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Hydrocarbon Contamination in the Canary Islands. II. Intertidal Limpet *Patella ulyssiponensis aspera*

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The Canary Islands are in an area of high tanker traffic, furthermore, the Canary Islands Stream and Trade Winds may carry over the pollution which originates far from the Island's coasts, De Armas et al. (1979) showed that more or less degraded oil slicks and tar balls in the sea near Canary Islands mostly belong to tank washings, ballast water and to accidental oil spills, and Conde et al. (1996) showed tar-balls and oil slicks in the beachs of this marine ecosystem can be associated to their original crudes. In recent years there has been a tendency towards a decrease in this kind of marine pollution probably due to the strengthening of international environmental protection laws as well as to the better design of pumping stations and tankers. The Last oil spills near the Canary Islands were on 19 December 1989 (Khark 5, about 220,000 t heavy Iranian crude) and 30-31 December 1989 (Aragon, 25,000 t Maya crude).

Marine organisms can be widely used as bioindicators and integrators of quality conditions in seawater ecosystems. In an aquatic organism, the bioaccumulation of lipophilic compounds such as n-alkanes, PAHs, PCBs,.. depends on their concentrations in ambient water and food (Granby and Spliid 1995; Kannan et al. 1995), on the mechanisms and kinetics that control their distribution between water and food, on the position of the organism in the food chain, on the metabolism, etc.

The objective of this paper, which is a part of a global monitoring project of the Canarian coastal ecosystem (Conde et al. 1996; Peña et al. 1996a,b,c), is to examine the content of n-alkanes and aromatics compounds (PAH and methyl-PAH) in the limpet *Patella ulyssiponensis aspera* (Mollusca: Gastropoda:Prosobranchia: Archaeogastropoda: Patellidae) readily found in this coast and appreciated as a food, and to provide baseline data for ongoing monitoring programmes.

MATERIALS AND METHOD

40 samples of *Patella ulyssiponensis aspera* were taken by hand along the shoreline

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at mid tide throught 1991-1993, at the three locations in the southeast coast of Tenerife (Fig. 1). Limpets were separated from theirs shells and wrapped in aluminium foil and stored, not longer than one month, at -20°C until analyzed. Analysis was carried out as stated elsewere (Peña et al. 1996a,b), on a composite sample for each sampling date and station, prepared from 10-15 specimens, which were freeze-dried and weighted (5-10g). Quality Control was carried out using CRM-1974 “Organics in mussel tissue”.

RESULTS AND DISCUSSION

Mean concentration as well as standard deviation for n-alkanes and aromatic compounds in *Patella ulyssiponensis* are summarized in Tables 2 and 4. The chromatograms of the n-alkane and PAH fractions (Fig. 2) from three sampling stations were characterized by the presence of the well known Unresolved Complex Mixture (UCM) along with peaks corresponding to acyclic isoprenoid hydrocarbons (pristane, phytane), and homologous series of methyl-substituted and parental PAH, which are recognized as indicators of petrogenic inputs (Pendoley, 1992)

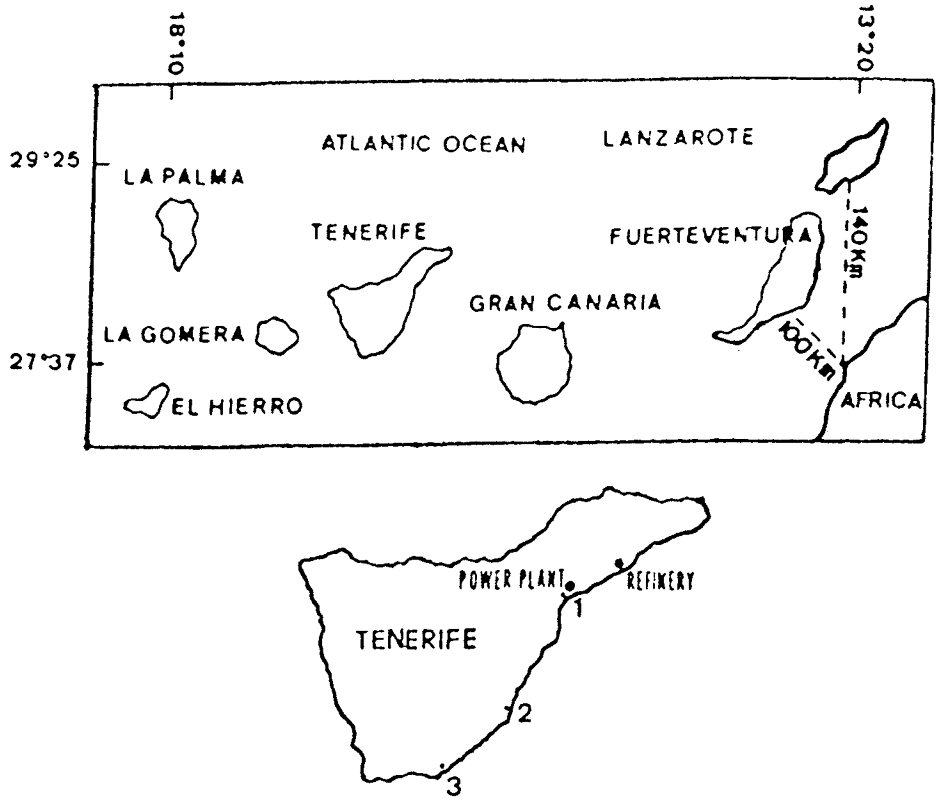

Figure 1. Map of sampling stations in the southeastern coast of Tenerife

The chromatogram of the saturate alkane fractions displayed an unusual bimodal distribution centered on n-C_{15}-nC_{20} and n-C_{21}-nC_{30}. Bimodal n-alkane distribution have also been reported in sediments (Noor et al. 1987) and fish (Al-Saad 1990) who proposed combined terrestrial plant wax and petroleum sources. Long chain components (> C_{24}) are known to be important constituents of terrestrial higher plants, and are very resistant to degradation (Najdek 1993). Occurrence of bimodal n-alkane peak distribution has been also reported in oyster (Pereira *et al* 1992), but for limpets could not be found in the available literature.

Table 1. Mean concentration (ng/g, dry weigth) and standard deviation for n-alkanes in *Patella ulyssiponensis* from the three sampling stations.

Variable	Las Caletillas		El Porís		El Médano	
	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
C_{11}	501.5	1,401	1,305	2,274	1,469	4,441
C_{12}	1,092	1,964	4,451	8,166	7,262	18,803
C_{13}	6,780	20,293	30,155	60,174	684.5	2,253
C_{14}	6,919	20,698	11,719	23,438	53.37	125,4
C_{15}	2,646	5,545	8,761	17,994	902.4	2,030
C_{16}	3,699	11,575	27,06	54,11	1,941	7,938
C_{17}	9,421	24,646	1,319	1,321	755.0	1,427
C_{18}	1,688	4,531	1,384	1,984	101.0	413.1
C_{19}	753.2	2,283	1,176	2,322	76.41	185.1
C_{20}	299.5	849.2	535.8	126.1	534.4	1,686
C_{21}	126.7	178.2	984.5	93.17	53.68	194.0
C_{22}	35.7	55.88	2,012	239.6	171.8	515.3
C_{23}	81.63	80.56	2,429	5,096	86.46	114.3
C_{24}	79.51	113.0	4,063	6,567	281.4	537.3
C_{25}	203.4	167.7	2,351	3,151	155.7	252.4
C_{26}	98.55	131.7	740.0	1,094	250.0	356.7
C_{27}	302.0	325.3	2,941	6,338	185.4	274.4
C_{28}	189.1	217.9	63.62	43,95	150.0	171.1
C_{29}	265.9	247.6	132.4	54,60	207.7	228.2
C_{30}	216.6	216.3	119.8	90,73	120.1	153.0
ΣAliph	45,560	110,355	64,198	108,853	14,082	32,856
ΣOdd	17,142	51,063	44,465	35,320	4,378	7,023
ΣEven	11,578	36,652	19,304	135,534	9,170	25,519

The individual concentrations of the n-alkanes with n<20 are dominated by n-C_{15} and

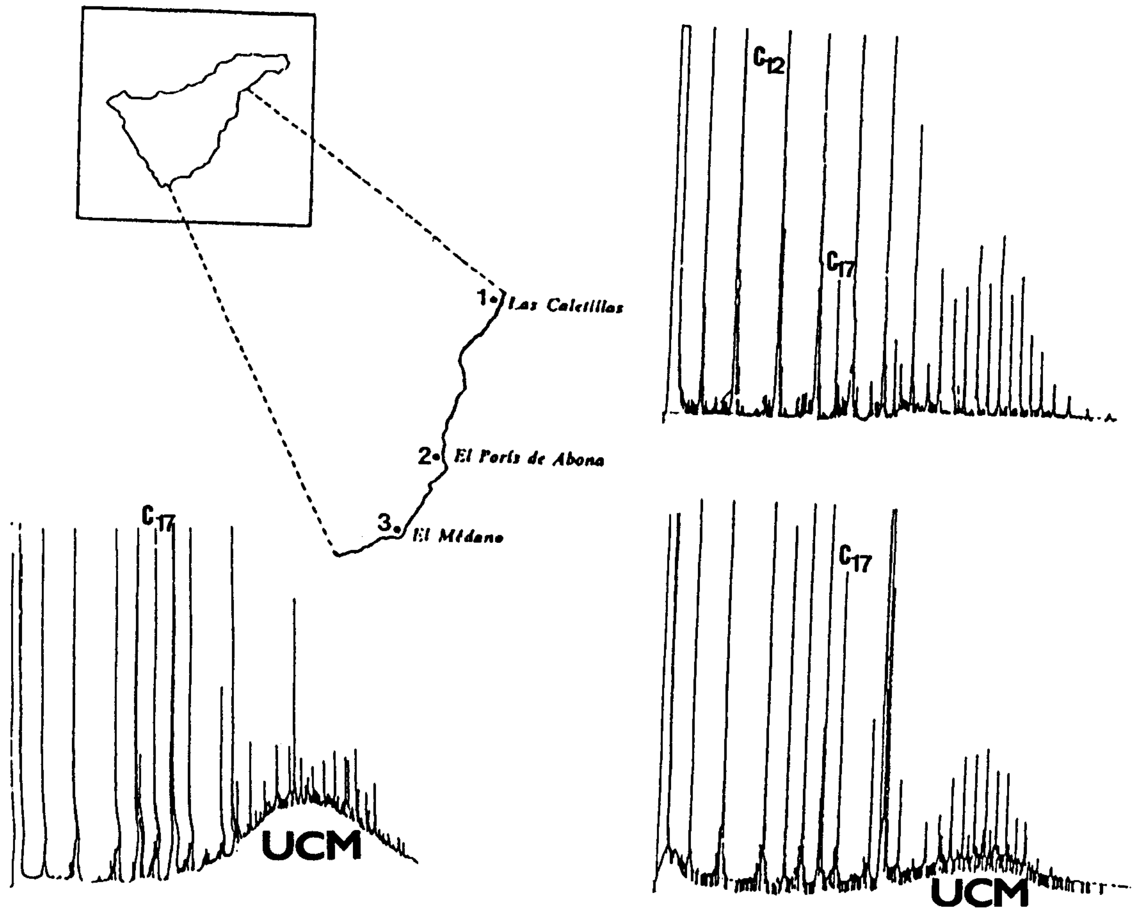

Figure 2. Typical chromatograms of the n-alkane fraction of contaminated samples

n-C_{17}, ocassionaly by n-C_{12} and n-C_{14}, which suggests a greater tendency for the accumulation of these odd hydrocarbons, Table 1, However, as odd carbon chain alkanes can be bio-synthesized in the marine environment, fluctuations in this source of input to the limpets or their own biosynthesis of such compounds can influence their concentration (Farrington and Meyers 1975).

The geochemical parameters Carbon Preference Index (CPI) and Pr/Ph were examined (Table 2). The pristane-to-phytane ratio has been proposed as a measure of the redox potential of sediments (Didyk 1978) as well as a way to identify oil-slicks and tar balls (Glover and Bullin 1989). Phytane is present in crude oils and is not found in most biota that have not been exposed to petroleum hydrocarbons. Pr/Ph ratios range from nd-1.4 in Las Caletillas, nd-20.6 in El Médano, and could not be evaluated in El Porís. The higher mean values for Pr/Ph observed in *P. ulyssiponensis* in Las Caletillas and El Médano stations may suggests that the phytyl side chain of chlorophyl probably is not degraded in the digestive system of this limpet (Peña 1996b).

Nevertheless, the Carbon Preference Index (CPI = ΣC-odd/ΣC-even) is more relevant in this sense (Table 3). CPI values are higher than one at the three sampling stations. Furthermore, CPI_{11-20} remains more or less constant near 5.5 at Las Caletillas and El Porís stations while is higher in El Médano, 12.46. The temporal variation of CPI_{21-30} is lesser than $CPI_{11-20,}$ which remains near 1.44-2. Taking into account the geographical situations of the sampling sites one can think of Las Caletillas and El Porís beaches as having an almost constant petrogenic pollution level and El Médano showing sporadic petrogenic inputs during the sampling period.

Table 2: Geochemical indices in *Patella ulyssiponensis*

Index	Las Caletillas		El Porís		El Médano	
	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
CPI	3.90	2.77	2.67	1.80	4.36	5.33
CPI_{11-20}	5.45	5.07	5.63	7.78	12.5	16.0
CPI_{21-30}	2.43	2.10	2.10	2.22	1.44	1.52
Pr/Ph	0.46	0.81	-	-	2.7	7.24

Not all the individual PAHs were detected in every analysed sample only naphtalene is present in all samples. ΣPAH (total sum of polycyclic aromatic hydrocarbons) is less than Σm-PAH (total sum of alkyl polycyclic aromatic hydrocarbons). El Médano beach presents thelesser mean value for Σm-PAH, 108.2ng/g, than samples from the other two stations which show close mean values, Las Caletillas 219.0ng/g, El Porís 213.0ng/g.

As one can see *Patella ulyssiponensis aspera* preferentially incorporates aliphatic compounds as compared to aromatic compounds in their tissues, this trend is no shared by other limpet, *Nacella concinna*, which incorporates mainly aromatic compounds (Kenicutt et al. 1992).

Table 3. Mean concentration (ng/g, dry weight) and standard deviation for aromatic compounds in *Patella ulyssiponensis* from the three sampling stations.

Variable	Las Caletillas		El Porís		El Médano	
	$\bar{x}$	S.D.	$\bar{x}$	S.D.	$\bar{x}$	S.D.
Naphtalene	67.84	149.2	659.2	538.5	238.8	362.7
Acenaphtilene	17.86	40.75	1.267	1.720	1.320	4.073
Acenaphthene	n.d.	-	2.820	6.900	703.6	3.083
Fluorene	n.d.	-	7.310	17.90	32.25	80.92
Phenanthrene	n.d.	-	n.d.	-	6.357	21.06
Anthracene	n.d.	-	60.50	66.62	26.15	82.03
Benzo[e]acephenanthrilene	0.762	2.140	59.12	144.8	2.914	13.97
Fluoranthene	0.888	3.205	3.156	7.732	1.826	6.298
Pyrene	4.255	11.10	7.214	17.67	239.1	745.7
Benzo[a]anthracene	n.d.	-	14.60	35.75	10.94	47.28
Chrysene	156.5	564.3	11.61	28.43	599.7	1,955
Benzo[b]fluoranthene	10.10	34.37	247.0	605.0	84.36	138.7
Benzo[a]pyrene	11.06	29.29	9.573	23.45	1.614	5.139
Benzo[e]pyrene	18.37	41.92	17.55	43.0	0.713	3.120
Perylene	949.7	3.181	235.5	577.0	11.10	45.05
Dibenzo[a,c]anthracene	1.632	5.878	31.52	77.22	8.750	28.33
Dibenzo[a,h]anthracene	227.4	617.0	n.d.	-	23.37	76.73
2-Methylnaphthalene	30.94	58.50	n.d.	-	0.713	3.190
1-Methylnaphthalene	89.46	178.2	n.d.	-	11.10	45.05
2,7-Dimethylnaphthalene	8.624	18.93	178.5	266.4	8.750	28.34
1,4-Dimethylnaphthalene	6.885	21.77	n.d	-	n.d.	-
1,2-Dimethylnaphthalene	n.d	-	n.d.	-	0.533	2.445
1.8-Dimethylnaphthalene	5.945	13.48	n.d.	-	5.783	25.86
1-Methylphenanthrene	46.17	129.6	21.10	25.62	13.94	40.44
2-Methylanthracene	43.74	126.8	-	n.d.	3.170	11.21
1-Methylantracene	20.48	33.42	12.81	12.61	34.0	102.4
3,6-Dimethylphenanthrene	22.47	37.04	44.86	74.81	34.10	75.20
9,10-Dimethylanthracene	218.7	420.9	24.11	31.86	70.0	146.1
ΣPAH	3.100	7.510	2.563	2.660	7.735	14.40
Σm-PAH.	219.0	421.0	213.0	238.0	108.2	172.3

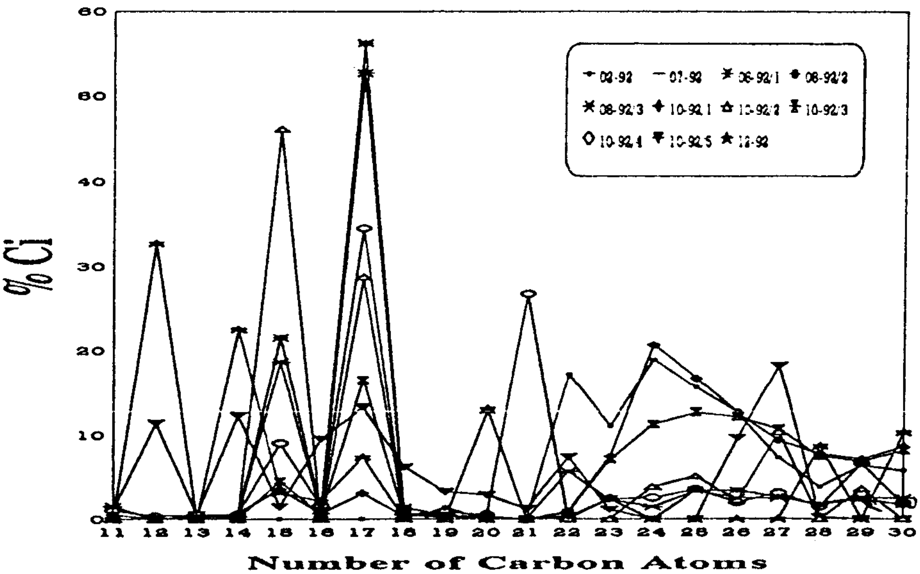

Figure 3. Variation of the relative percentaje of n-C_i hydrocarbons along the sampling period in El Médano station. Legend for dates in box.

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