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Heavy Metals in the Coastal Environment of Las Galletas, Tenerife, Canary Islands, Spain

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Urban and industrial activities in coastal areas introduce significant amounts of trace metals into the marine environment, causing permanent disturbances in coastal marine ecosystems, and leading to environmental and ecological degradation (Berrow, 1991). This ecological significance is due to their toxicity and cumulative behaviour which constitute a potential hazard for marine biota, and can generate risk when they enter the food chain. Thus monitoring systems are essential to study long-term pollution processes in coastal environments especially when they are affected by the impact of increasing tourist populations which disturb normal activities in the area. Few authors have studied metal concentrations in the sea near the Canary Islands. Thus, Chester & Stoner (1974), Gardiner (1975) and Boyle *et al.* (1982) performed several analyses during their cruises in 1973 and 1978, respectively, and Díaz *et al.* (1990) studied trace metal contents in the coastal waters of the city of Santa Cruz de Tenerife.

It is necessary to bear in mind that industrial development in these island is very scant, there being only a oil refinery (Tenerife), fuelled power stations in each island and transformation industries, but the number of visitors increases. The entire island of Tenerife with 677,845 inhabitants received as many as 4,641,804 tourists throughout 1999 (3,438,462 of whom were located in the southeast-southwest zone of Tenerife island to which this small environment belongs).

This mass tourism is mostly concentrated in resorts around the coast, attracted by the very uniform year-round weather, which led to the intensive and continuous development of coastal tourist resorts. The diversity of the habitats of these volcanic islands, which have only a small platform, with sandy, rocky and pebbly beaches, and cliffs, produces diverse edible marine fauna.

Fishing activities have been established around the islands and in the neighbouring Sahara Bank, influenced by the northeastern Africa upwelling. In recent years increased seafood farming activities have been established in some coastal areas. The concurrence of these conflicting activities prompts the establishment of pollution monitoring-research programmes.

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The main objectives of this work were to establish background levels for Mn, V, Cr, Ni, Co, Cu, Ag, Cd, and Pb in the seawater of a small coastal ecosystem in the south of Tenerife (Canary Islands, Spain), near a large tourist resort where the main economic activities are tourism and commercial and sport fishing, and to evaluate the impact, if any, of the tourist population on the marine ecosystem.

MATERIALS AND METHODS.

This study has been carried out in the coastal ecosystem of the village of Las Galletas located 80 km southwest of Santa Cruz de Tenerife. Noteworthy features include a fishing port with about 100 boats for both commercial and sport fishing, and an occasionally operational underwater sewage outfall, which discharges at about 200m from the shoreline at a depth of 15m.

Varian SpectrAA-10Plus atomic absorption spectrophotometer with flame atomizer and Varian SpectrAA-640Z atomic absorption spectrophotometer equipped with graphite furnace GTA 100 and Zeeman background correction were used to perform analysis. Niskin Hydrobios 1.5L plastic sampling bottles with a nylon rope were used for sampling, and polyethylene bottles were used to store samples.

One thousand ppm Panreac and Supelco certified stock solutions for the metals analysed. Ammonium pyrrolidine dithiocarbamate (APDC) (Aldrich) 1% and ammonium diethyl dithiocarbamate (DDC) (Aldrich) 1% aqueous solution purified by extraction with carbon tetrachloride (Merck). Ultra pure Milli-Q water and nitric acid (Merck, Suprapur) were used to prepare solutions and for sample dilutions. Acetic acid-ammonium acetate pH 5.0 buffer solution previously extracted with APDC-DDC/Cl_4C was used for pH adjustment. All laboratory ware and sampling equipment was thoroughly cleaned by extensive washing with 10% nitric acid solution.

110 samples of seawater (5L) were taken between 1992 and 1994 at five sampling stations at a depth of 1m. Samples were acidified in situ with nitric acid. Trace metals were extracted with APDC-DDC/Cl_4C solution at pH 5.0, and back extracted into 1 ml concentrated nitric acid. Extraction was repeated twice to ensure quantitative recoveries (Dannielson et al. 1978). The reference material (NOAA 1987, 1989, Wade et al. 1988) NBS SRM 1643b "Trace elements in water" to which sufficient sodium chloride (Merk Suprapur) was added to reach 35‰ salinity was used to validate the analytical methodology and was re-analysed each 20 samples (Table 1).

RESULTS AND DISCUSSION.

Average trace metal concentrations found in the five sampling stations are given in Table 2, together with their basic statistical parameters. Values found here for Pb, Cu, Fe and Ni are significantly lower compared to those given by Diaz *et. al* (1990) for the coast of Santa Cruz de Tenerife
city, more highly industrialized and populated. Nevertheless, Cd and Zn show

Table 1. Results of NIST 1643b analysis (ng.g^{-1}, Mean±SD).

	Mn	Ni	Cd	Cr	Cu
Certified	28±2	49±3	20±1	18.6±0.4	21.9±0.4
Mean Found	33.1±1.4	50.4±6.0	19.3±1.4	17.5±0.2	20.2±1.1
	Co	V	Pb	Ag	
Certified	26±1	45.2±0.4	23.7±0.7	Aprox. 9	
Mean Found	28.2±0.2	45.6±2.6	23.0±3.2	13.2±0.8	

similar values in both places.

Zn concentrations are similar to those found in other studies for both the ocean and coastal environments (Kokovides et al., 1992, McManus et al., 1996, Achterberg et al., 1996, Bruland et al., 1980, Moore et al., 1976, Dassenakis et al., 1996). Iron values are higher than those found for oceanic waters by Jong et al. (1998), McLeod et al.(1981), and Pai et al. (1990) but lower than values for other coastal environments (Kokovides et al., 1992, McLeod et al., 1981, Pohl et al. 1998, Dassenakis et al. 1996).

Several metals such as Cu, Pb and Ag present increased concentrations during the months immediately following holiday periods: August-September (summer), December-January (Christmas) and April-May (Easter), as shown in Fig. 1 for copper and lead concentrations, which can be related to increased tourism activities.

Variations in heavy metal concentrations have been statistically analysed with regard to sampling station, sampling date and season, and the analysis of variance shows statistically significant differences at the 95% confidence level for Cu, Zn, and Ni between station 1, the one closest to the port, and the other sampling stations. These differences can be related to the metallic objects used in fishing activities, such as galvanic protected metallic nets, nails and sacrificial anodes (Zn), and copper and nichrome (Cu, Ni) base alloys in fishing lines. No other significant differences were found for sampling date or season.

A study was first carried out on the binary metal-to-metal inter-relations for the overall data and several inter-metallic correlations were found with correlation coefficients (r) higher or near 0.4 and significance levels (p) lower than 0.0001 as shown in Table 3. The correlation between Ni and Cu concentrations can be explained in terms of their use in many marine metallic objects.

The correlation between Zn and Cd may be due to their chemical similitudes. Lead seems to be an impurity for Cu and Ni and the correlation between Mn and Cr may be due to the formation of colloids as chromium tends to adsorb on manganese colloid formed at seawater pH (8.2-8.3) (Turner et al. 1981).Correlations between Pb, Cu, Zn, Ni, Fe can be explained by their similar origin, which is either mineralogical or due to pollution. The silver and vanadium correlation could be explained by the formation of insoluble silver vanadate as shown by Turner et al. (1981), which can dissolve under treatment with the preserving agent (nitric acid, pH=2).

Table 2. Levels of heavy metals and basic statistical parameters (ng/L^{-1})

Overall	Ag	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn*
Av. (n = 110)	12.9	278	85.7	0.35	5.20	16.8	0.50	1.65	0.52	16.9
S. D.	9.5	460	422	0.30	6.76	46.2	0.38	2.66	0.52	36.8
Min.	0.3	12	2.4	0.09	1.56	0.6	0.12	0.23	0.03	0.6
Max.	45.6	2586	4359	2.37	57.0	481	2.48	19.3	2.45	261
Station 1										
AV. (n = 22)	11.7	148	45.2	0.39	3.70	13.1	0.49	2.30	0.48	5.5
S. D.	6.7	141	91.2	0.16	1.81	9.8	0.14	4.32	0.49	3.2
Min.	2.4	25	2.4	0.21	1.62	0.8	0.29	0.26	0.03	1.8
Max.	31.0	529	436	0.77	10.5	35.4	0.87	19.3	1.69	12.9
Station 2										
Av.	15.9	265	242	0.46	6.02	34.8	0.58	1.55	0.46	23.3
S. D.	10.1	365	925	0.56	6.74	101	0.57	1.89	0.47	36.0
Min.	1.2	24	4.6	0.15	1.56	3.5	0.22	0.27	0.08	0.9
Max.	36.0	1338	4359	2.37	26.3	481	2.48	8.08	2.32	132
Station 3										
Av. (n = 22)	13.0	248	66.4	0.29	7.02	14.1	0.41	1.45	0.38	20.2
S. D.	11.3	402	126	0.17	11.6	16.8	0.17	2.66	0.25	43.7
Min.	0.4	21	4.5	0.09	1.70	0.6	0.15	0.33	0.09	0.6
Max.	45.6	1952	484	0.86	57.0	72.7	0.94	13.1	1.12	196
Station 4										
Av. (n = 22)	13.5	421	34.2	0.29	4.97	10.7	0.51	1.41	0.67	21.5
S. D.	10.9	703	68.6	0.28	5.06	9.2	0.45	1.59	0.69	58.1
Min.	0.5	12	7.1	0.09	1.57	4.3	0.12	0.23	0.19	1.3
Max.	44.8	2586	314	1.38	21.9	44.9	2.27	6.74	2.26	261
Station 5										
Av. (n = 22)	10.4	315	21.2	0.28	3.56	9.9	0.43	1.47	0.55	14.4
S. D.	8.0	524	23.6	0.11	3.10	7.4	0.22	2.02	0.55	21.3
Min.	0.3	19	3.6	0.11	1.91	1.5	0.12	0.23	0.13	0.6
Max.	28.1	2385	113	0.56	16.8	37.0	0.91	8.86	2.45	90.2

*µg L^{-1}

As differences among the data set based solely on the visual examination of the variables did not unequivocally demonstrate if the samples were the same or different, because of the small differences between the respective values and the large number of samples and variables, in order to ascertain the possibility of identifying where the samples come from or the origin of their contamination, factor analysis and principal components were applied (Malinowski and Howery, 1980, Massart *et al.*, 1988), and the results support/validate those conclusions. Table 4 shows eigenvalues and cumulative variance for the system. As can be seen, the first four factors account for nearly 76% of the total system variance and simultaneously all of them appear with eigenvalues higher than 1, such that these four factors were extracted to reduce matrix dimensionality.

When a varimax rotation was applied to the data matrix, the eigenvector components in the rotated matrix (Table 4) show that Cr and Mn have strong loadings on the first

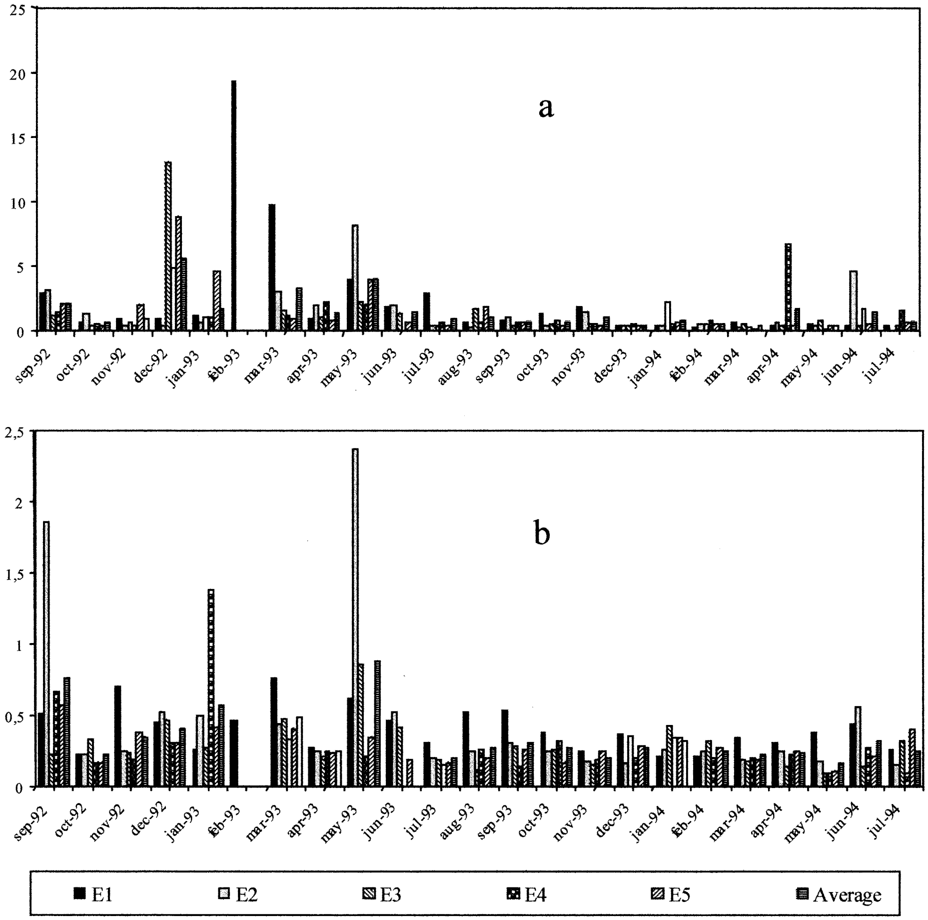

Figure 1. (a) Pb and (b) Cu concentrations (ng L^{-1}) by sampling month.

factor, vanadium and silver have strong loadings on factor 2, Zn and Cd have strong loadings on factor 3 while Pb has the higher factor loading on factor 4.

These results confirm those obtained in the correlation study and probably show a different source for lead than for the rest of the metals studied.

Therefore, in order to sort samples into groups of similar characteristics (sampling date, sampling station, season, ...) a "cluster analysis" was carried out, using the Euclidean similarity "distances" and the "nearest neighbour" strategy to group the objects (Willet, 1987), and including the continuous evaluation of the significance of the groups formed by calculating both the Mahalanobis distance between groups and the *F* statistic of the grouped samples. The use of different similarity measurements or clustering strategies (Massart and Kaufman 1983) leads to similar results. For the first trial the variables Mn, V, Cd and Pb, which show the higher/highest loadings on the four factors, were chosen. The corresponding dendrogram shows no clustering of samples. Besides the biplot in Fig. 2, which shows the simultaneous plot of the

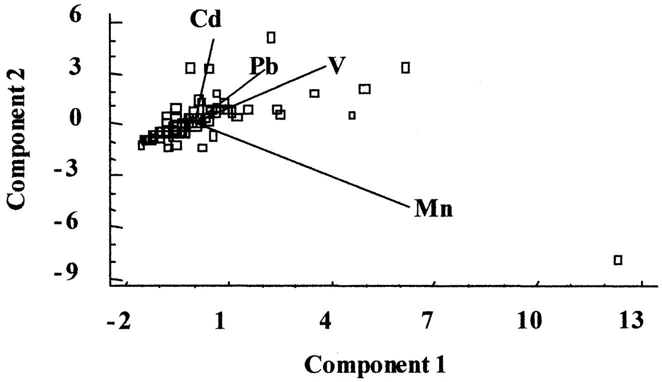

Figure 2. Biplot of eigenvectors and samples on the PC-1/PC2 plane.

Table 3. Direct, logarithmic and semilogaritmic correlations ($p<0.001$, $r \geq 0.4$)

Variables	R	p
[Ni] *vs* [Cu]	0.4821	0.0000
log[Cu] *vs* [Ni]	0.4983	0.0000
log[Ni] *vs* [Cu]	0.4911	0.0000
log[Ni] *vs* log[Cu]	0.5207	0.0000
log[Zn] *vs* [Ni]	0.4701	0.0000
log[Zn] *vs* log[Ni]	0.5220	0.0000
[Mn] *vs* [Cr]	0.4433	0.0000
log[Cr] *vs* [Mn]	0.4460	0.0000
log[Mn] *vs* log[Cr]	0.4463	0.0000
[Pb] *vs* [Cu]	0.4228	0.0000
log[Pb] *vs* [Cu]	0.4329	0.0000
log[Pb] *vs* log[Cu]	0.4061	0.0000
log[Pb] *vs* [Ni]	0.4185	0.0000
log[Ni] *vs* log[Fe]	0.4003	0.0000
log[Cd] *vs* [Zn]	0.3985	0.0001
log[Cd] *vs* log[Zn]	0.4411	0.0000
[V] *vs* [Ag]	0.3538	0.0007

selected variables (metals) and samples on the plane defined by PC-1 and PC-2, displays a high number of samples near the coordinate origin and the fact that sudden contamination events appear along the sampling time.

Even though Pb is well correlated to many other metals, factor analysis shows a different behavior pattern which can be explained by a different source for lead than for the remainder of the metals studied. Since no classification of samples by sampling date or season is observed one can conclude that the pollution in this coastal ecosystem is very uniform but sudden contamination events appear which cannot be

Table 4. Factor analysis and varimax rotated factor loadings matrix.

	Factor1	Factor2	Factor3	Factor 4
Eigenvalues	3.0042	1.8921	1.5071	1.1883
% Cumulative variance	30.04	48.96	64.03	75.91
Pb	0.0257	-0.1424	0.0340	**0.8999**
V	0.0663	**0.8647**	0.0004	0.0245
Cr	**0.9639**	-0.0584	-0.0163	-0.0823
Mn	**0.9730**	0.0065	0.0095	-0.0294
Fe	0.4769	0.4295	-0.0224	0.4445
Ni	0.6807	0.3898	0.0080	0.2851
Cu	-0.0128	0.3139	0.0919	0.6591
Ag	0.0360	**0.7741**	0.0638	0.0764
Zn	-0.0141	0.1436	**0.8993**	0.0322
Cd	0.0082	-0.0727	**0.9050**	0.0732

related to local pollution events or other local anthropogenic origins but rather to the influence of tourism-related activities.

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