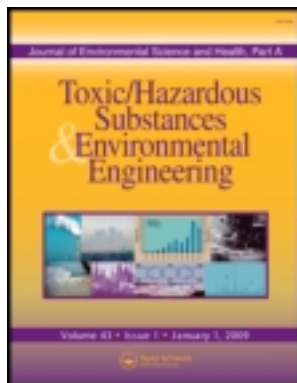


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Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments from the Neuquen River, Argentine Patagonia

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Spatial distribution and probable sources of aliphatic and polyaromatic hydrocarbons (AHs, PAHs) were investigated in surface sediments collected along the bank of the Neuquen River, Argentina. Total concentrations of aliphatic hydrocarbons ranged between 0.41 and 125 $\mu\text{g/g}$ dw. Six stations presented low values of resolved aliphatic hydrocarbons and the *n*-alkane distribution indexes applied suggested a clear biogenic source. These values can be considered the baseline levels of aliphatic hydrocarbons for the river sediments. This constitutes important information for the assessment of future impacts since a strong impulse in the exploitation of shale gas and shale oil in these zones is nowadays undergoing. For the other 11 stations, a mixture of aliphatic hydrocarbons of petrogenic and biogenic origin was observed. The spatial distribution reflects local inputs of these pollutants with a significant increase in concentrations in the lower course, where two major cities are located. The highest values of total aliphatic hydrocarbons were found in this sector which, in turn, was the only one where individual PAHs were detected.

Keywords: Neuquen River, sediments, hydrocarbon pollution, biogenic source, petrogenic source, evaluation indexes, baseline levels.

Introduction

The Province of Neuquen is part of the northern region of the Argentine Patagonia, where the most relevant economic activities are the exploitation of energy resources, agriculture and tourism. To the west lies the Andes Mountain Range, the border between Argentina and Chile, where starts a large river system that flows to the east, across a vast semi-desert zone. Urban and industrial activities are concentrated in the lowlands, in the center of the province. The oil and gas fields located in this area produce 48% and 23%, respectively, of Argentina's total production, totaling 23,336.3 MMm^3 of gas and 8,310.7 Mm^3 of oil in the year 2009.^[1] Therefore, this zone is exposed to oil pollution mainly derived from drilling, production and transport of crude oil, although it also receives urban, agricultural and

industrial waste. The Neuquen River is the second largest in the province, draining a basin of 32,450 km^2 . This river is the only water supply for approximately 400,000 inhabitants, mostly settled on the eastern edge of the province.

Petroleum hydrocarbons in the air and water can enter river sediments by adsorption and deposition and, at the same time, petroleum hydrocarbons in sediments can re-enter the air and water by geochemical circulation, increasing secondary pollution.^[2] The mutagenic and carcinogenic effects of some high-molecular-weight polyaromatic hydrocarbons have been clearly recognized for several years and due to their high persistence and hydrophobic nature, these pollutants constitute a potential risk to the biota and to human health.^[3,4] Although hydrocarbons are naturally occurring compounds which can be present at low concentrations in different environmental matrices, anthropogenic activities are mainly responsible for high concentration levels reported worldwide, both in the sediments of rivers and marine coasts.^[5–7] Sediments are considered nonpolluted if hydrocarbon levels are not greater than 10 $\mu\text{g/g}$ of dry weight.^[8]

Although the Neuquen River is an important source of water supply for human, agricultural and industrial

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activities in the region, no systematic studies have been conducted to evaluate hydrocarbon levels. The goals of this study were (i) to determine the current levels and spatial distribution of aliphatic and polyaromatic hydrocarbons in sediments from the river, (ii) to evaluate their possible sources by applying *n*-alkane distribution indexes and (iii) to find the baseline levels of hydrocarbons in the sediments from the river.

Material and methods

Study area

The Neuquen River starts in the Andes and flows southeast to the Atlantic Ocean, with a length of approximately 500 km. It is a typical mountain river with an average flow rate of 300 m³/s which increases substantially during the snow melt season.^[9] The river is regulated by a dam in the middle course. The study area (Fig. 1) was divided into three sectors: RNQN1 Upper Course, near the city of Chos Malal (37°22'S, 70°16'W) (3 stations); RNQN2 The Lakes, where the Cerros Colorados Hydroelectric Complex and the Loma La Lata gas exploitation field (38°30'S, 68°50'W) are located (2 stations); and RNQN3 Middle and Lower Courses, including two major cities, Neuquen (38°56'S, 68°04'W) and Cipolletti (38°55'S, 67°59'W), oil exploitation fields and the agricultural area (12 stations).

Sample collection and storage

Sampling was carried out from August 2007 to March 2008. Each location was accessed by GPS assistance. Surface sediment samples (0–3 cm) were collected from six random points at each station using stainless steel spatulas. The composite samples were preserved in clean, solvent-rinsed glass jars, transported in portable coolers and frozen immediately at 18°C below zero, until analysis. Defrosted samples were homogenized, air dried at 32°C, and divided into subsamples for the determination of grain size, water content, ignition loss and hydrocarbon concentrations.

Grain size analysis

A subsample of each site was divided into three fractions by sieving through meshes of 75 μm and 200 μm. They consisted of: the silt and clay fraction <75 μm, the sand fraction between 75 μm and 200 μm and the gravel fraction >200 μm.

Ignition loss analysis

Sediment samples were placed in pre-weighed crucibles and dried at 105°C for 48 h to determine dry weight and then calcined in a muffle furnace at 450°C for 4 h to obtain ignition loss. In this study it was assumed that ignition loss

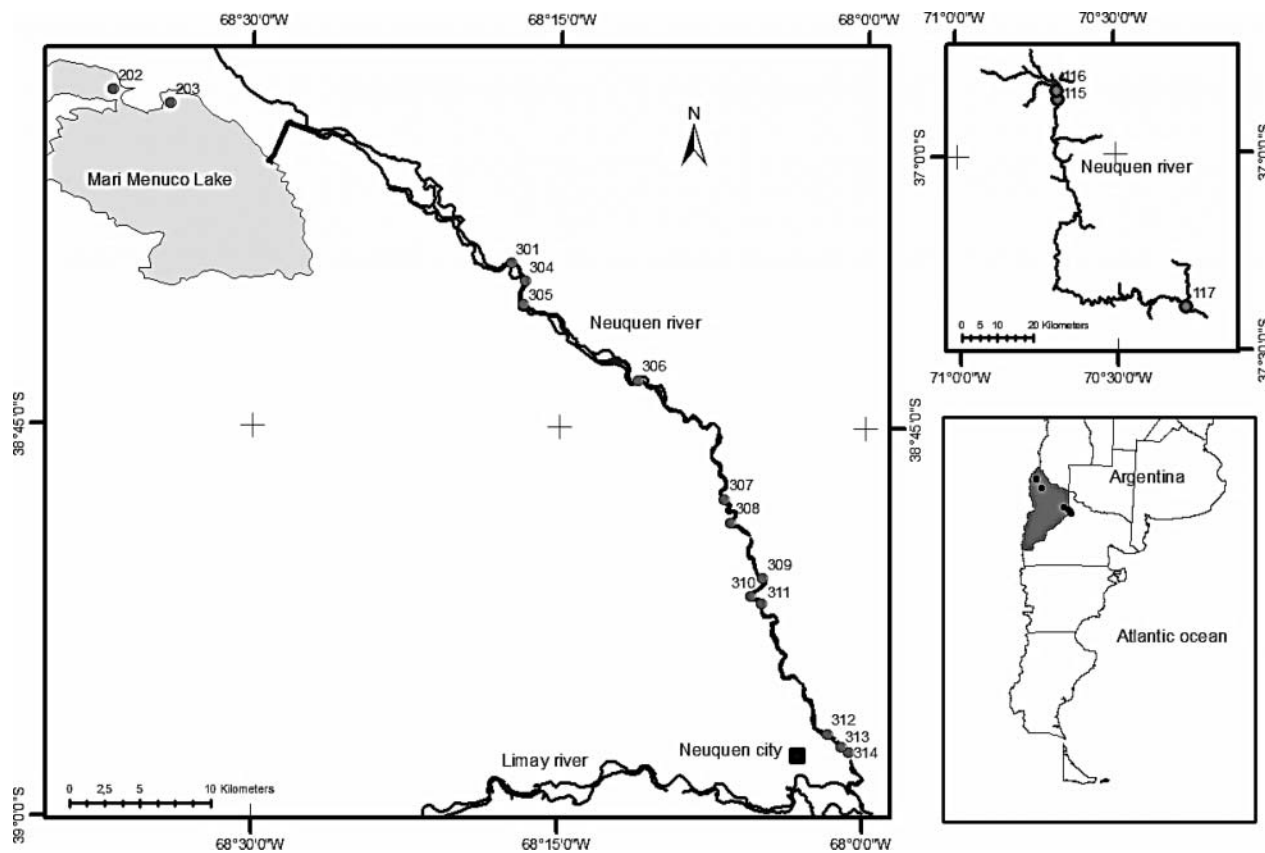


Fig. 1. Sediment sampling locations along the Neuquen River bank.

represents an approximation of the organic matter content (OM) in the samples.

Hydrocarbon analysis

Extraction and fractionation of hydrocarbons

Hydrocarbon analyses were performed according to the Method for the Determination of Extractable Petroleum Hydrocarbons of the Massachusetts Department of Environmental Protection (MADEP),^[10] EPH-04 Revision 1.1. Accurately weighted sediment samples (about 10 g) were refluxed in Soxhlet extractors with dichloromethane (16 h, 3–4 cycles/h); activated Cu was added to remove sulfur. The extract was rotary evaporated up to around 10 mL; the solvent was exchanged to *n*-hexane and finally concentrated to 1 mL under a gentle nitrogen stream in thermostatic bath at 35°C.

Clean-up and fractionation of the AHs and PAHs were carried out using a glass chromatographic column packed with pre-activated silica gel (Sigma-Aldrich [Steinheim, Germany], 923 grade, 100–200 mesh). The total extract (1 mL) was added to the top of the column using a glass pipette. The AHs fraction (F_1) was eluted with 20 mL of *n*-hexane and a second fraction (F_2), for the separation of PAHs, was eluted with 20 mL of dichloromethane. Each fraction was concentrated to 1 mL under a nitrogen stream, transferred to a glass vial and quantitated by gas chromatography.

Gas chromatography analysis

Aliphatic and polyaromatic hydrocarbons were analyzed separately using an Agilent (Miami, USA), 6890 gas chromatograph equipped with a ZB-5 fused silica capillary column (30 m x 0.25 mm i.d., 0.25 μ m film thickness), split/splitless injection system and a flame ionization detector (FID). Analyses were conducted in splitless mode using nitrogen as a carrier gas at a flow rate of 2 mL/min. The column temperature was programmed from 60°C to 300°C at a rate of 6°C/min and held at 300°C for 5 min. Injector and detector temperatures were held at 300°C. Resolved aliphatic hydrocarbons (rAH) were identified by comparison of retention times with standards ranging from *n*-C₉ to *n*-C₃₃. Both rAH and unresolved complex mixture (UCM) were quantified based on the standard calibration curves.

The same scheme was used for the identification and quantitation of the 16 EPA priority PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, 1–2 benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene and benzo[*ghi*]perylene. The structure of the PAHs was confirmed by gas chromatography/mass spectrometry (Agilent 6890N GC, Agilent 5973 MSD). The

analysis was performed on a 30 m HP-5 MS fused silica column (0.25 mm i.d., 0.25 μ m film thickness). Helium was used as a carrier gas at a flow rate of 1.5 mL/min and the following temperature program for the column was applied: 38°C (1 min) to 300°C with ramping at 6°C/min and held 5 min at 300°C. The samples (5 μ L) were injected with a PTV (Programmed Temperature Vaporization) injector at 250°C. Samples were run in the electron impact mode at 70 eV and in the selected ion monitoring (SIM) mode with a 4.04 s scan time over a 50–450 amu range resolution. Each compound was recognized by a target ion and two qualifiers.

Quality assurance/quality control

The analytical method was subject to a previous quality control. For aliphatic compounds, replicates ($n = 3$) showed recovery values of $81.4 \pm 0.74\%$ using *n*-C_{16_d} and *n*-C_{12_d} as internal and surrogate standards, respectively, while the recoveries of PAHs were $93.5 \pm 0.62\%$ using 5- α -androstane as an internal standard and *o*-terphenyl as a surrogate. The detection limit (LOD) was $0.022 \pm 0.008 \mu\text{g/g dw}$ for *n*-C_{9–20}; $0.040 \pm 0.010 \mu\text{g/g dw}$ for *n*-C_{21–33}; and $0.023 \pm 0.005 \mu\text{g/g dw}$ for the 16 PAHs. Solutions of synthetic standard mixtures (AccuStandard, New Haven, CT, USA) containing *n*-C_{8–40} and the 16 PAHs, respectively, were used as calibration standards. Procedural blanks (solvent) and procedural controls (standards spiked into solvent) were run along with each batch of samples processed. In addition, surrogate compound *o*-terphenyl was added to all the samples and blanks to monitor procedural performance and matrix effects. The mean recovery for surrogate in sediment samples was better than 90%. The results reported in this study were not corrected by recoveries.

Evaluation indexes

To assess the possible origin of the hydrocarbons found in this study a combination of several indexes was applied in addition to the assessment of absolute concentrations at each station. The indexes selected and used in this study were:

- Low molecular weight to high molecular weight ratio (LMW/HMW). It is defined as the concentration ratio of low molecular weight (sum of *n*-alkanes \leq C₂₀) to high molecular weight (sum of *n*-alkanes \geq C₂₁). It has been reported that LMW/HMW ratios < 1 usually represent *n*-alkanes produced by higher plants and sedimentary bacteria, while ratios close to 1 suggest *n*-alkanes that are mainly from petroleum and plankton sources.^[11] Higher LMW/HMW ratios suggest the presence of fresh oil in sediments.^[12]
- Carbon Preference Index (CPI). The CPI is a robust indicator that is used to distinguish between sources

- of hydrocarbons from vascular plants and those from fossil fuel contamination. The CPI was calculated as $2(C27 + C29)/(C26 + 2C28 + C30)$. CPI values ranging from 3 to 6 are typical of vascular plant contribution while petrogenic hydrocarbons and highly degraded organic matter show CPI values close to 1.^[13, 14]
- (c) Major hydrocarbon (MH). It denotes the highest *n*-alkane concentration. This index is often around C18 for crude oil while C15, C17, C19 and C21 have been described as components of different types of algae. Odd *n*-alkanes in the range of C23 to C31 are associated with vascular land plants.^[15-17]
- (d) Even to odd ratio (Even/Odd). Petroleum typically shows a wide range of *n*-alkanes while in most plant waxes odd chain alkanes are 8 to 10 times more abundant than even chain *n*-alkanes.^[18]
- (e) Pristane/Phytane ratio (Pri/Phy). Pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetra-methylhexadecane) are present in most oils and they can also occur as a result of diagenetic processes. Thus, they are often considered as good indicators of petroleum contamination. However, a high concentration of pristane may reflect a zooplankton contribution while phytane is practically absent in uncontaminated recent sediments.^[18, 19] Values of the Pri/Phy ratio close to 1 suggest petroleum derived hydrocarbons and values from 1.4 to 6.7 suggest biogenic hydrocarbons.^[15, 20]
- (f) Sum of resolved aliphatic hydrocarbons/unresolved complex mixture ratio (rAH/UCM). The UCM is considered to be a mixture of many structurally complex isomers and homologues of branched and cyclic hydrocarbons that cannot be resolved by capillary GC columns and appear as a hump in the chromatogram.^[21] The UCM magnitude is related to the degree of anthropogenic contribution. Although the UCM is associated with petroleum hydrocarbons, it can also result from bacterial degradation of organic matter.^[22] Low values of the rAH/UCM ratio suggest degraded or weathered petroleum residues but are also associated with others sources of degraded organic matter.^[23]
- (g) *n*-C17/Pristane and *n*-C18/Phytane. These ratios are used to indicate microbial degradation. Biodegradation rates for *n*-alkanes are faster than those of isoprenoids. Low values for these indexes suggest the presence of degraded oil. When hydrocarbon concentrations are also high, higher indexes suggest fresh oil inputs.^[16, 24]

Resolved aliphatic hydrocarbons and total organic matter

The ratio of compounds classes (i.e., hydrocarbons) or individual compounds at trace levels, present in ng/g or $\mu\text{g/g}$, compared to a bulk parameter, such as total organic carbon (TOC), present in mg/g, can be used to evaluate existing geochemical ratios and to evaluate future incremental additions. An increase in the concentration of the trace param-

ter due to an oil input may cause a marked increase in levels at a given station, but have little effect on the value of the bulk parameter. Consequently, these ratios can be used as a sensitive indicator of anthropogenic input of petroleum hydrocarbons to the sediments.^[13] In sediments that are receiving a normal input of a polluting agent within one given region, a specific rAH/TOC ratio is characteristic of the "province geochemistry".^[25]

Results and discussion

Granulometry and organic matter

Grain size composition of the sediments varied according to the sampling site. In most of the samples, the sediments were mainly gravel and sand (Table 1). Fine material greater than 3% was found at stations 301, 304, 307 and 310. At station 115 a high value (56%) was observed due to the volcanic origin of the sediments in this zone. The organic matter levels ranged from 0.91% to 2.78% at 16 stations and only at station 310 was it 22.04%, probably due to the discharge of a juice processing plant located upstream. Numerous studies have demonstrated that organic matter plays a crucial role in the accumulation of organic pollutants, including hydrocarbons.^[7, 26]

Total aliphatic hydrocarbon concentrations showed a strong correlation with organic matter ($r = 0.78$, $p < 0.05$, $n = 17$), yet the correlation between total concentration of aliphatic hydrocarbons (tAH) and fine material was $r = 0.29$ ($p < 0.05$, $n = 16$, station 115 excluded).

The correlation coefficient between fine material and OM was $r = 0.49$ ($p < 0.05$, $n = 16$, station 115 excluded).

Hydrocarbon concentrations and evaluation indexes

The amount of *n*-alkanes and UCM was combined to provide the total concentration of aliphatic hydrocarbons (tAH). Total concentrations ranged from 0.41 $\mu\text{g/g}$ dw to 124.96 $\mu\text{g/g}$ dw and UCM was detected at 6 stations. Table 2 shows the results at each station. The trend of the absolute concentrations of tAH expressed as $\mu\text{g/g}$ dw is preserved when these are normalized by the OM content (Fig. 2) with only two exceptions: samples from stations 304 and 310, which would suggest the presence of OM from different origins at these stations.^[7] The OM at station 310 is the highest found in this study and can be explained by the contribution of the effluent of a juice plant located upstream from this station.

RNQN1

In sector RNQN1 neither industrial activities nor petroleum exploitation take place; however, the chromatograms showed an important contribution of UCM to the tAH concentrations at stations 116 and 117. Even

Table 1. Grain size composition and organic matter in surface sediment samples from the Neuquen River.

Station	Location	Fine % ^a	Sand % ^b	Gravel % ^c	OM%
RNQN 115	Confluence of the rivers Varvarco and Upper Neuquen	56.6	39.1	4.3	2.10
RNQN 116	Upper Neuquen River	0.0	5.8	94.2	1.38
RNQN 117	Chos Malal City	0.0	6.8	93.2	1.56
RNQN 202	Barreales Lake	1.4	10.2	88.4	1.87
RNQN 203	Mari Menuco Lake	1.7	11.5	86.8	1.45
RNQN 301	Oil Field "Río Neuquen" st. 1	4.7	27.6	67.7	2.00
RNQN 304	Downstream drainage channel El Chañar	10.4	80.1	9.5	2.65
RNQN 305	El Chañar Beach	0.0	21.4	78.6	1.32
RNQN 306	Oil Field "Río Neuquen" st. 2	2.9	30.5	66.6	1.92
RNQN 307	Drainage channel Costa de Reyes	5.5	23.0	71.5	2.78
RNQN 308	Downstream drainage channel Costa de Reyes	1.4	20.4	78.2	1.25
RNQN 309	Centenario City North	1.7	17.7	80.6	0.91
RNQN 310	Drainage channel Nueva España	7.4	13.9	78.7	22.04
RNQN 311	Centenario City South	1.0	10.5	88.5	2.00
RNQN 312	Neuquen City-Northern access	1.3	13.7	85.0	1.50
RNQN 313	Cipolletti City st. 1	2.1	42.8	55.1	1.90
RNQN 314	Cipolletti City st. 2	2.4	19.6	78.0	2.29

^aFine fraction <75 μm .

^bSand fraction between 75 μm and 200 μm .

^cGravel fraction >200 μm .

though the concentrations of rAH remained low (1.11 $\mu\text{g/g}$ dw to 6.03 $\mu\text{g/g}$ dw), tAH levels in the Upper Neuquen River (116) and Chos Malal (117) can be compared with those reported in polluted areas of the Chubut River in Patagonia.^[17] The tAH represents 5.19‰ of the total organic carbon in sample 116 and 6.65‰ in 117, while this value falls to 0.26‰ at station 115. These relationships suggest an anthropogenic hydrocarbon input at the first two stations, reinforced by the presence of *n*-C24 as the MH which reflects bacterial activity.^[27] Long-chain homologues were predominant at the three sites studied of this sector, as shown by the LMW/HMW < 1 ratio, but only at

station 115 does the Even/Odd ratio reflect the prevalence of odd chain *n*-alkanes (Table 3) where C29 was the MH. Pristane was found at stations 115 and 117 at 0.02 $\mu\text{g/g}$ dw while phytane concentrations reached 0.03 $\mu\text{g/g}$ dw and 0.05 $\mu\text{g/g}$ dw, respectively (values not shown in Table 3).

In uncontaminated sediments, phytane levels should not exceed 1 ng/g dw.^[14,28] At the same time, the homologous series of *n*-alkanes was observed at the three stations with a prevalence of low molecular weight hydrocarbons (Fig. 3). Besides the chromatographically resolved compounds, an unresolved complex mixture of branched and cyclic hydrocarbons eluting between *n*-C19 and *n*-C29 was present

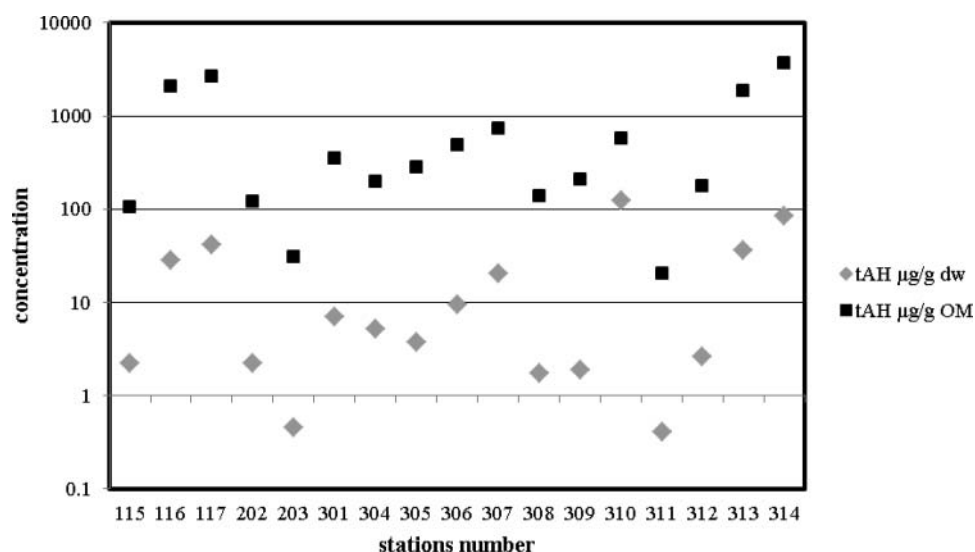
**Fig. 2.** Total aliphatic hydrocarbon (tAH) concentrations expressed in $\mu\text{g/g}$ dw and $\mu\text{g/g}$ OM.

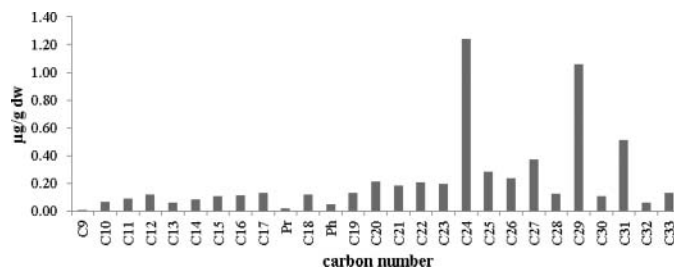
Table 2. Concentrations of resolved aliphatic hydrocarbons, unresolved complex mixture and total aliphatic hydrocarbons in surface sediment samples from the Neuquen River in $\mu\text{g/g dw}$.

Station	rAH ^a	UCM ^b	tAH ^c
115	2.22	nd	2.22
116	1.11	27.56	28.67
117	6.03	35.48	41.51
202	2.25	nd	2.25
203	0.45	nd	0.45
301	6.92	nd	6.92
304	5.26	nd	5.26
305	3.75	nd	3.75
306	9.45	nd	9.45
307	8.20	12.28	20.48
308	1.73	nd	1.73
309	1.89	nd	1.89
310	54.05	70.91	124.96
311	0.41	nd	0.41
312	2.64	nd	2.64
313	10.92	24.81	35.73
314	3.75	81.37	85.12

^arAH: resolved aliphatic hydrocarbons.^bUCM: unresolved complex mixture.^ctAH: total aliphatic hydrocarbons.

nd: not detected.

in the samples from stations 116 and 117, which represented 96% and 85%, respectively, of the tAH concentrations at these stations, with rAH/UCM ratio values of 0.04 and 0.17, respectively. The AH levels at stations 116

**Fig. 3.** *n*-alkanes and isoprenoids distribution pattern in surface sediments from the Neuquen River at st.117. Mixtures of petrogenic and biogenic hydrocarbons.

and 117 may be explained by the discharge of the Chos Malal sewage plant and/or local inputs near the locations. Although station 115 showed the lowest concentration of tAH in the sector ($2.22 \mu\text{g/g dw}$), it cannot be considered a baseline value due to the presence of homologous series of *n*-alkanes. Future studies must be conducted in this area.

In summary, the results described above allow for the hydrocarbons found in this sector to be classified as a mixture of terrigenous and biogenic, with a low anthropogenic contribution at station 115 and moderate anthropogenic inputs at stations 116 and 117.

RNQN2

This area comprises the major oil and gas fields in the region without urban settlements. In this sector the absolute concentrations of rAH found were $2.25 \mu\text{g/g dw}$ at

Table 3. Evaluation indexes for aliphatic hydrocarbons in surface sediment samples from the Neuquen River.

Station	MH ^a	LMW/HMW ^b	CPI ^c	rAH/UCM ^d	<i>n</i> -C17/Pr	<i>n</i> -C18/Ph	Pr/Ph	Even/Odd ^e
115	C29	0.46	4.15	—	6.69	3.87	0.61	0.55
116	C26	0.30	1.16	0.04	—	5.24	—	1.09
117	C24–29	0.27	4.80	0.17	6.95	2.43	0.38	0.83
202	C20	1.19	1.47	—	6.27	—	0.19	1.09
203	C29–31	0.26	4.24	—	—	—	—	0.56
301	C29–31	0.36	8.53	—	1.58	1.55	1.04	0.34
304	C29	0.04	10.95	—	—	—	—	0.16
305	C27–29	0.51	7.52	—	1.39	1.41	1.02	0.43
306	C29	0.48	8.87	—	1.95	2.04	0.82	0.41
307	C29	0.13	11.08	0.67	—	1.40	—	0.21
308	C29	0.11	14.36	—	—	—	—	0.26
309	C29	0.24	10.61	—	—	—	—	0.43
310	C27	0.25	1.36	0.76	0.20	2.66	1.12	0.79
311	C29	0.09	—	—	—	—	—	0.62
312	C29	0.25	9.00	—	—	—	—	0.41
313	C29	0.14	6.16	0.44	0.80	0.71	0.79	0.39
314	C24–29	0.20	13.37	0.05	—	2.54	—	0.33

^aMH *n*-alkane detected at the highest concentration.^bLMW/HMW = $\sum_{\leq n-C20} / (\sum_{\geq n-C21})$; ^cCPI = $2(n-C27+n-C29)/(n-C26+2n-C28+n-C30)$.^drAH/UCM = resolved aliphatic hydrocarbons/unresolved complex mixture ratio.^eEven/Odd = $\sum n-C\text{even} / \sum n-C\text{odd}$.

(–) Not calculated due to most compounds were not detected.

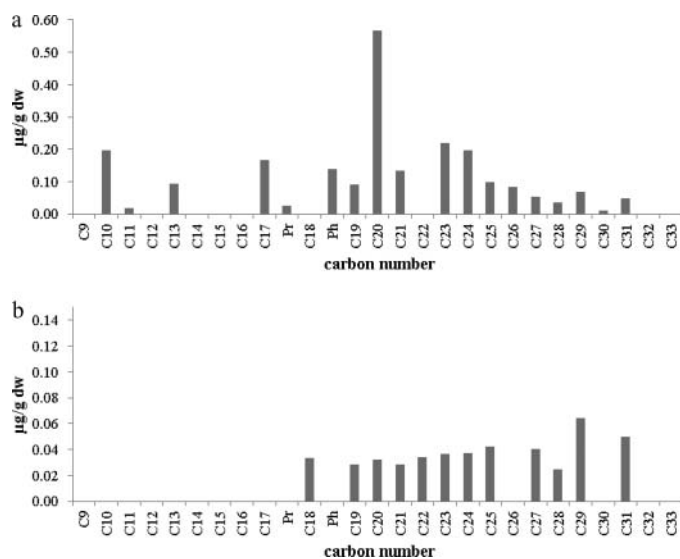


Fig. 4. *n*-alkanes and isoprenoids distribution pattern in surface sediments from the Neuquen River at a) st. 202, petrogenic hydrocarbons in low concentrations; b) st. 203, terrigenous biogenic hydrocarbons.

station 202 (Barreales Lake) and $0.45 \mu\text{g/g dw}$ at station 203 (Mari Menuco Lake). UCM was not detected. Even though the concentrations found were quite low, the distribution pattern between sites showed significant differences. In the Barreales Lake sample a homologous series of *n*-alkanes with the MH in C20 was observed (Fig. 4a); pristane and phytane concentrations were $0.03 \mu\text{g/g dw}$ and $0.14 \mu\text{g/g dw}$, respectively (not shown). The LMW/HMW, Even/Odd and CPI indexes denote a petrogenic source of the hydrocarbons found at this station (Table 3), whereas

the sample pattern of Mari Menuco Lake (Fig. 4b), based on the same indexes, suggests a terrestrial biogenic source.

The results of the rAH/TOC ratio were 3.01×10^{-4} at station 202 and 7.76×10^{-5} at station 203. The fine material and OM content are consistent with the geographical characteristics of the region: sparse shrub steppe. Much higher ratios would be expected if a significant amount of unweathered petroleum were incorporated in the sediments.^[29, 30] Despite the presence of petrogenic hydrocarbons in the sediments of Barreales Lake (202), the tAH concentrations at both stations can be compared with those reported in nonpolluted areas of the Atlantic Coast of Patagonia.^[31] The values found in Mari Menuco Lake (203) can be considered as the baseline value for aliphatic hydrocarbons in the area.

RNQN3

Absolute concentrations of rAH in all stations of this sector ($n = 12$) ranged between $0.41 \mu\text{g/g dw}$ and $54.05 \mu\text{g/g dw}$ (Table 2). Stations 304, 308, 309 and 311, located in the agricultural zone, and station 312, located along the northern access of the city of Neuquen, showed an absolute concentration of rAH $<6 \mu\text{g/g dw}$ without the presence of UCM (Fig. 5). The MH was C29 and the isoprenoids pristane and phytane were not detected or detected only at traces levels. The LMW/HMW and the Even/Odd ratio values denote the predominance of chains with an odd number of carbons and high molecular weight (Table 3). The absence of homologous series of *n*-alkanes and the low concentrations of tAH of a biogenic source associated with terrestrial plants (Fig. 6a and 6b) allow the origin of the compounds found in these samples to be classified as

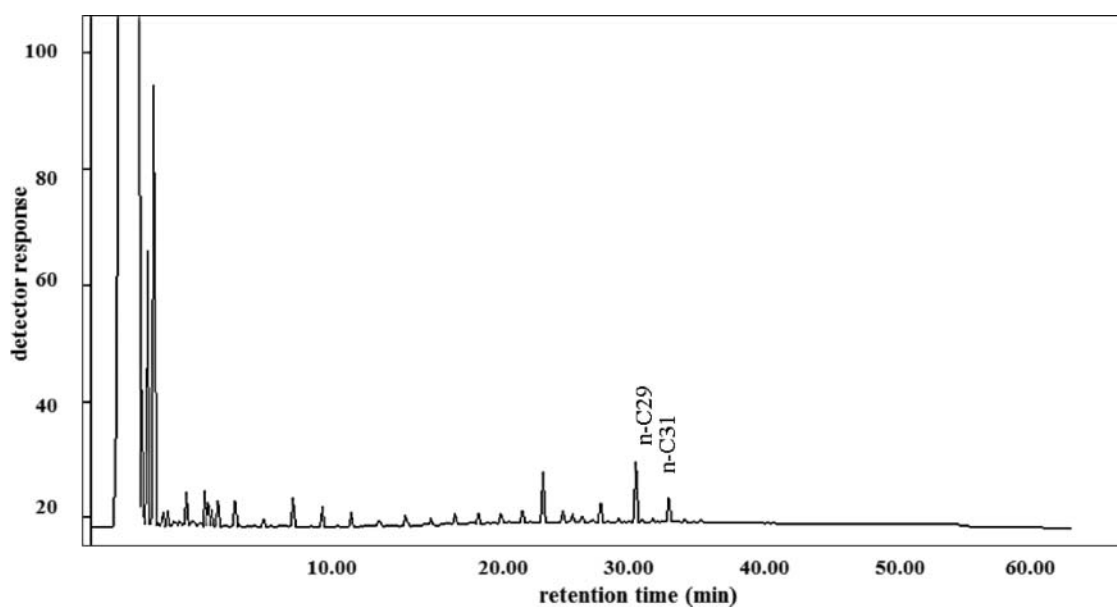


Fig. 5. GC-FID chromatogram of aliphatic hydrocarbons from surface sediments from the Neuquen River at st. 311, biogenic aliphatic hydrocarbons, low total concentration and MH *n*-C29.

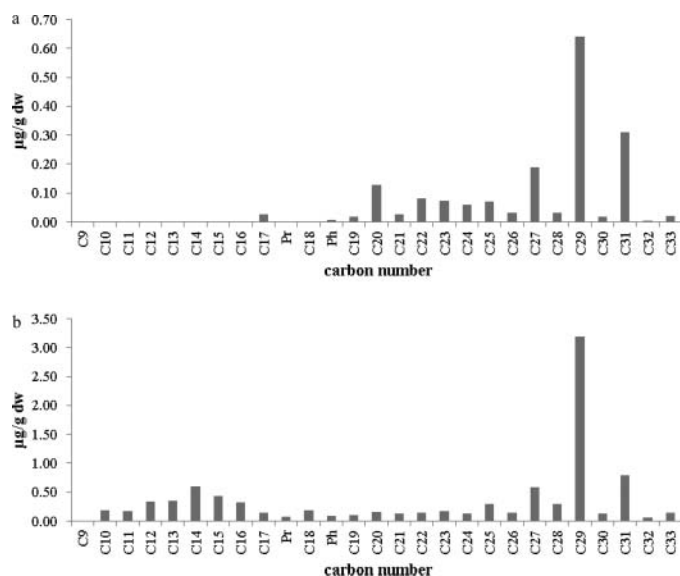


Fig. 6. *n*-alkanes and isoprenoids distribution pattern in surface sediments from the Neuquen River at a) st. 308, biogenic hydrocarbons in very low concentrations; b) st. 306, petrogenic hydrocarbons in low concentrations, homologous series of *n*-alkanes.

terigenous biogenic hydrocarbons. The results found at these 5 stations suggest that the sediments in these samples can be considered as nonpolluted and therefore these values constitute the baseline for aliphatic hydrocarbons in the middle and lower course of the Neuquen River and may be used to evaluate future impact.

At sites 301, 305 and 306, located along the oil fields, rAH concentrations were $<10 \mu\text{g/g dw}$ and UCM was not detected. However, a probable petrogenic input was evidenced by the presence of an even chain distribution

of *n*-alkanes in the range C10–C32, with a maximum in C14. Pristane and phytane concentrations ranged between $0.08 \mu\text{g/g dw}$ and $0.20 \mu\text{g/g dw}$ and the Pri/Phy ratio was close to 1; this ratio varies within oils types and is thought to reflect the depositional environment of the original source rocks.^[32] The *n*-C17/Pr and *n*-C18/Ph ratio values suggest a recent input of contaminants, probably mixtures of oil-derived compounds.

Besides petrogenic hydrocarbons, those associated with terrestrial plants contributed to tAH concentrations, as is emphasized by the low values of the LMW/HMW ratio, the Even/Odd indexes and the MH in *n*-C29. In summary, it can be assumed that the origin of the hydrocarbons found at these stations is a biogenic and petrogenic mixture, in low concentrations. The remaining 4 stations, situated downstream from the discharge of agricultural drainage channels (307 and 310) and along the riverside near the city of Cipolletti (313 and 314), presented a significant contribution of UCM to the tAH concentrations.

The rAH concentrations ranged between $3.75 \mu\text{g/g dw}$ and $54.05 \mu\text{g/g dw}$, and the tAH concentrations from $20.48 \mu\text{g/g dw}$ to $124.96 \mu\text{g/g dw}$ (Table 2) with homologous series of *n*-alkanes in all the samples. The stations corresponding to the agricultural production zone showed higher tAH concentrations with a moderately degraded UCM, centered in C29. These channels are steady; however, their flow rate increases substantially during the irrigation season, from October to March. The pollution at these stations can be attributed to local human inputs, such as household and agricultural solid wastes. Similar effects were observed at the stations situated downstream from the urban area (313 and 314), where the UCM greatly contributed to the tAH concentrations found (Fig. 7); in these cases it was more

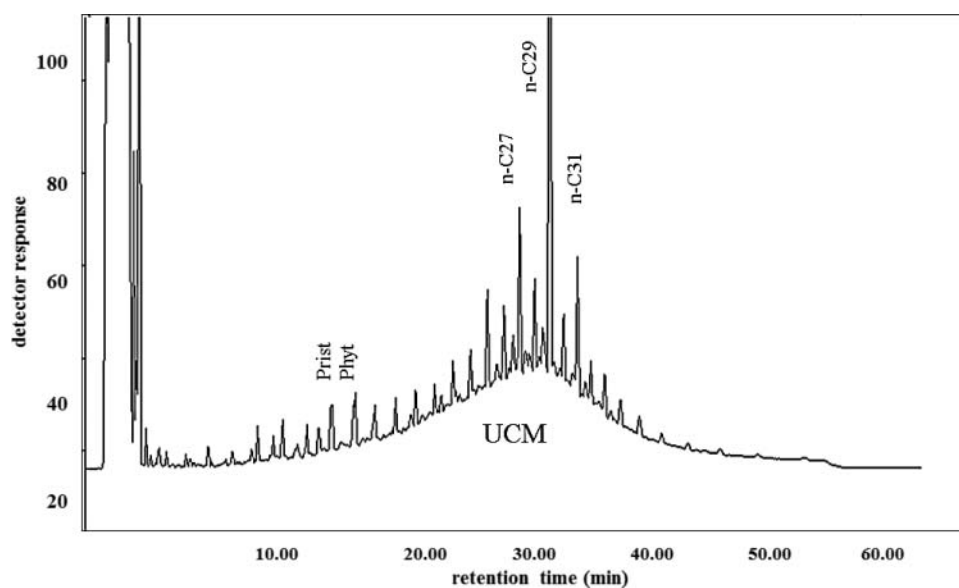


Fig. 7. GC-FID chromatogram of aliphatic hydrocarbons from surface sediments from the Neuquen River at st. 313, MH *n*-C29, homologous series and UCM; low to moderate degradation.

degraded and there was evidence of bacterial activity. This sector of the river receives the discharges of two sewage plants.

The highest value for this sector corresponded to station 310 where the MH was C27, an odd chain carbon related to plant wax. However, the Even/Odd ratio and CPI value close to 1 reflect the presence of a homologous series of *n*-alkanes. Pristane and phytane concentrations at this station were 0.87 $\mu\text{g/g dw}$ and 0.78 $\mu\text{g/g dw}$, respectively, the highest recorded in this study. The (Pr+Ph)/*n*-C17 ratio was 9.25 (not shown in Table 3), which suggests the presence of degraded crude oil.^[25]

The results and combination of the indexes denote mainly an anthropogenic origin of the hydrocarbons found in the samples studied. In summary, it can be observed that the spatial variability of the concentrations of aliphatic hydrocarbons in sediments is mostly affected by local inputs. The pollutants accumulate in the drainage channels, which are almost stagnant much of the year, and seem to reach the river during the irrigation season. Nevertheless, at the stations located along the river downstream from the channels (308 and 311) hydrocarbon levels remained low, reflecting the dilution effect.

At station 313, naphthalene and pyrene were found at 40 ng/g dw and 50 ng/g dw, respectively. At the 16 remaining stations the PAHs analyzed were not detected. Even though the total PAHs concentrations found are in line with those reported in nonpolluted zones, such as Jubany Station, Antarctica,^[33] the individual concentrations are close to the maximum levels established in the Canadian Soil Quality Guidelines.^[34] The presence of PAHs at station 313 can be attributed to different sources, such as the sewage input and/or pyrolytic origin. In order to assess the extent of the pollution and the impact to the ecosystem, a more exhaustive study should be carried out in this sector of the river.

Resolved aliphatic hydrocarbons/ Total organic carbon

The values of the rAH/TOC ratio for all stations ranged from 5.13×10^{-5} to 1.44×10^{-3} with an average of $5.69 \times 10^{-4} \pm 3.87 \times 10^{-4}$ ($n = 17$). This ratio showed clear differences between the stations with hydrocarbons of biogenic origin and those of anthropogenic origin. The lower values corresponded to the stations that are considered as baseline values for hydrocarbons in this study (203 and 311), which represented less than the 0.08‰ of TOC, mainly associated with terrigenous and riverine biogenic inputs. On the other hand, the hydrocarbons found at station 313 represented 1.44‰ of TOC, which suggests an important input of pollutants. Similar results have been reported by Commendatore and Esteves for the Chubut River (Argentine Patagonia),^[17] where hydrocarbons in TOC were not higher than 0.1‰ in the nonpolluted sediments.

Conclusions

This study represents the first scientific contribution to the knowledge of environmental pollution by hydrocarbons in an area where intensive oil exploitation has been conducted for more than 60 years, near a growing urbanization. The main rivers in the region are located in the area studied, which are of great relevance to co-existing economic activities (agricultural, ichthyic), and in turn provide the only source of drinking water for adjacent communities.

Assessment of the spatial distribution and the probable source of hydrocarbons in sediments of the Neuquen River are provided first time. The results provide current information regarding the river conditions. In general, the sediments of the Neuquen River present a relatively low degree of contamination, according to the recommendations of the UNEP.^[8] In the different areas studied, it was possible to locate sectors where the levels of hydrocarbons found can be used as baseline values, with the presence of hydrocarbons of biogenic origin in very low concentrations. This information is important in view of possible future dumping which may occur in these sectors. Furthermore, the results obtained in the most populated areas highlight the vulnerability of this watercourse in terms of anthropogenic pressure. In the sectors along the outskirts of the cities of Cipolletti and Neuquen, a monitoring plan should be implemented, given that the values found in these sectors and the evaluation indexes applied denote a greater degree of deterioration.

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