Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina)

M.G. Commendatore [a,*], J.L. Esteves [a,b]

[a] *Centro Nacional Patagónico (CONICET), Bv. Brown S/No, 9120 Puerto Madryn, Chubut, Argentina*
[b] *Fundación Patagonia Natural, Marcos A. Zar 760, 9120 Puerto Madryn, Chubut, Argentina*

Abstract

In march of 2001 a study was carried out to evaluate hydrocarbon levels in the lower course of the Chubut River. The study included 12 sample stations along the river from San Cristóbal Bridge to the confluence with the sea, in a 25 km straight-line extension in a urbanized area. In the first 11 stations, resolved aliphatic (RAli) hydrocarbons presented low values, between 0.07 and 0.96 µg/g dry weight (dw); the unresolved complex mixture (UCM) between 0.42 and 2.72 µg/g dw, and the total aliphatic (TAli) hydrocarbons between 0.55 and 3.07 µg/g dw. In the last station, at the mouth of Chubut river, these values increased to 460, 284, and 741 µg/g dw for RAli, UCM and TAli, respectively. The *n*-alkanes distribution indices and the compositional parameters suggested a predominantly biogenic origin in eleven stations, and a predominantly anthropogenic origin in the last station, with the highest hydrocarbon values. It is possible to conclude that the stations with low hydrocarbon values and biogenic origin predominance would constitute the baseline of aliphatic hydrocarbons for river sediments at this zone. The station with the highest hydrocarbon concentration and predominantly anthropic origin was related to the presence of Rawson city's port, where its activities (harbor and fishing vessels) generate hydrocarbon wastes unrelated to the river base profile in the study zone. Offshore, but within the river influence, there is an important fishing area of Argentine Red and Patagonian shrimps (*Pleoticus muelleri* and *Artemesia longinaris*, respectively).
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1. Introduction

The arid portion of the Patagonian region has very few rivers and, therefore, these are of fundamental importance for agricultural activities and water supply for human consumption. In the Chubut Province, the Chubut river is the only water supply for close to 200,000 inhabitants, distributed in three major neighboring cities (Rawson, Trelew and Puerto Madryn) and other less populated ones as Gaiman, Dolavon and 28 de Julio. In addition, the river is the source for irrigation channels, which are used for agricultural purposes. However, despite concentrating a large percentage of the Province's population (52%), the Chubut river drainage basin has not undergone extensive industrial and agricultural development. Both Trelew and Rawson cities,

located on the margins along the lower course of the river, have relatively low industrial activity. Nevertheless, Rawson city has an active fishing port.

Hydrocarbons can be environmental polluting agents of risk for ecosystems and human population health. Hydrocarbons of anthropogenic origin, such as petroleum and derived products, are introduced to the environment as a result of activities related to oil operation, petroleum transport, harbor activities, and domestic and industrial effluents. Crude oil and its derived products have been widely recognized as important pollutants (Clarck, 1992; Ho et al., 1999). On the other hand, hydrocarbons of biogenic origin naturally occur at low concentrations in different substrates, such as water and sediment, and are part of the natural hydrocarbon baseline of an ecosystem. According to UNEP (1992), hydrocarbon concentrations in non-polluted sediments are not greater than 10 µg/g dry weight (dw).

Water for human consumption, electricity generation, and land irrigation, are among the most important

* Corresponding author. Tel.: +54-2965-451024; fax: +54-2965-451543.

E-mail address: commenda@cenpat.edu.ar (M.G. Commendatore).

uses of the river. At the lower course it receives urban, agricultural, and industrial sewage. Despite the significance of the Chubut river as a water source in the region, no studies have yet evaluated hydrocarbon concentrations throughout its course. The definition of a baseline level of hydrocarbons is essential when attempting to determine chemical changes introduced by anthropogenic effects. The goals of this study were (a) to determine the current levels of aliphatic hydrocarbons along the lower course of the Chubut river and (b) to determine their possible sources using *n*-alkane distribution indices.

2. Material and methods

2.1. Study area

The Chubut river starts more than 500 km west in the Andes, flowing southeast, where an important flow feeds the ground water and the rest empties into the sea (Atlantic Ocean). It is a typical mountain river that receives the largest amount of water during snow and glacier melt, when the water flow increases. In the valley downstream of Florentino Ameghino dam (150 km west

from the mouth), it runs with a markedly meandrous course and flows to the Atlantic Ocean, crossing areas with the highest population density and agricultural and industrial activities (Sastre et al., 1994). A fishing port is located at the mouth. Offshore, but within the river influence, there is an important fishing area for Argentine Red and Patagonian shrimps (*Pleoticus muelleri* and *Artemesia longinaris*, respectively).

In this study, hydrocarbon presence was evaluated from the San Cristóbal bridge to the river mouth (between 43° 18.08′S, 65° 23.75′W and 43° 20.40′S, 65° 03.16′W) (Fig. 1).

2.2. Sediment sampling

The sampling was made on the riverside sediments using plexiglass tubes 25 cm long with 4.5 cm internal diameter, which were introduced vertically into the sediment. Surface sediment (0–3 cm) samples were collected from five random points at each sampling location and placed in a cleaned, solvent rinsed glass flask. All samples were frozen immediately after collection at −20 °C until analysis. Collected sediments were homogenized and subsampled for the determination of water content and ignition loss, grain size analysis, and
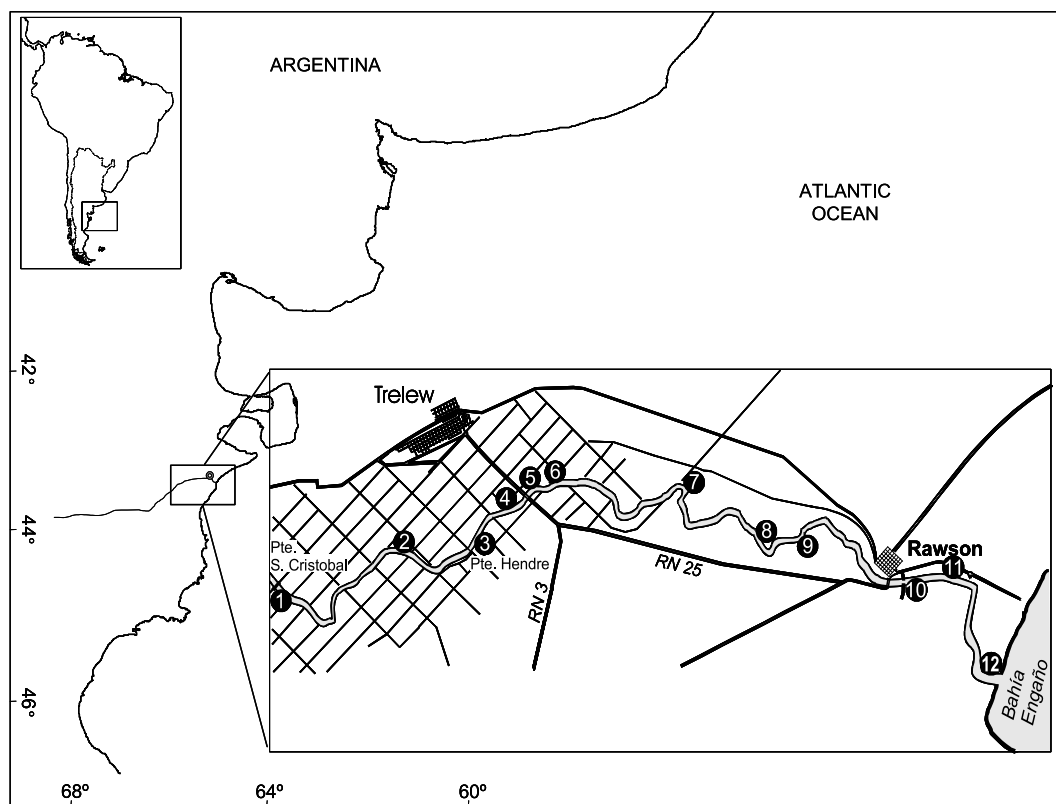

Fig. 1. Study area and sampling stations: 1. San Cristóbal Bridge, 2. Industrial park water intake, 3. Hendre Bridge, 4. Madryn city water intake, 5. Trelew city water intake, 6. Wool industry, 7. Irrigation channel intake, 8. Rawson city water intake, 9. Rawson Zoo, 10. New Bridge, 11. Rawson sewage, 12. Rawson port.

extraction of organic compounds. Sampling stations were selected according to the following criteria: stations potentially subject to anthropogenic impact, water intakes for the cities or sources of drinking waters (Trelew, Rawson and Puerto Madryn), and the return of the irrigation channel to the river.

2.3. Hydrocarbon analysis

2.3.1. Extraction and fractionation of hydrocarbons

Hydrocarbon analysis was carried out according to UNESCO (1982) and Manual Caripol (Gold et al., 1987). Wet sediments were digested with methanol and KOH. The non-saponificable fraction was extracted with hexane. The combinated extracts were dried with anhydrous sodium sulphate and evaporated at room temperature to near 2 ml. The volume was reduced with a soft flow of nitrogen gas to 0.2 ml. The final extract was seeded in totally activated alumina column to carry out the clean-up and isolation of hydrocarbons. A fraction F1 corresponding to aliphatic hydrocarbons was obtained by elution with hexane and was measured by high resolution gas chromatography (HRGC).

2.3.2. Determination of aliphatic hydrocarbons through gas chromatography

High resolution gas chromatography was conducted on a gas chromatograph, equipped with a DB1 fused silica column (30 m × 0.25 mm i.d.), split/splitless capillary injection system, and a flame ionization detector (FID). Samples were analyzed in the splitless mode using nitrogen as carrier gas, at a rate of 1 ml/min. The injector and detector temperatures were maintained at 250 and 320 °C, respectively. The column temperature was programmed from 60 °C (2 min hold) to a final temperature of 290 °C at a rate of 8 °C/min. The identification of resolved aliphatic hydrocarbons was made by comparison of retention times with standards. Resolved aliphatic hydrocarbons (RAli) and unresolved complex mixtures (UCM) were calculated using the response factors of n-alkanes. Procedural blanks and standards were run in association with samples. Recovery assays were made by spiking a pristine sample. The results were $94.5 \pm 11.6\%$ ($n = 5$) for C20–C28 n-alkanes. Results were not corrected for recoveries. The reproducibility of the method for the synthetic standard mixture at the spiked level of 1 µg/g of dw sediment varied from 9.3% to 16.5%. The detection limit for total aliphatic hydrocarbons was 14 ng/g. For each station, the individual n-alkane concentrations from n-C11 to n-C31, the isoprenoid pristane and phytane concentrations, the total resolved n-alkanes, the UCM and the total aliphatic (TAli) fractions were calculated. The UCM involves cycloalkanes, branched alkanes, and other compounds unresolved by the capillary column which show as a "hump" below the resolved compounds. The TAli was defined as the sum of the identifiable aliphatic (RAli) peaks and, if present, the UCM.

2.4. Grain size analysis

The sediment was dried in oven and sifted in an automatic equipment during 20 min. Sieves of 2 and 0.063 mm mesh size were used; three fractions were thus obtained: gravel, particle sizes >2 mm; sand, particle sizes between 0.063 and 2 mm; and fine (silt–clay), particle sizes <0.063 mm.

2.5. Ignition loss

Sediments were dried at 105 °C during 48 h to obtain the dry weight and then calcined in muffle at 450 °C during 4 h to obtain ignition loss of the samples. We can assume that the ignition loss at 450 °C is approximately the organic matter (OM) content in the samples.

2.6. Resolved aliphatics hydrocarbon/total organic carbon

The ratio of "trace-level" individual compounds or compound classes (i.e. individual or total saturated or aromatic hydrocarbons) present at the $ng\,g^{-1}$ (ppb) or $\mu g\,g^{-1}$ (ppm) level to a bulk parameter (i.e. total organic carbon, TOC) present at $mg\,g^{-1}$ level can be used to evaluate existing geochemical relationships and to gauge future incremental additions. An increase in the concentration of the trace parameter due to an input of petroleum might double or triple the levels at a given station but have little effect on the value of a corresponding bulk parameter such as TOC. Therefore, this type of relationship can be used as a sensitive indicator of anthropogenic inputs of petroleum hydrocarbons to sediments (Bohem and Requejo, 1986). In sediments that are receiving a normal input of a polluting agent within one given region, a specific relation RAli/TOC is characteristic of the "province geochemistry" (UNEP, 1995). In this study the TOC values were obtained from OM values according to Billen (1978).

2.7. Evaluation indices

Different parameters in addition to absolute concentration have to be analyzed in order to evaluate the probable origin of hydrocarbons (anthropogenic or biogenic) due to the high complexity of natural samples. In addition, the combination of different indices applied to the same sample strengthens this assessment. The anthropogenic source may be petroleum, but it can also be recycled organic matter of different origin, such as sewage, soil organic matter washed by rains or effluents from treatment plants. Biogenic sources may be, for example, algae, plankton, marine animals, terrestrial

vascular plants or bacteria. Evaluation indices selected in this study were:

(a) Major hydrocarbon (MH): denotes the highest *n*-alkane concentration. This index is often around C18 for crude oils. C15, C17, C19 and C21 have been described as important components in different types of algae (both macro and micro-algae), and C23, C25, C27, C29 and C31 for vascular land plants (Broman et al., 1987; Colombo et al., 1989).

(b) The low/high molecular weight hydrocarbons (LMW/HMW): it is the ratio of the sum of *n*-alkanes $\leqslant$ C20 over the sum of *n*-alkanes $\geqslant$ 21. Ratio values of 1.0 have been reported for petroleum, while sedimentary bacteria, seawater, marine animals, higher plants, and sediments show relatively lower values. Ratio values >1.0 indicate algae and plankton hydrocarbon inputs.

(c) *n*-C16 ratio: it is the sum of all *n*-alkanes/*n*-C16. This ratio tends to be small (<15) for petroleum-contaminated samples, while it is larger (>50) for biological samples (Clarck and Finley, 1973).

(d) Carbon preference index (CPI): it is defined as $2(C27 + C29)/C26 + (2C28) + C30$ (Bohem and Requejo, 1986). Petrogenic hydrocarbons show values around 1, while vascular plants and uncontaminated sediments range from 3 to 6 (Colombo et al., 1989).

(e) Even to odd ratio (even/odd). Petroleum usually shows a wide distribution range of *n*-alkanes and the even/odd ratio shows no predominance. In contrast, in most plant waxes, odd-chain alkanes are 8–10 times more abundant than even-chain *n*-alkanes (Volkman et al., 1992).

(f) Pristane/Phytane ratio (Pri/Phy). Values close to 1 indicate petroleum derived hydrocarbons (Broman et al., 1987) and values from 1.4 to 6.7 indicate biogenic hydrocarbons (Lecaros et al., 1991).

(g) *n*-C17/Pristane and *n*-C18/Phytane indices (*n*-C17/Pri, *n*-C18/Phy). These indices evaluate the presence of oil and the relative biodegradation of *n*-alkanes. Low values for these indices suggest the presence of degraded oil while higher indices suggest low degradation. When hydrocarbon concentrations are also high, higher indices indicate fresh oil inputs (Colombo et al., 1989).

(h) Sum of the resolved aliphatic/unresolved complex mixture index (res/UCM). This index estimates the relative degradation degree; low values suggest a degradation process, while high values suggest fresh oil presence. The UCM magnitude is related to the degree of anthropogenic contribution. UCM presence is usually associated with petroleum hydrocarbons. It has been suggested that UCM can result from bacterial degradation of organic matter (Venkatesan and Kaplan, 1982).

3. Results

3.1. Organic matter and granulometry

The organic matter presented values ranging between 1.1% and 3.9%. Values greater than 3% corresponded to stations 6, 7, 8, 9 and 12. No correlation was found between the percentages of organic matter and fine sediment ($r^2 = 0.18$, $p < 0.05$), which varied between 5.9% and 39.5%. Total aliphatic hydrocarbon concentrations showed no correlation with the organic matter or the fine material ($r^2 = 0.05$, $p < 0.05$, and $r^2 = 0.19$, $p < 0.05$, respectively). Table 1 shows the organic and granulometry values obtained at each station.

3.2. Absolute hydrocarbon concentrations

Stations 1–11 showed low values for RAli, UCM and TAli concentrations (Fig. 2). The highest value of TAli was 3.1 μg/g dw at the Rawson Sewage (Station 11), where the UCM made an important contribution (2.72 μg/g dw) in comparison to the RAli (0.35 μg/g dw). In contrast, Station 12 presented relatively high concentrations of RAli (458 μg/g dw), UCM (284 μg/g dw), and TAli (741 μg/g dw), the highest recorded in the studied stations (Fig. 3). Fig. 4 shows TAli concentration values

Table 1
Organic matter and granulometry by the Chubut River sediments

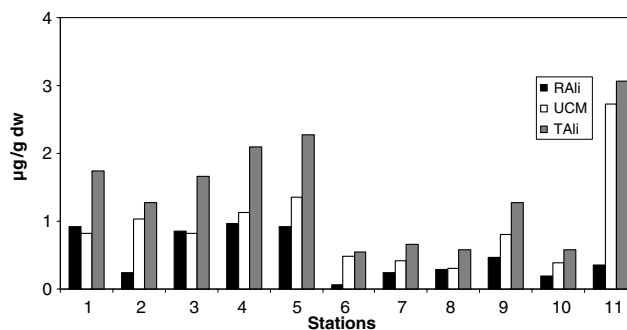| STATION	OM %	Gravel %	Sand %	Fine %
1	1.7	0.1	79.7	20.2
2	2.1	0.2	68.4	31.3
3	2.6	0.5	78.6	20.9
4	1.7	0.0	90.6	9.3
5	2.6	0.1	71.8	28.1
6	3.9	0.1	77.4	22.6
7	3.5	2.7	73.9	23.4
8	3.1	1.2	59.3	39.5
9	3.4	1.0	71.7	27.4
10	1.1	2.6	91.5	5.9
11	2.1	5.5	75.2	19.3
12	3.2	47.8	44.9	7.3

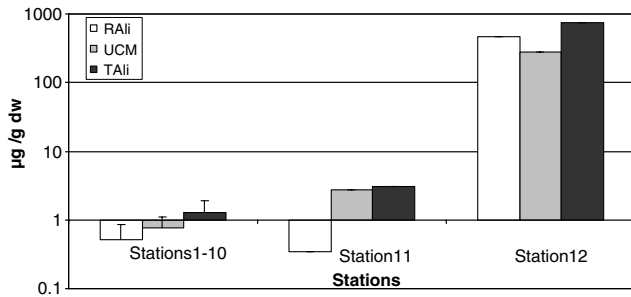Fig. 2. Aliphatic hydrocarbon concentrations at stations 1–11.

Fig. 3. Hydrocarbon concentrations at stations 1–10 (the bar represents +1sd), station 11 and station 12.

normalized with the organic matter content of the sediments.

3.3. Origin of hydrocarbons

3.3.1. Even/odd, LMW/HMW, n-alk/n-C16, and CPI ratios

At stations 1–11, the Even/Odd and LMW/HMW indices presented low values (<1) (Table 2), showing a clear hydrocarbon predominance of chains with odd number of carbons and high molecular weight (C > 20).

In all cases, the n-alk/n-C16 relationship presented values higher than 15. The CPI index showed high values at all stations, except for Station 2 (Industrial Park water intake), which presented a value of 0.25. In this last case, as a result of the presence of the alkanes n-C22, n-C24 and n-C26, both the Even/Odd and LMW/HMW relationships had relatively higher values than in the rest of the stations (0.74 and 0.61, respectively). Evaluation indices for Station 12 showed different values than those found for the rest of the stations (except for Station 2), particularly the Even/Odd, LMW/HMW, and n-alk/n-C16 relationships (0.82, 7.03, and 7.2, respectively). Absolute concentration values at Station 12 were three orders of magnitude greater in relation to those at the other stations (Rali = 457.6 µg/g dw; UCM = 283.7 µg/g dw; Tali = 741.2 µg/g dw).

3.3.2. Pri/Phy ratio

At stations 1–11, values for Pristane and Phytane remained low. Values for these isoprenoids were highest at station 11, with 0.015 and 0.025 µg/g dw, respectively. In the other stations, values remained very low for Pristane (mean = 0.0038 µg/g dw, sd = ±0.0042 µg/g dw; $n = 10$) and Phytane (mean = 0.004 µg/g dw, sd = ± 0.0044; $n = 10$). At station 12, the values for Pristane
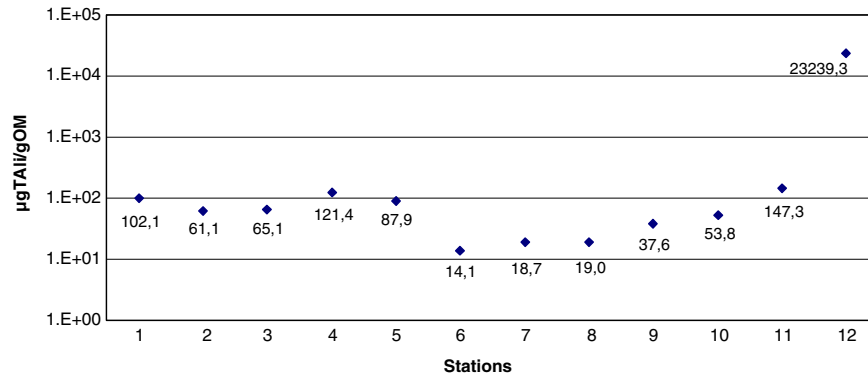

Fig. 4. TAli concentrations expressed in µg/g of OM.

Table 2
Evaluation indices for Chubut river samples

Station	MH	Even/Odd	LMW/HMW	n-alk/n-C16	CPI	Pri/Phy	n-C17/Pri	n-C18/Phy	RAli/UCM
1	n-C27–n-C25	0.4	0.31	17.9	14.62	–	124.31	–	1.1
2	n-C17–n-C24	0.74	0.61	34.37	0.25	0.75	7.74	–	0.24
3	n-C27–n-C25	0.34	0.25	29.23	10.39	–	11.76	–	1.04
4	n-C27–n-C29	0.25	0.16	36.07	11.95	1.06	3.99	5.19	0.85
5	n-C25–n-C27	0.42	0.36	34.49	6.34	1.02	5.65	3.16	0.68
6	n-C27–n-C25	0.06	0.07	–	14.24	–	–	–	0.14
7	n-C25–n-C27	0.03	0.32	–	26.2	0.92	13.22	–	0.56
8	n-C27–n-C17	0.14	0.33	–	12.58	–	–	–	0.94
9	n-C27–n-C25	0.13	0.24	62.52	21.72	0.61	12.3	0.01	0.59
10	n-C29–n-C31	0.06	0.1	–	13.64	0.83	1.93	–	0.48
11	n-C27–n-C25	0.11	0.46	–	53.93	0.56	2.61	–	0.13
12	n-C19–n-C16	0.82	7.03	7.2		0.89	1.1	0.85	1.61

and Phytane were relatively high, 0.045 and 0.05 µg/g dw, respectively. The Pri/Phy relationship at the analyzed stations varied between 0.6 and 1.1 (Table 2).

3.3.3. Major hydrocarbon

At stations 1–11, except station 2, the largest peaks were the higher molecular weight odd-carbon number alkanes (Table 2). The predominant odd-carbon number alkanes were *n*-C27, *n*-C25 and/or *n*-C29, depending on the station. At station 2, *n*-C17 was the major peak in the lower molecular weight range whereas, at station 12, was *n*-C19.

3.3.4. Unresolved complex mixture

UCM values for stations 1–11 remained low, with the highest value of 2.72 µg/g dw at station 11. At station 12, the value for UCM was 284 µg/g dw, two order of magnitude higher than that at station 11.

3.3.5. Classification of stations according the source of hydrocarbons

On the basis of the previous analysis, the studied stations can be classified into four categories:

(1) Terrigenous biogenic hydrocarbons: Stations 1, 3, 4, 5, 6, 9, and 10, where the presence of odd-carbon number hydrocarbons such as *n*-C23, *n*-C25, *n*-C27, *n*-C29, and *n*-C31 in the sediments could be explained by the contribution of terrestrial plants.
(2) Riverine biogenic hydrocarbons (micro and macroalgae): Station 2, where the presence of odd-carbon number hydrocarbons such as *n*-C15, *n*-C17, *n*-C19 and *n*-C21 in the sediments could be explained by the contribution of different micro and macroalgaes types.
(3) Mixture of terrigenous and riverine biogenic hydrocarbons: stations 7, 8, and 11 (both low and high molecular weight odd hydrocarbons).

(4) Petrogenic hydrocarbons: station 12, where the UCM feature and the homologous series of *n*-alkanes were present.

To confirm the type of biogenic source at stations 1–11, a relationship was calculated as the sum of odd hydrocarbons from *n*-C23 to *n*-C31 divided by the sum of odd hydrocarbons from *n*-C15 to *n*-C21 (Fig. 5). Values higher than 1 can be seen for the Stations 1, 3, 4, 5, 6, 9 and 10, smaller than 1 can be seen for the station 2 and intermediate can be seen for the stations 7, 8 and 11.

Figure 6 presents RAli hydrocarbon concentrations and their distribution pattern at three different stations along the river, which show a clear predominance of each of the three different types of contributions (terrigenous biogenic, riverine biogenic and petrogenic).

3.4. Resolved aliphatics hydrocarbon/total organic carbon

Values of the RAli/TOC relationship for all stations are presented in Fig. 7. Values for stations 1–11 ranged between 4×10^{-6} and 1×10^{-4}, with an average of $6 \times 10^{-5} \pm 5 \times 10^{-5}$, while the value calculated for Station 12 was 3×10^{-2}.

4. Discussion

No correlation was found between total aliphatic hydrocarbon concentrations and organic matter or fine material. TAli concentration values normalized to the organic matter content of the sediments showed a similar trend to the one found for concentrations expressed on sediment dry weight basis. This result confirms the lack of association between hydrocarbon concentrations and organic matter contents on the analyzed sediments.

Except station 12, hydrocarbon values were low in all stations. According to UNEP (1992), hydrocarbon
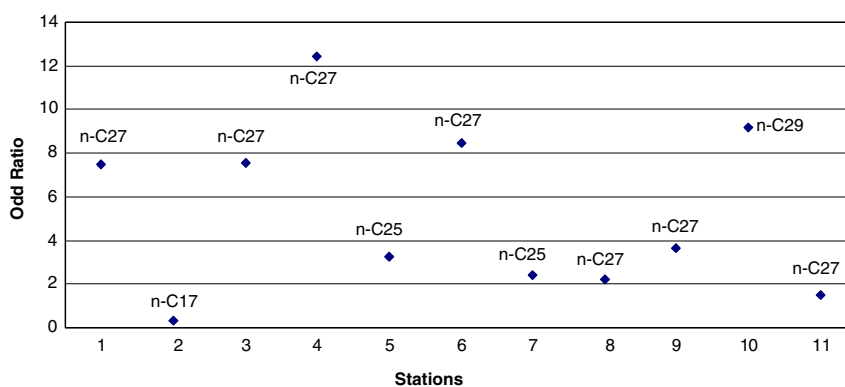

Fig. 5. Relationship of terrestrial biogenic hydrocarbons (plants) and riverine biogenic hydrocarbons (algaes) (Odd ratio $\sum n$-C23, *n*-C31 to $\sum n$-C15, *n*-C21). The MH for each station is presented.
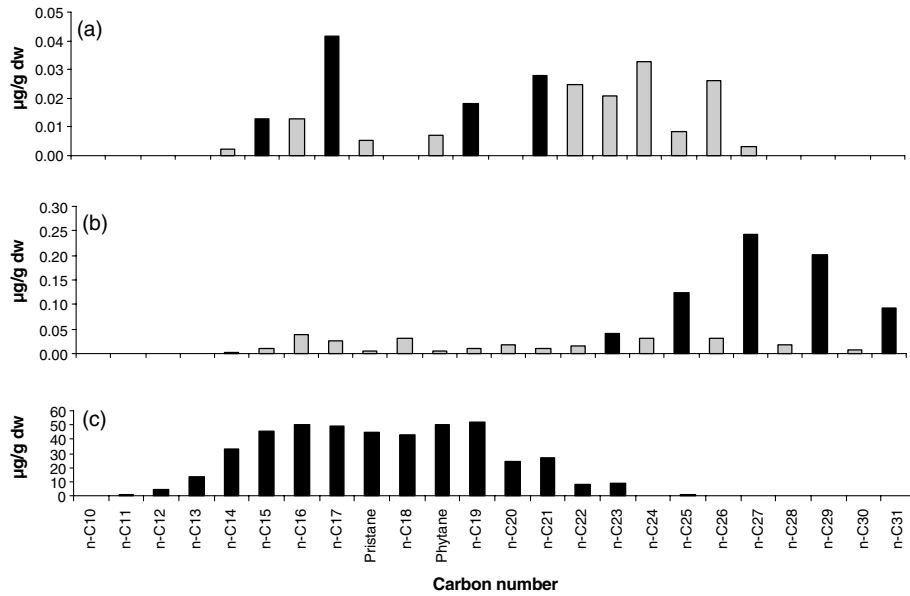
Fig. 6. Station number 2 (a), algaes derived hydrocarbons predominance (*n*-C15, *n*-C17, *n*-C19 and *n*-C21); Station number 4 (b), terrestrial plants derived hydrocarbons predominance (*n*-C23, *n*-C25, *n*-C27, *n*-C29 and *n*-C31); and Station number 12 (c) petrogenic hydrocarbons predominance (homologous series of *n*-alkanes). Peaks of interest are in dark color.
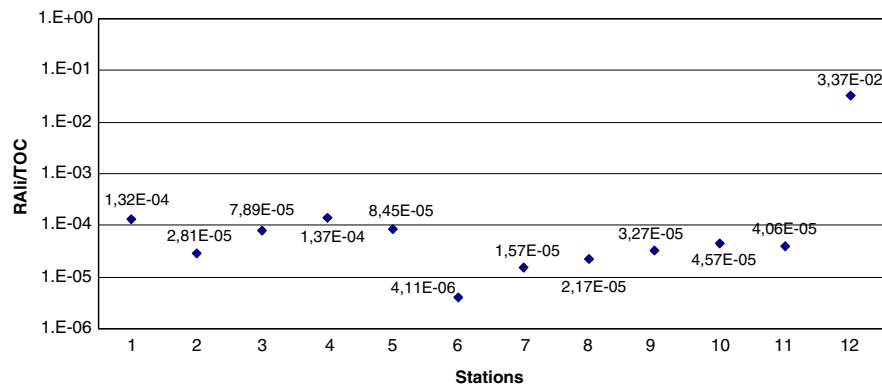

Fig. 7. Relationship of resolved saturated hydrocarbons/total organic carbon content.

concentrations in non-polluted sediments are not greater than 10 μg/g dry weight. The highest value of TAli at the Rawson Sewage (Station 11), where the UCM made an important contribution in comparison to the RAli, indicates the presence of degraded waste, probably associated to sewage. In the rest of the stations, the contribution of UCM was smaller and in many cases similar to the RAli value.

At station 12 (Rawson port), hydrocarbon values were similar to the highest values found at accumulation zones of the Patagonian marine coast due to marine current action, and greater to those found at port areas such as Comodoro Rivadavia or San Antonio Oeste (Commendatore et al., 2000). Port activities are the main source of hydrocarbon contamination at the Rawson area, and future studies should analyze nearby areas to evaluate the extent of their impact. The UNEP

(1992) reports values between 10 and 1000 μg/g dw as possible for sediments in industrial and harbor zones.

The unresolved complex mixture is a result of overlapping elution of a complex mixture of petroleum hydrocarbons over the entire boiling point range. Therefore, the UCM signal in the gas chromatogram may indicate petroleum pollution, whereas the differentiation of biogenic sources primarily from marine plankton and terrestrial vascular plants is often facilitated by the distribution of hydrocarbons in restricted boiling point ranges (Venkatesan et al., 1980). At stations 1–11, UCM was present at very low levels and all evaluation indices and compositional parameters, including the absence of the homologous series of *n*-alkanes, indicate a clear biogenic origin.

The distribution of hydrocarbons with predominance of odd high molecular weight *n*-alkanes, principally

n-C27 how MH, suggests that the most important biogenic hydrocarbon contribution would be associated with terrestrial plants. A minor contribution would be associated to algaes (MH *n*-C17, station 2). Station 2 showed the presence of *n*-alkanes C22, C24, and C26. In addition, a low value of CPI index and both the Even/Odd and LMW/HMW relationships with relatively high values suggest a small hydrocarbon contribution of anthropogenic origin at this station.

According to Broman et al. (1987), values close to 1 for the Pri/Phy relationship indicate petroleum derived hydrocarbons. The Pri/Phy ratio found in this study (between 0.6 and 1.1) would therefore suggest some anthropogenic hydrocarbon input. This is the case at station 11 (Rawson sewage), where the value for this ratio was 0.56 as the phytane concentration was the second highest (0.026 μg/g dw). However, phytane concentration values in other stations (except for station 12) were very low, with an average of 0.004 μg/g dw. Seagars and Garlich-Miller (2001) argue that low concentrations of phytane occur only in unoiled sediments (<0.001 μg/g). The phytane concentration values for stations 1–10 were in the same order of magnitude than those considered as unoiled sediments, suggesting low or no anthropogenic input. In addition, phytane occurs in the lipids of bacteria and could be abundant in anaerobic sediments (Volkman et al., 1992), and might also come from diagenetic sources (Blumer and Snyder, 1965; Mille et al., 1992).

The above considerations, in addition to the low absolute hydrocarbon concentrations and to the clear absence of homologous series of *n*-alkanes, demonstrate the predominant biogenic origin of hydrocarbons at these stations. Values found in the analyzed stations of the lower course of the Chubut river can be considered as the baseline for aliphatic hydrocarbons.

Station 12 had a clear anthropogenic impact reflecting the harbor activities and it does not comprise the baseline established for the rest of the stations analyzed. According to Gearing et al. (1976), relatively large amounts of *n*-C16 together with an even distribution of *n*-alkanes in the range C14–C20 and a substancial unresolved envelope, all point out to a fossil fuel input. In agreement with this fact, the presence of homologous series of *n*-alkane hydrocarbons from *n*-C10 to *n*-C25 indicates petroleum hydrocarbons (probably gas oil or gas oil–fuel oil mixtures). High RAli/UCM value (1.6) would indicate the contribution of fresh oil to the sediments. The presence of light *n*-C10 confirms this contribution. According to UNEP (1995) the (Pri + Phy/ *n*-C17) ≫ 1 relationship indicates the presence of degraded crude oil. The value of this relation for Station 12 was 0.22, which confirms fresh oil contribution and recent pollution from the source. Values of *n*-C17/Pri and *n*-C18/Phy relationship (1.1 and 0.8, respectively) could indicate degradation processes. In order to assess the extent of the port activities impact on the ecosystem, it is necessary to carry out a more exhaustive study at this region.

RAli/TOC relationships in river sediments showed a clear difference between the "biogenic" and "anthropogenic" stations. The lower values corresponded to river hydrocarbon baseline stations and the higher value to the station at port Rawson, where an important input of fresh derived petroleum hydrocarbons was found in the sediments. For example, Venkatesan et al. (1980) found differences in this relationship in sediments of two basins of southern California Bights. While in polluted sediments of San Pedro Basin the *n*-alkane/TOC relationship was 0.0009, in San Nicolas Basin it was lower by one order of magnitude. At the river hydrocarbon baseline stations, resolved aliphatic hydrocarbons represented 0.01% to 0.0004% of the total organic carbon and they were associated with terrigenous and riverine biogenic inputs. Much higher ratios would be expected if a significant amount of unweathered petroleum were incorporated in the sediments (Palacas et al., 1976). The significantly higher relationship showed at the Rawson port, where resolved aliphatic hydrocarbons represented 3.4% of the total organic carbon, suggests an important input of petroleum hydrocarbons. The relationship determined for the river hydrocarbon baseline can be used as a basis to assess future hydrocarbon inputs.

5. Conclusions

Hydrocarbon concentrations found in sediments of the Chubut river lower course can be considered as a baseline. These hydrocarbons have a predominant biogenic origin, mainly associated to terrestrial plants input to river sediments, while a minor contribution would be associated to algaes. These sediments can therefore be considered as non-polluted and may be used as reference for future studies. An exception was the station located at the Rawson Port, which showed net anthropogenic hydrocarbons at the highest concentration. The specific ratio RAli/TOC found is characteristic of the "province geochemistry" of the Chubut river and this relationship can serve as a sensitive indicator of future anthropogenic inputs of petroleum hydrocarbons to sediments. Future studies should include a more exhaustive evaluation of the impact of port activities. In addition, strict regulations are necessary to improve the environmental quality of this region and to avoid the impact of hydrocarbon contamination on fishing activities.

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