

# Higher plant *n*-alkane average chain length as an indicator of petrogenic hydrocarbon contamination in marine sediments

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## Abstract

The *n*-alkane average chain length (ACL) is the weight-averaged number of carbon atoms of the higher plant C<sub>25</sub>–C<sub>33</sub> *n*-alkanes. The abundance of individual *n*-alkanes from higher plant sources generally increases with increasing carbon number in coastal marine sediments around Taiwan, but this trend is reversed for petrogenic hydrocarbons. The ACL would potentially be lowered if petrogenic hydrocarbons were added to sediments containing biogenic hydrocarbons alone. To test this idea, a marine environment off southwestern Taiwan known to contain both biogenic and petrogenic hydrocarbons and two nearby rivers were selected for investigating possible difference in ACL values between their sediments. The average CPI of C<sub>25</sub>–C<sub>33</sub> *n*-alkanes was 4.08±2.04 (range 1.90–8.96, *n*=15) for the river sediments and 1.70±0.16 (range 1.43–1.97, *n*=15) for the marine sediments. The ACL of C<sub>25</sub>–C<sub>33</sub> *n*-alkanes for river sediments ranged from 29.2 to 30.5 (average 29.9±0.4), and for marine sediments from 28.4 to 29.3 (average 28.9±0.3). The ACL difference between marine and river sediments was significant (Student's *t* test at 99% confidence) although it appeared small. It is suggested that the ACL can be an additional indicator for detection of petrogenic hydrocarbons in coastal marine sediments.

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## 1. Introduction

In the coastal marine environment, hydrocarbons are generally dominated by inputs from terrigenous sources. For instance, the *n*-alkane distribution exhibits high odd-to-even predominance of long-chain (C<sub>25</sub>–C<sub>35</sub>) *n*-alkanes, which characterizes hydrocarbons from vascular land plants versus those in petroleum and bacteria (Gearing et al., 1976; Farrington, 1980; Cranwell, 1982). One common parameter derived from this predominance

is the carbon preference index (CPI). The CPI is an indication of *n*-alkane source. Hydrocarbons composed of a mixture of compounds originating from land plant material show a predominance of odd-numbered carbon chains with CPI ~ 5–10 (Rieley et al., 1991; Hedges and Prahl, 1993), whereas petrogenic inputs have a CPI approximating 1.0 (Farrington and Tripp, 1977; Eganhouse and Kaplan, 1982; Nishimura and Baker, 1986; Saliot et al., 1988; Pendoley, 1992). CPI values close to one also are thought to indicate greater input from marine microorganisms and/or recycled organic matter (Kennicutt et al., 1987). In organic geochemistry, CPI is used to indicate the degree of diagenesis of straight-chain geolipids, and is

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a numerical representation of how much of the original biological chain length specificity is preserved in geological lipids (Meyers and Ishiwatari, 1995).

Another parameter is the higher plant *n*-alkane average chain length (ACL), which describes the average number of carbon atoms per molecule based on the abundance of the odd-carbon-numbered higher plant *n*-alkanes (Poynter and Eglinton, 1990). Vegetation types are the main influence on chain length of terrigenous leaf lipids. Leaf

lipids derived from grasslands may on average have longer chain lengths than do leaf lipids from plants in forests (Cranwell, 1973). It has been suggested that plants produce longer-chain compounds in warmer climates (Poynter et al., 1989). Simoneit et al. (1991) have analyzed continental aerosols from China and reported that higher molecular weight *n*-alkanes ( $C_{31}$ ) of the aerosols predominate in the warmer climate of southern China. Distributional variations in plant biomarker homologs

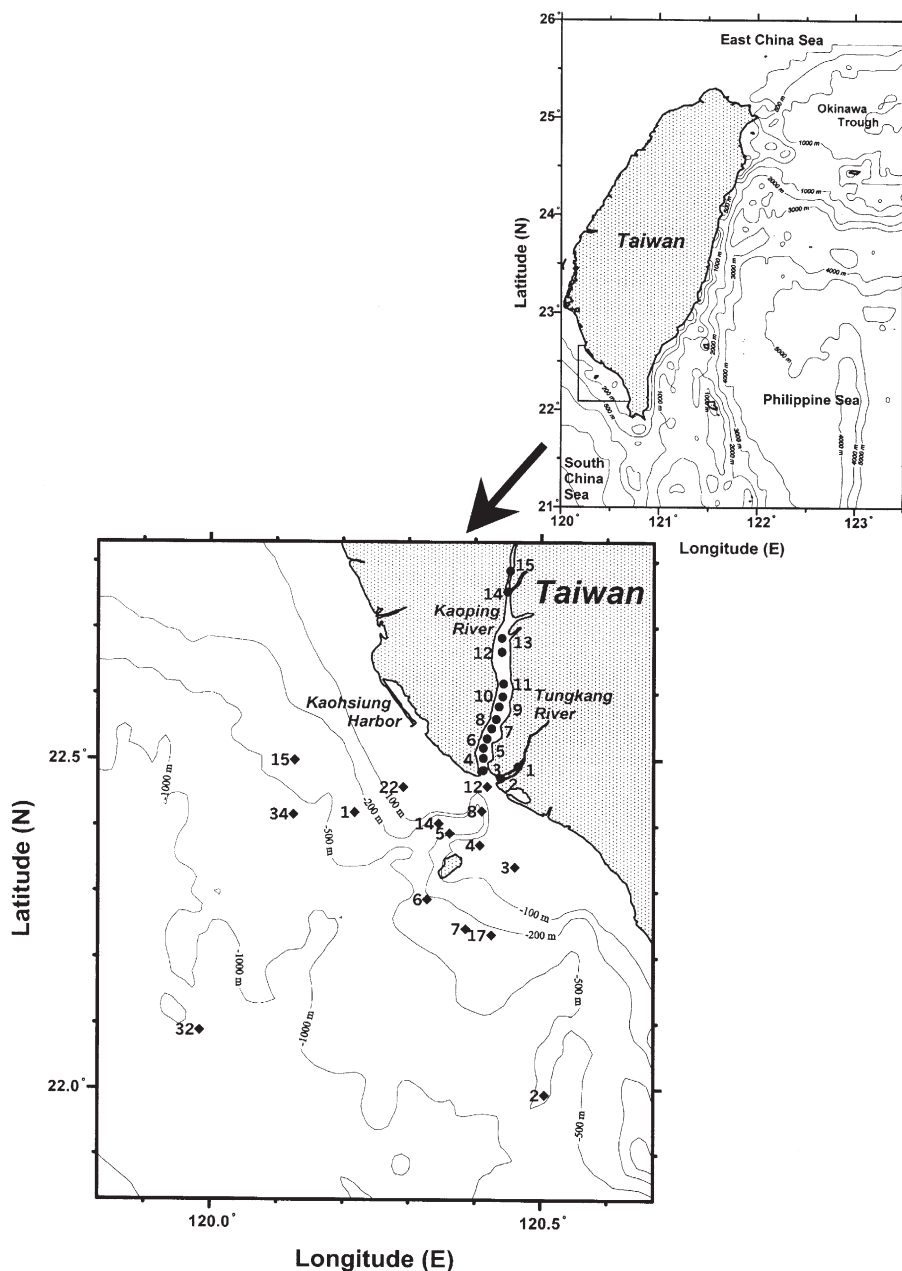


Fig. 1. Sampling locations off southwestern Taiwan and the nearby rivers. Filled diamonds, marine sediments; filled circles, river sediments.

also record differences between “arid” and “humid” vegetation sources. For instance, atmospheric dust samples collected in transects along the west African coast reveal changes in the chain length distributions of *n*-alkanes responding to aridity in the source regions (Huang et al., 2000; Schefuss et al., 2003). ACLs for alkanes in Oregon conifers decrease with increasing distance away from the Coastal Range, which suggests an adaptation by conifers to humid climate conditions (Oros et al., 1999). It has been found that the modal carbon number of a higher plant *n*-alkane distribution is broadly related to latitude (Poynter et al., 1989; Poynter and Eglinton, 1990), with higher modal carbon numbers occurring at lower latitudes. Further, the distribution of ACL has been linked to the geographical distribution of fluvial and eolian inputs and source regions (Poynter and Eglinton, 1990). In other words, for coastal marine sediments, ACL in a given area can be considered a constant if all these factors are the same.

Often times, a common source of hydrocarbons introduced to coastal marine environments is petrogenic hydrocarbons through human activities like tanker operations and accidents, coastal refineries, among others. The abundance of the *n*-alkanes from terrigenous sources reflected in coastal marine sediments around Taiwan is generally  $C_{25} < C_{27} < C_{29} < C_{31}$  (Jeng et al., 2003); on the other hand, for petrogenic hydrocarbons the trend is reversed. The ACL could be lowered if there is an addition of petrogenic hydrocarbons to sediments containing biogenic hydrocarbons alone. To date, no study of using ACL along this line has been conducted. In this study, we explored the possibility of applying ACL in this aspect. In order to test this idea, a two river-marine system of Taiwan was chosen for this study. The Kaoping River has a high annual sediment discharge of 35.6 MT (Water Resources Bureau, 1998) to the sea off the southwestern Taiwan coast, contributing predominantly terrigenous lipids to the marine sediments. Furthermore, the marine environment off southwestern Taiwan is subjected to repeated oil spills due to heavy tanker traffic and operations, other ship traffic, and industrial activities (Jeng, 1986; Jeng et al., 1997), a hot spot being at Kaohsiung Harbor (Jeng and Han, 1994).

## 2. Experimental

In the present study, to obtain samples containing both biogenic and petrogenic hydrocarbons, fifteen samples were taken from the vicinity of a major river mouth off the southwestern Taiwan coast (Fig. 1). Marine sediment samples were collected using a box corer on board R/V *Ocean Researcher I* on Dec. 10–11, 1992. The top 3–

4 cm of sediment was stored in stainless steel boxes (pre-cleaned with solvent) and kept frozen ( $-20\text{ }^{\circ}\text{C}$ ) until analyzed. Fifteen river sediment samples were collected from the Kaoping and Tungkang Rivers using a dredge (for covering a wider area of sediment) because the braided Kaoping River has many bars, forming semi-isolated areas. Samples were taken near the middle of the main channel on 1–2 December 2004. Most samples were collected on a motorboat (care was taken not to contaminate the samples); however, the northernmost 3 stations were sampled on temporary bridges or by wading in water. The river sediments were kept in an ice chest at the dry ice temperature and brought to the lab. In the lab, sediment samples were thawed and freeze-dried.

Following the addition of an internal standard ( $n\text{-C}_{24}\text{D}_{50}$ ), the dried sediment was extracted with a mixture of dichloromethane and methanol (1:1, v/v) for 24 h in a Soxhlet apparatus. The lipid extract was then saponified by reflux for 3 h with 0.5 N KOH solution in methanol. The non-saponifiable lipids were isolated by hexane extraction four times and concentrated by solvent evaporation under a  $\text{N}_2$  gas stream. The aliphatic hydrocarbon fraction was isolated from the neutral lipids by silica gel (deactivated with 5%  $\text{H}_2\text{O}$ ) column chromatography.

For GC analysis, an HP 5890A gas chromatograph equipped with a split/splitless injector and a flame ionization detector (FID) was used. An SGE (Australia) OCI-5 cool on-column injector was also fitted in the gas chromatograph for quantitation. Separation of aliphatic hydrocarbons was achieved by an SPB-1 capillary column ( $30\text{ m} \times 0.25\text{ mm i.d.}$ ). Oven temperature programming was  $45\text{--}90\text{ }^{\circ}\text{C}$  at  $15\text{ }^{\circ}\text{C min}^{-1}$  and  $90\text{--}270\text{ }^{\circ}\text{C}$  at  $3\text{ }^{\circ}\text{C min}^{-1}$  for analyzing aliphatic hydrocarbons. Identification was made with co-injection of authentic standards and GC-MS. Based on replicate analyses, the analytical precision of lipid abundances was calculated to be 2–8%. The gas chromatography-mass spectrometry (GC-MS) analyses were performed with an HP 6890 GC (HP-1MS crosslinked methyl siloxane column,  $30\text{ m} \times 0.25\text{ mm i.d.}$ ) interfaced directly to an HP 5973 quadrupole mass selective detector (electron ionization, electron energy 70 eV, scanned from 50 to 550 Da).

## 3. Results and discussion

Representative GC traces for marine and river sediments are shown in Fig. 2. In river sediments, higher molecular weight (HMW,  $>C_{23}$ ) *n*-alkanes strongly outweighed lower molecular weight (LMW,  $<C_{23}$ ) ones with strong odd-to-even preference in the HMW range,

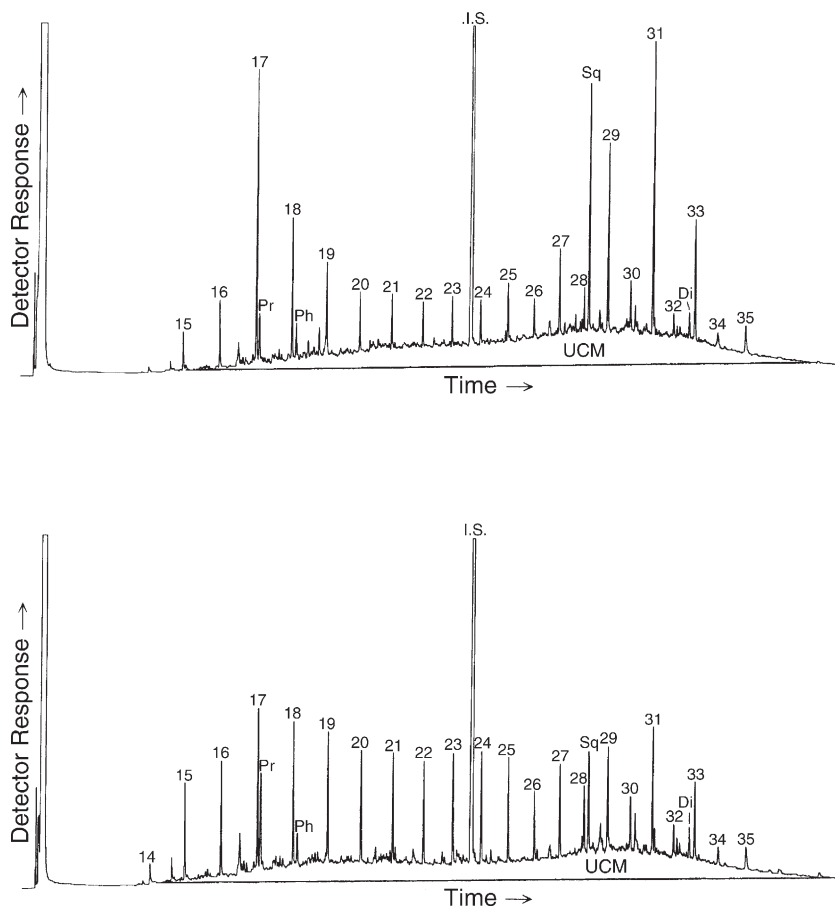


Fig. 2. GC traces of aliphatic hydrocarbons from station R6 (upper) and station M5 (lower). Numbers above peaks indicate carbon chain lengths. Pr = pristane, Ph = phytane, Sq = Squalene, Di = diploptene, UCM = unresolved complex mixtures.

suggesting a predominant contribution from higher plant sources (Rieley et al., 1991). In addition, all samples showed a baseline elevation, the so-called “unresolved complex mixture” (UCM). For marine sediments, HMW and LMW *n*-alkanes accounted for approximately similar proportions. Moderate odd-carbon predominance in the C<sub>25</sub>–C<sub>33</sub> range was noted, but was not as strong as those of river samples. This suggests at least two hydrocarbon sources contributing to the marine sediments—biogenic and petrogenic. In addition, *n*-alkanes were prominent, indicating little weathering.

Due to the CPIs of terrestrial higher plant waxes yielding high values, usually ~5–10, higher CPI values found in sediment or soil show greater contribution from vascular plants (Rieley et al., 1991; Hedges and Prahl, 1993); CPI values close to unity are thought to indicate greater input from microorganisms, recycled organic matter, and/or petroleum (Bray and Evans, 1961; Farrington and Tripp, 1977; Kennicutt et al., 1987). In the present study, the average CPI was  $4.08 \pm 2.04$  (range 1.90–8.96)

for river sediments and  $1.70 \pm 0.16$  (range 1.43–1.97) for marine sediments (Table 1). This reflects that all marine sediments and some river sediments (R3, R10–15) are probably contaminated with petrogenic hydrocarbons based on CPI values <3 indicating oiled sediments (Farrington and Tripp, 1977).

UCM, consisting of cyclic and branched alkanes, is known to resist microbial degradation more effectively than *n*-alkanes and thus has a greater tendency to remain in the environment after *n*-alkanes have degraded (Gough and Rowland, 1990; Bouloubassi and Saliot, 1993). All river and marine sediments analyzed generally contained a medium UCM (Fig. 2, Table 1) with the exception of R2 ( $1300 \mu\text{g g}^{-1}$ ). This does not necessarily reflect the content of degraded petroleum in the sediments since in some cases concentrations of  $\text{UCM} < 10 \mu\text{g g}^{-1}$  are common in coastal marine environments far from petrogenic hydrocarbon sources (Matsumoto, 1983; Tolosa et al., 1996). UCM has a linkage to degraded or weathered petroleum residues (Venkatesan et al., 1980; Readman et al.,

Table 1

Hydrocarbon data for river (R) sediments of southwestern Taiwan and marine (M) sediments off southwestern Taiwan

	River samples														
	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15
C <sub>15</sub>	5.03	3330	164	103	–	94.0	–	176	49.3	–	23.5	–	–	90.4	25.7
C <sub>16</sub>	52.5	3980	249	161	93.8	135	110	287	169	26.1	69.2	34.7	50.7	134	118
C <sub>17</sub>	252	8600	1080	501	1110	571	3810	1460	552	148	435	288	411	316	434
Pr	50.1	7320	491	153	207	128	305	294	155	44.0	92.5	92.5	184	115	161
C <sub>18</sub>	189	4050	430	294	737	279	1580	725	417	85.8	206	195	301	179	235
Ph	77.5	8930	221	122	249	81.9	385	249	199	18.5	54.6	66.5	104	49.3	61.2
C <sub>19</sub>	148	4670	435	373	590	266	1440	442	341	80.6	167	189	307	157	254
C <sub>20</sub>	57.8	3430	304	211	279	136	372	257	191	60.8	114	131	217	118	180
C <sub>21</sub>	57.6	2900	321	168	293	132	384	279	246	61.8	95.1	131	246	110	169
C <sub>22</sub>	40.5	1840	295	116	212	103	241	214	142	52.2	77.1	111	134	93.2	149
C <sub>23</sub>	68.9	1590	333	136	236	115	321	277	205	57.5	90.4	125	189	96.7	156
C <sub>24</sub>	85.3	1120	286	129	218	96.1	286	257	140	51.5	79.3	96.5	155	78.8	130
C <sub>25</sub>	90.5	1030	350	236	365	123	554	509	335	60.3	119	121	306	99.8	159
C <sub>26</sub>	42.1	587	241	160	194	84.2	356	300	152	46.6	94.8	108	206	85.5	125
C <sub>27</sub>	206	1540	432	293	590	188	995	941	779	63.1	144	126	357	97.6	220
C <sub>28</sub>	70.8	746	270	145	274	87.9	497	472	273	41.6	114	69.2	269	80.8	172
Sq	593	5670	350	313	872	524	1520	2250	2130	122	548	204	3450	230	323
C <sub>29</sub>	589	3780	792	629	1750	423	2730	2890	2530	104	367	194	864	226	328
C <sub>30</sub>	123	1110	265	113	265	98.1	565	554	336	46.5	113	57.6	280	109	188
C <sub>31</sub>	984	6010	1050	756	2540	625	4330	4680	4010	139	412	232	710	203	449
C <sub>32</sub>	95.8	443	184	54.8	144	57.1	320	294	188	18.0	68.2	30.3	167	51.9	86.2
Di	313	2000	155	76.9	150	66.3	368	234	165	38.2	99.5	82.1	146	49.4	81.6
C <sub>33</sub>	663	4390	574	268	1040	294	2050	2280	1990	76.1	260	147	502	193	275
C <sub>34</sub>	111	583	102	71.1	97.2	48.8	278	255	115	23.8	102	71.0	235	132	110
C <sub>35</sub>	298	2170	295	99.3	351	111	793	1000	902	28.7	113	59.8	246	130	150
UCM	42.3	1300	33.1	21.4	41.5	14.5	113	41.7	34.2	9.74	33.0	19.6	97.4	33.0	24.9
U/Σn	10.0	22.5	3.92	4.26	3.64	3.56	5.14	2.25	2.43	7.67	10.1	7.78	15.8	11.9	6.06
CPI	5.90	4.51	2.79	3.82	6.10	4.15	5.28	6.03	8.96	2.14	2.71	2.36	2.46	1.90	2.07
ACL	30.5	30.3	29.7	29.5	30.1	29.9	30.2	30.3	30.4	29.2	29.8	29.4	29.5	29.7	29.6
C <sub>17</sub> /Pr	5.03	1.17	2.20	3.27	5.36	4.46	12.5	4.97	3.56	3.36	4.70	3.11	2.23	2.75	2.70
C <sub>18</sub> /Ph	2.44	0.45	1.95	2.41	2.96	3.41	4.10	2.91	2.10	4.64	3.77	2.93	2.89	3.63	3.84
	Marine samples														
	M1	M2	M3	M4	M5	M6	M7	M8	M12	M14	M15	M17	M22	M32	M34
C <sub>15</sub>	–	–	–	10.1	221	–	11.8	430	41.6	106	182	257	5.66	–	121
C <sub>16</sub>	–	–	4.88	47.3	213	31.1	67.0	393	132	144	163	218	51.1	3.73	195
C <sub>17</sub>	54.5	27.6	72.4	111	271	123	172	506	236	197	209	306	134	67.3	334
Pr	46.6	26.6	61.8	115	234	102	149	474	198	173	203	252	122	59.5	300
C <sub>18</sub>	148	83.9	182	132	262	182	200	444	265	182	188	246	168	158	304
Ph	37.3	21.3	40.9	39.4	82.7	44.4	51.4	137	64.0	52.7	58.7	72.0	44.4	62.4	91.1
C <sub>19</sub>	202	114	252	128	237	209	208	412	263	166	167	220	154	210	288
C <sub>20</sub>	218	132	274	120	196	205	193	382	251	158	144	195	136	226	264
C <sub>21</sub>	223	142	281	121	194	209	195	374	252	156	147	189	131	232	251
C <sub>22</sub>	233	145	277	121	183	199	190	368	248	157	132	191	132	236	246
C <sub>23</sub>	252	159	296	133	203	211	207	387	256	172	151	205	144	240	259
C <sub>24</sub>	243	145	304	152	207	206	193	370	242	165	170	203	131	220	246
C <sub>25</sub>	243	146	295	132	203	209	202	372	235	174	184	204	132	228	257
C <sub>26</sub>	184	123	213	94.0	143	159	150	309	199	139	107	147	95.3	183	187
C <sub>27</sub>	225	146	270	113	177	198	200	375	216	169	193	187	119	200	255
C <sub>28</sub>	176	114	175	80.9	132	151	143	265	171	123	123	150	86.9	169	203
Sq	152	45.0	185	91.8	227	265	79.6	225	53.5	67.4	154	161	239	335	237
C <sub>29</sub>	251	163	248	114	206	235	251	449	205	196	194	245	109	243	297
C <sub>30</sub>	126	91.7	111	56.5	99.2	114	101	179	110	85.0	96.9	110	58.7	155	144

Table 1 (continued)

	Marine samples														
	M1	M2	M3	M4	M5	M6	M7	M8	M12	M14	M15	M17	M22	M32	M34
C <sub>31</sub>	291	182	265	147	241	294	315	526	197	234	226	320	111	325	380
C <sub>32</sub>	105	72.8	76.5	39.2	71.3	82.1	77.7	124	70.8	63.7	89.3	86.9	48.1	165	132
Di	62.0	18.6	73.1	90.0	66.7	93.1	82.6	82.9	23.1	22.3	76.2	94.3	36.7	74.4	153
C <sub>33</sub>	160	112	137	76.1	137	166	168	271	103	136	150	177	65.5	247	211
C <sub>34</sub>	44.7	35.3	29.1	20.2	36.7	45.9	40.0	63.7	33.9	34.1	40.1	40.7	14.9	179	64.3
C <sub>35</sub>	143	64.8	83.2	38.3	86.2	136	124	144	50.1	63.8	103	108	53.9	229	163
UCM	11.1	2.34	7.37	2.16	13.2	8.20	7.38	12.0	4.95	5.40	23.6	5.86	8.78	13.5	9.01
U/Σn	3.15	1.06	1.91	1.09	3.55	2.43	2.16	1.68	1.31	1.79	7.47	1.46	4.22	3.44	1.88
CPI	1.62	1.54	1.70	1.69	1.74	1.78	1.97	1.86	1.43	1.81	1.85	1.88	1.53	1.43	1.73
ACL	28.8	28.9	28.5	28.7	28.9	29.0	29.1	29.0	28.4	29.0	28.9	29.1	28.5	29.3	29.1
C <sub>17</sub> /Pr	1.17	1.04	1.17	0.97	1.16	1.21	1.15	1.07	1.19	1.14	1.03	1.21	1.10	1.13	1.11
C <sub>18</sub> /Ph	3.97	3.94	4.45	3.35	3.17	4.10	3.89	3.24	4.14	3.45	3.20	3.42	3.78	2.53	3.34

Note:

Hydrocarbon concentrations are in ng g<sup>-1</sup> with the exception of UCM in μg g<sup>-1</sup>.

Sq = squalene, Di = diploptene, UCM = unresolved complex mixture, U/Σn = UCM/total *n*-alkanes, – = less than 1 ng g<sup>-1</sup>

CPI = carbon preference index

$$= \frac{1}{2} \left( \frac{nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}}{nC_{24} + nC_{26} + nC_{28} + nC_{30} + nC_{32}} + \frac{nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}}{nC_{26} + nC_{28} + nC_{30} + nC_{32} + nC_{34}} \right)$$

ACL = average chain length

$$= \frac{25(nC_{25}) + 27(nC_{27}) + 29(nC_{29}) + 31(nC_{31}) + 33(nC_{33})}{nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}}$$

River averages:

CPI=4.08±2.04, ACL=29.9±0.4, C<sub>17</sub>/Pr=4.09±2.62, C<sub>18</sub>/Ph=2.96±1.03

Marine averages:

CPI=1.70±0.16, ACL=28.9±0.3, C<sub>17</sub>/Pr=1.12±0.07, C<sub>18</sub>/Ph=3.60±0.50

1987); a weathering index, variously defined as the ratio of unresolved to resolved compounds, provides an estimate of the extent of degradation of a particular oil. In Table 1, 4 river samples (R2, R11, R13 and R14) gave UCM/Σ*n*-alkanes ratios >10, likely indicating the presence of degraded petroleum hydrocarbons (Simoneit, 1982; Matsumoto, 1983). In addition, UCM is an important component of the aliphatic hydrocarbon fraction since it has higher concentrations than total *n*-alkanes in marine and river sediments (Table 1). However, it exhibited no linear correlations with CPI or ACL for river or for marine sediments alone, and was weakly correlated with CPI ( $r=0.49$ ,  $p=0.007$ ) and with ACL ( $r=0.62$ ,  $p=0.0003$ ) when data for river and marine sediments were combined. The cause for these no correlations is that when two (or more) components characterized by different values of a biomarker ratio (like CPI or ACL) are mixed, the value of the ratio for the mixture usually varies nonlinearly (and disproportionately) with the weight percentages of the end members (Hedges and Prahl, 1993).

In two marine environments in the western Pacific free from petrogenic hydrocarbon contamination, it has been reported that all (23 samples) coastal marine sediments off northeastern Taiwan and all (9 samples) but one sediments from the East China Sea Shelf exhibit a trend of  $C_{25} < C_{27} < C_{29} < C_{31}$  (Jeng et al., 2003; Jeng and Huh, 2004), which is typical of more tropical sources. In the present study, 13 out of 15 river sediments exhibited this trend, but only 2 (M8 and M15) out of 15 marine sediments showed this trend (Table 1). This result can be attributed to the probable input of petrogenic hydrocarbons to 2 river (R13 and R14) and 13 marine sediments since this chain length trend is reversed in petrogenic hydrocarbons.

The *n*-alkane/acyclic isoprenoid ratios are often used for diagnosing petrogenic hydrocarbon contamination in environmental samples based on the fact that they are generally <1 for crude oils (Pavlova and Papazova, 2003) and >1 for uncontaminated samples. In the present study, the average *n*-C<sub>17</sub>/Pr ratios were 4.09±2.62 for river sediments and 1.12±0.07 for marine sediments (Table 1),

suggesting incorporation of more fossil hydrocarbons in the marine samples. However, the  $n\text{-C}_{18}/\text{Ph}$  ratios averaged  $2.96 \pm 1.03$  for river sediments and  $3.60 \pm 0.50$  for marine sediments (Table 1); this result contradicts the preceding one. This can be explained as follows. The Kaoping and Tungkang Rivers have been heavily polluted, particularly from pig-farming along the Kaoping River (Jeng et al., 1996). Most river samples were in the reducing environment as indicated by the presence of black color and strong  $\text{H}_2\text{S}$  odor. Additional phytane was presumably generated in the river sediments under the reducing condition (Didyk et al., 1978), resulting in the  $n\text{-C}_{18}/\text{Ph}$  ratio unable to reflect the addition of petrogenic hydrocarbons to the marine sediments.

It is reported that ACL distribution broadly varies with latitude (Poynter et al., 1989; Poynter and Eglinton, 1990). For instance, surface (top 2 cm) sediments from off NW Africa ranging from  $\sim 0\text{--}40^\circ$  N have  $n$ -alkane ACL values of 28.3–29.9 (Huang et al., 2000). As another example, ACL for a north to south latitudinal transect ( $5\text{--}30^\circ$  S latitude) of Holocene sediment in the SE Atlantic increases from 29.9 to 30.8 (Rommerskirchen et al., 2003). This means a change of  $\sim 0.04$  ACL units for crossing  $1^\circ$  latitude. In northeastern Taiwan, a watershed in the Fushan Experimental Forest (a nature reserve) was considered the least-disturbed site and was used as a reference station. The total suspended matter from this nature reserve has an ACL of 29.7 (calculated from data of Jeng and Kao, 2002). The ACL range of 12 marine sediments (latitude  $24^\circ 50'$  to  $25^\circ 20'$ ) from the lower slope (900–1600 m) of the southernmost Okinawa Trough (off northeastern Taiwan) is 29.6–29.8 averaging  $29.7 \pm 0.1$  (calculated from Jeng et al., 2003), identical to that of Fushan Forest suspended matter, indicating a predominant input of biogenic (recent) hydrocarbons. This is supported by other studies that the lower Okinawa trough sediments are located in an area with apparent sedimentation rates ranging from 0.10 to 0.52  $\text{cm yr}^{-1}$  (Chung and Chang, 1995) and are generally considered to be of recent origins, not relict sediments (Chen et al., 1995). In the present study, river sediments (latitude  $22^\circ 30'$  to  $22^\circ 50'$ ) gave an average ACL value of  $29.9 \pm 0.4$ . An increment of 0.2 ACL units for a latitude difference of ca.  $2.0^\circ$  can probably be attributed to variation of ACL in plant species and, to a lesser extent, to latitude effect.

Compared with the ACL range (29.6–29.8) of Okinawa Trough sediments, the present river sediments had a relatively wide range (29.2–30.5). One possible cause can be the ACL variation of different plant species. In addition, as discussed above, some river sediments were contaminated with petrogenic hydrocarbons. Based on their  $n$ -alkane distribution (abundance decreasing with

increasing carbon number), petrogenic hydrocarbons are expected to have low ACL values (in the  $\text{C}_{25}\text{--}\text{C}_{33}$  range). Three fossil fuel hydrocarbon samples were analyzed and gave ACL values of 27.8 (crude oil 1 from the refinery complex located between Kaohsiung Harbor and the Kaoping River mouth, Fig. 1, not shown), 27.9 (crude oil 2 from an oil spill near Kaohsiung Harbor, Fig. 1, not shown) and 28.4 (fuel oil from the same refinery complex as crude oil 1). Input of petrogenic hydrocarbons with varying amounts to natural samples (containing biogenic hydrocarbons without oil seepage) can result in lower ACL values, thus making the ACL range wider.

As shown in Table 1, the ACL values (28.4–29.3) of marine sediments were lower than those (29.2–30.5) of river sediments (Student's  $t$  test at 99% confidence). The difference in ACL values between river and marine sediments suggests that ACL may be a useful tool for distinguishing samples from the two areas. Marine samples were taken from the sediment surface (top 3–4 cm), and most samples were located in shallow water ( $< 300$  m) with the exception of few deep-water stations (e.g., M14, 452 m; M15, 374 m; M34, 679 m; and M32, 990 m) (Fig. 1). Therefore, these samples are considered contemporary in age, and presumably have no difference in ACL values due to water column diagenesis. Sediment diagenesis is considered to be minimal due to high sedimentation in this area (ca.  $0.72 \text{ cm yr}^{-1}$ , Tsai and Chung, 1989) and only surface sediment (top 3–4 cm) being analyzed. In other words, the ACL values of marine sediments should be very close to or possibly equal to the average of those of river sediments if they are well mixed and transported to the sea. The present result can be explained by petrogenic hydrocarbon inputs to marine sediments, supporting earlier studies (Jeng, 1986; Jeng et al., 1997).

The amount of plant wax in the petroleum-contaminated samples can be determined following the approach of Simoneit et al. (1990). The concentrations of the wax  $n$ -alkanes were calculated by subtraction of the average of the next higher and lower even carbon numbered homologs:

$$\text{Wax } C_n = [C_n] - 1/2[(C_{n+1}) + (C_{n-1})]$$

Using these wax concentrations of odd carbon numbered alkanes ( $\text{C}_{25}\text{--}\text{C}_{33}$ ), the average ACL of plant wax in marine sediments was calculated to be  $30.0 \pm 0.4$  (range 29.1–30.3), which presumably represents the ACL from the Kaoping River (assumed to be the source). However, the measured ACL for river sediments was  $29.9 \pm 0.4$  (range 29.2–30.5); a lowering of 0.1 ACL

units can therefore be ascribed to some river sediments being polluted.

Both ACL and CPI are calculated using *n*-alkanes data derived from higher plants, and they are expected to be related. Linear regression of ACL vs. CPI for 15 river sediments gave an equation:

$$ACL_r = 29.2 + 0.165 \text{ CPI}_r \quad (r = 0.83, p < 0.001)$$

where subscript *r* denotes river; linear regression for 14 marine sediments yielded another relationship:

$$ACL_m = 26.8 + 1.20 \text{ CPI}_m \quad (r = 0.77, p = 0.0014)$$

where subscript *m* denotes marine (Fig. 3). Sample M32 was an outlier and therefore excluded for regression since it is located far from the river mouth (Fig. 1), receiving less contribution from land and in the deepest water of 990 m, possibly resulting in hydrocarbon diagenesis in the water column. Further, the influence of the Kuroshio loop current (Wang and Chem, 1988) might supply hydrocarbons from additional sources to M32. From Fig. 3, it is notable that the regression line for marine sediments is very close to that of fossil hydrocarbons (ACL=28.0, average of the three fossil hydrocarbon samples analyzed and CPI=1), pointing to a close relation between them. In addition, it is seen from Fig. 3 that marine and river

sediments are separated by two regression lines with different slopes, demonstrating that ACL and CPI may be equally useful tools for distinguishing sediments containing biogenic hydrocarbons alone from those containing both biogenic and petrogenic hydrocarbons.

For marine sediments, ACL was correlated significantly with CPI. Proportions of petrogenic hydrocarbons in marine sediments can be estimated using this correlation if we assume the two predominant hydrocarbon sources to marine sediments are from the Kaoping and Tungkang Rivers and from fossil fuels. By using a two-end-member mixing assumption, the fractional contributions of the two end-member sources to marine sediments can be estimated. The petrogenic end-member has ACL=28.0 and CPI=1.0. The ACL (29.9) and CPI (4.08) of river end-member were the averages of 15 river sediments. Estimation was made by the following two equations:

$$\text{CPI}_m = \text{CPI}_p X + \text{CPI}_r (1-X)$$

$$\text{ACL}_m = \text{ACL}_p X + \text{ACL}_r (1-X)$$

where subscripts *m*, *p* and *r* refer to marine sediment, petroleum and river sediment, respectively; *X* and  $1-X$  respectively stand for hydrocarbon fractions of petroleum and those of river sediments in marine sediments. The

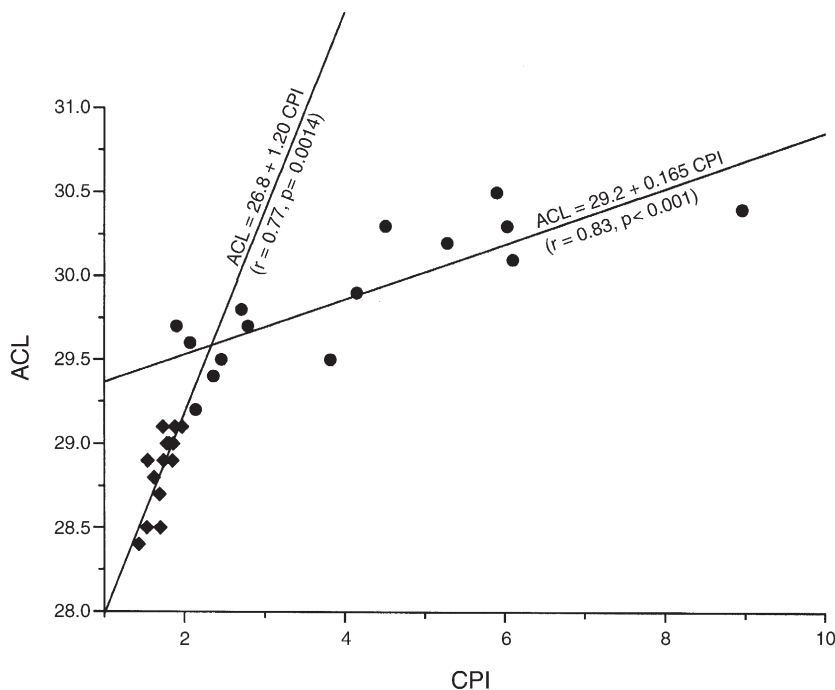


Fig. 3. Plot of ACL vs. CPI for all samples. Filled diamonds, marine sediments; filled circles, river sediments.



minimum and maximum values of marine sediments for CPI were respectively 1.43 and 1.97 (Table 1), and the corresponding ACL values were calculated using the regression equation to be 28.5 and 29.2, respectively. Therefore, the percentages of petrogenic normal hydrocarbons contained in marine sediments were estimated to be between 86% and 69% using CPI and from 74% to 37% using ACL. The difference between estimations using CPI and ACL can be attributed to the fact that the value of the ratio for the mixture usually varies non-linearly (and disproportionately) with the weight percentages of the end members when two components characterized by different values of a biomarker ratio are mixed (Hedges and Prahl, 1993)

Mature fossil hydrocarbons can be characterized by a number of parameters such as CPI, pristane formation index, unresolved complex mixture (UCM), and steroidal and hopanoidal hydrocarbon maturity parameters, etc. (Killops and Killops, 1993). Catastrophic events are generally studied by these conventional tools (Hostettler et al., 1992; Readman et al., 1996). In the present study, ACL is proposed as an additional tool for studying petrogenic hydrocarbons in marine sediments or for comparing the relative amounts of vascular plants (CPI=5–10) and mature fossil hydrocarbons (CPI= $\sim$ 1) within an environmental sample. CPI values of a sedimentary area tend to vary over a wide range, but ACL values may vary less, such as the case for river sediments (Fig. 3). In another example, lower Okinawa Trough sediments have a CPI range of 2.49–6.06 with an average of  $3.38 \pm 1.01$  (Jeng et al., 2003) and an ACL range of 27.6–27.8 (discussed earlier). ACL values could approximate a “constant” in an unpolluted area (within few degrees in latitude) as long as natural source inputs remain unchanged with time and sediments are well mixed. Under the natural conditions, ACL values of sediments for a given area can be precisely determined as a database and used as a reference for an oil spill. It is suggested that ACL can be an additional indicator for *n*-alkane contamination only. Note that like CPI, ACL is a diagenetically insensitive ratio because it is based on the relative abundances of chemically similar compounds within a limited molecular weight range (Hedges and Prahl, 1993). Compared with the approach of using more sophisticated geochemical techniques like isotopic analyses of *n*-alkanes, the ACL method is a rapid screening tool and for labs without state-of-the-art instruments.

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