration in fish muscle and fork-length is not particular for Hg but it can be found for other metals, toxic or not, in several fish species, even though these positive correlations seem to be less frequent than negative correlations. In this sense Hg displayed the most peculiar behavior. Besides, the low slope values obtained in some species indicate that the fishes residing in this coastal ecosystem must be in an almost steady state with their aquatic environment with respect to some metals. This constancy of the concentration of a given metal in the muscle tissue of a fish suggests that the exchange rates of these metals are essentially constant, except for trace accumulation by new tissues. The significant decrease with fork-length of the concentration of other metals could be due to compositional changes in muscle, dilution by growth or a decrease of intake of the metal in the diet of the older fish.

Further statistical analysis was carried out to investigate whether a relation existed between metal concentrations to establish whether there were correlations significant enough within these species to show possible metabolic or pollution relations between these metals.

Table 4 summarizes the results of simple regression for the metal-to-metal correlations, whose R^2 values ($P<0.04$) indicate the relation of each pair in these species. Other correlations exist, showing lower correlation and

Table 4. Results of the logarithmic metal-to-metal regressions (log [Y, ppm] = a log [X, ppm] + b).

Species	Y-X	a	b	R^2	P
Pagellus acarne N=16	Zn-Fe	0.504	0.247	0.291	0.031
	Zn-Pb	0.312	0.635	0.290	0.031
	Zn-Cd	0.546	1.211	0.337	0.023
	Cu-Pb	0.600	0.034	0.355	0.015
	Cu-Ni	0.954	0.201	0.578	0.004
	Cu-Cd	0.947	1.016	0.336	0.024
Sarpa salpa N=13	Zn-Pb	-0.543	0.757	0.822	0.000
	Cd-Fe	-0.700	-1.776	0.485	0.025
	Pb-Ni	-1.129	-0.270	0.626	0.006
Chromis limbatus N=17	Zn-Fe	0.792	0.029	0.656	0.000
	Zn-Pb	0.638	0.504	0.496	0.005
	Pb-Fe	0.690	-0.290	0.450	0.009
	Cd-Fe	1.068	1.656	0.963	0.000
	Pb-Ni	1.499	0.409	0.588	0.016
Abudefduf luridus N=19	Hg-Pb	0.941	-0.764	0.450	0.003
	Hg-Ni	1.436	-0.363	0.338	0.037
	Zn-Fe	0.649	0.166	0.583	0.000
	Zn-Pb	0.471	0.635	0.318	0.018
	Cu-Ni	1.312	0.249	0.432	0.015
	Cu-Cd	0.593	0.714	0.359	0.030
	Ni-Cd	0.364	0.251	0.539	0.004
Sparisoma cretense N=17	Hg-Zn	-0.748	-0.165	0.365	0.017
	Zn-Pb	0.939	0.579	0.651	0.003
	Zn-Cd	0.681	1.470	0.658	0.008
	Pb-Fe	0.500	-0.343	0.587	0.006
	Cu-Ni	1.144	0.218	0.482	0.038
Pseudocaranx dentex N=15	Hg-Zn	-0.780	0.080	0.547	0.002
	Cu-Fe	0.548	-0.178	0.443	0.007
	Cu-Pb	1.184	0.279	0.637	0.032
	Cd-Fe	1.068	-1.656	0.963	0.000
Trachinotus ovatus N=12	Hg-Fe	1.600	-1847	0.631	0.004
	Hg-Pb	1.104	0.454	0.540	0.016
	Cu-Fe	0.609	-0.474	0.662	0.002
	Pb-Fe	1.096	-0.978	0.692	0.002
Pagellus erythrinus N=12	Zn-Fe	0.253	0.466	0.614	0.004
	Ni-Fe	0.437	-0.743	0.669	0.002
Monacanthus hispidus N=11	Hg-Fe	-0.667	-0.001	0.436	0.038
	Zn-Fe	0.342	0.398	0.642	0.003
	Cu-Ni	0.953	0.238	0.799	0.000
	Cu-Fe	-0.457	0.294	0.587	0.010

Table 5. Equations resulting from the multiple regression analysis of the data ([ppm]).

Equation	Multiple R
Pagellus acarne (N=16)	
log[Cu]= -0.172 + 0.765log[Ni] + 0.796log[Hg] + 0.544log[Pb] + 0.124log[Cd]	0.949
log[Zn]= 0.766 + 0.539log[Pb] + 0.349log[Fe] + 0.432log[Cd] - 0.137log[Cu]	0.853
log[Pb]= -0.373 + 0.304log[Cu] + 0.666log[Zn] + 0.079log[Ni]	0.842
log[Cd]= -1.266 + 0.252log[Cu] + 0.416log[Zn]	0.689
Sarpa salpa (N=13)	
log[Fe]= 1.617 + 0.667log[Cd] - 0.104log[Cu]	0.705
log[Cu]= 0.544 - 0.744log[Zn] + 0.249log[Ni]	0.458
Chromis limbatus (N=17)	
log[Fe]= -0.297 + 1.012log[Zn] - 0.364log[Cd] + 0.265log[Cu]	0.787
log[Pb]= -0.424 + 0.490log[Zn] + 0.278log[Fe] + 0.034log[Cd]	0.799
Sparisoma cretensis (N=17)	
log[Zn]= 1.332 + 0.648log[Pb] + 0.529log[Cd] + 0.113log[Fe]	0.975
log[Ni]= -0.237 + 0.446log[Pb] + 0.228log[Cu]	0.702
Pseudocaranx dentex (N=15)	
log[Fe]= 0.783 + 2.039log[Pb] - 0.343log[Cu]	0.698
log[Zn]= 0.248 - 0.631log[Hg] + 0.276log[Cu]	0.812
Trachinotus ovatus (N=12)	
log[Fe]= 0.885 + 0.294log[Pb] + 0.679log[Cu] + 0.126log[Hg]	0.963
Pagellus erythrinus (N=12)	
log[Zn]= 0.316 + 0.333log[Fe] - 0.182log[Ni]	0.963
Monacanthus hispidus (N=11)	
log[Ni]= 0.024 + 0.629log[Cu] - 0.229log[Fe] + 0.015log[Hg]	0.953
log[Zn]= 0.379 + 0.344log[Fe] + 0.171log[Pb]	0.822

significance values. Even though the same metal-to-metal correlation was not found in all the species studied, it can be seen that very often the concentrations of several metals were related to that of iron with positive correlation coefficients, which can be tentatively related to the presence of coloidal iron in this seawater (*Conde* and *García Montelongo*, personal communication). It has yet to be studied if the strong correlations shown by the pairs Cu-Cd, Hg-Cu, Cd-Zn and Hg-Cd could be explained in terms of the presence of metallothioneins in these fish species as suggested by others (Noël-Lambot et al. 1980; Overnell & Abdullah 1988). Table 4 shows that for some of these fish species two or more metal concentrations were related to a common metal concentration. Thus, analysis of multiple regression was carried out on data for *P. acarne, S. salpa, C. limbatus, S. cretensis, P. dentex, T. ovatus, M. hispidus* and *P. erythrinus* to determine if the concentration of the "common" metal could be explained in terms of the concentrations of the correlated metals. Results in Table 5 show the high multiple-R value by most of these multiple correlations. However, further studies are clearly needed to explain these simple and multiple inter-metallic correlations from metabolic and/or pollution standpoints.

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