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Application of some physical organic chemistry models to the study of oil spills residues in Patagonian soils

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The present study focuses on the application of some physical organic chemistry (POC) models for a better understanding of the interactions between oil spills and soil. By studying the sorption behavior of pure compounds, it was possible to examine the application of the multilayer model to the prediction of crude oil isotherms. The difference between the predicted and experimental oil isotherms was only 13%, which indicates the reliability of the model. The distribution coefficients, K_d, of soil samples containing oil residuals of different ages, were also determined using methanol as a co-solvent. Desorption experiments showed that they are a function of the polarity of the liquid phases; the K_ds, calculated by applying a model derived from the solvophobic theory, increase with increasing age. On the other hand, the natural attenuation of oil spills was studied by using GC and ^{1}H NMR techniques. Signals for four types of aliphatic and for the aromatic protons were clearly assigned; signals for alcohol (O*H*) and carboxylic (COO*H*) protons were also observed; compounds exhibiting these polar groups are usually not detected in the GC–FID conventional analysis. The principal component analysis (PCA) of K_d, and the parameters determined by GC and NMR, showed that the first and second PC, accounted for more than 95 and 81% of variance, for NMR and GC parameters, respectively. The detailed results suggest that the ^{1}H NMR data would be more useful than GCs to evaluate the environmental transformations that oil spills undergo in Patagonian soils. Nevertheless, direct extrapolation of the present results to other environments is not possible because the changes depend strongly on the original chemical composition of the crude oil and the variable exposure conditions along the time. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

The fate of organic chemicals in the environment is strongly dependent on the different degree of sorption of the chemical species to soil; a good understanding of the factors affecting sorption is essential for the assessment of the potential adverse impacts. The degree of sorption not only affects the chemical mobility but also other transport parameters and transformation reactions. Thus, the rates of volatilization, photolysis, hydrolysis, and biodegradation of many organic chemicals in the oil spills are directly dependent on the extent of sorption.[1] Empirical models to predict partition coefficients have been developed and research is also focused on the application of sorption and desorption kinetics of organic compounds in sediments[2] and soils,[3,4] as well as the effects of water on sorption and transport in soils.[5]

One of the purposes of this study was to examine the interactions between oil and soil in a range of concentrations, by using models developed for the sorption of pure compounds. Sorption determinations were carried out with pyridine, phenanthrene, and phenol in soil, to test the validity of the sorption model, after which the behavior of different oil fractions was studied. There are abundant reports in the literature on the development and extensive use of the mathematical relationships, and linear and Freundlich sorption isotherm models.[6–8] On the other hand, the Langmuir isotherm is a more general expression, and it is useful for the empirical 'fitting' of the sorption data[9–11] because of the presence of two constants. The Brunauer, Emmett, and Teller (BET) isotherm is another common expression. The major difference between the BET isotherm and the Langmuir isotherm lies on the consideration of multilayer sorption for the former. Nevertheless, in many cases it is not possible to fit all the sorption data with only one model.

Many efforts have been undertaken for a better determination of the risk associated with the presence of pollutants in soil.

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Selection of the technical options and implementation of management practices, must include an understanding of the fundamental relationships between the components of the complex mixtures in the environment (soil, water, natural organic matter, contaminants, etc.).[12] The behavior of the oil in aqueous phase is of critical importance because solute transport and transformation processes are known to occur predominantly in water.[3,13] As oil residuals are basically mixtures of hydrophobic compounds, the solubility in water is very low, but the concentrations in the aqueous phase can be increased by means of a co-solvent of a lower polarity, miscible in varied proportions.[5,14] Our previous work showed that variations observed in the concentrations and distribution coefficients of the oil residues, in the presence of different fractions of an organic co-solvent (methanol), can be interpreted by the solvophobic theory,[5] previously proposed for single solutes. On this basis, the aqueous concentrations and distribution coefficients in complex mixtures could be estimated. This is interpreted as an indication that, in principle, the oil residuals could be treated as a global solute of variable hydrophobic characteristics. Our results also showed that the distribution coefficients are affected by the ionic strength of the equilibrium aqueous phase and the soil salinity.[15] The effect of the aging of the residuals on the estimation of the distribution coefficients as well as its correlation with compositional and structural changes is described.

When petroleum is spilled in soil, its components undergo various physical and chemical modifications. Evaporation, biodegradation, photooxidation, etc. all contribute to the removal of hydrocarbon molecules from the geosphere. It is known that the more volatile fractions evaporates and biodegrades more rapidly,[3] that *n*-alkanes are more easily biodegraded than the branched alkanes,[16] and that aromatics are sensitive to photo- and biodegradation.[17] Since accidental spills of oil often cause serious damage to the natural environment, different parameters have to be analyzed in order to evaluate the natural attenuation. Several models have been proposed recently, most of them use gas chromatography (GC–FID or GC–MS),[18,19] based essentially on the identification and processing of chemical groups that have an enhancing or retarding effect on degradability.[20,21]

Two 'weathering' ratios evaluate the degree of biodegradation of *n*-alkanes, those are n-C_{17}/Pristane and n-C_{18}/Phytane, where Pristane is 2,6,10,14-tetrametylpentadecane, $C_{19}H_{40}$, and Phytane, 2,6,10,14-tetrametyl hexadecane, $C_{20}H_{42}$.[22] The ratio of *n*-alkanes to isoprenid alkanes gives information on the degree of weathering or freshness of the samples. For example, the chemical composition of the naturally weathered oil residues released over a period of 15 years in the Egyptian Western Desert was investigated by GC/MS spectrometry and a fresh crude oil sample was analyzed to provide a comparative data.[21] In another recent work, older fuel spill (1982) and younger fuel spill (1999) in Antarctica were examined using GC–FID characterization; the composition of fresh reference fuels were used for comparison with weathered soil samples.[23]

Other indexes based on GC are total extractable hydrocarbons (TEH, the total integration area of the n-C_{10}–n-C_{30} hydrocarbons that are extracted with methylene chloride); and the total resolvable hydrocarbons (TRH, only the hydrocarbons that are resolved as specific peaks in the same n-C_{10}–n-C_{30} zone, are taken into account). The ratio TRH/TEH measures the increase of the unresolved complex mixture (UCM) with the exposure time (the UCM is shown as a 'hump' in the GC: see Supplementary Material). Changes in the global residues volatility and molecular weight may be estimated by the average retention time (ART, calculated by average of the retention times in the chromatogram weighting in terms of peak area/concentration), by the equation: $\mathrm{ART} = \Sigma A_p \mathrm{RT}_p / \Sigma A_p$, where A_p is the peak area and RT_p is the corresponding retention time.

On the other hand, nuclear magnetic resonance (NMR) is one of the most important spectroscopic analytical techniques. It allows a fast and detailed insight into structural parameters and it can be applied to high molecular weight fractions and to hydrocarbon mixtures.[17,24] Although well known in organic chemistry, it has been applied to the study of petroleum fractions only since the last decade.[17,25–27] In most of those papers, three types of aliphatic and the aromatic protons were distinguished, while in the present study seven types of protons could be detected in some samples.

The goal of this work was determine the above-defined parameters (n-C_{17}/Pristane, n-C_{18}/Phytane, TRH/TEH, and ART) plus the NMR studies, to quantify the degree of compositional changes and to test the validity of some models to evaluate natural attenuation, by comparing results with assisted degradation of oil spills in the Patagonian environment.

RESULTS AND DISCUSSION

Sorption isotherms

Sorption from solutions is a complex equilibrium process. Only substitution of one molecule by another is possible at the interface, since there are no vacancies in either the surface layer or the bulk solution. In such case, the sorption isotherm represents the interactions between all the components in solution and the solid phase. Our experiments intend to determine the conditions that would prevail after an oil spill on surface soil, taken into account that each component of the crude oil, is mixed with a variety of other components in a liquid organic phase. The applicability of the BET model, proposed for pure compounds, is tested in this work by considering the oil residual as only one solute

$$\frac{q_e = K_1 K_2 \sum_{i=1}^{m} i C_e^i}{\left(1 + K_1 \sum_{i=1}^{m} C_e^i\right)} \tag{1}$$

In Eqn (1), K_1 is a constant related to the heat of sorption ($\mathrm{L\,mg^{-1}}$) and K_2 is a constant related to the monolayer coverage ($\mathrm{mg\,kg^{-1}}$), '*i*' is the number of the layer, and the upper limit of the summation was taken as a finite number, *m*. A similar expression was derived for the treatment of the gas sorption in a fractal environment.[28] When the surface coverage is only one monolayer, then $i = 1$ and the BET isotherm takes the Langmuir shape. The finite number of layers sorbed (*m*), is usually dependent on the monolayer coverage (K_2), and on the initial sorbate concentration (C_0). Equation (2) shows this possible dependence.

$$m = q_e / K_2 = a C_0^b \tag{2}$$

where q_e is the equilibrium soil–sorbate concentration, '*a*' and '*b*' are fitting parameters. The K_1, K_2, *a*, and *b* constants account for the interactions among the components in liquid phase and for the overall interactions of each of them with the mineral matrix.[29]

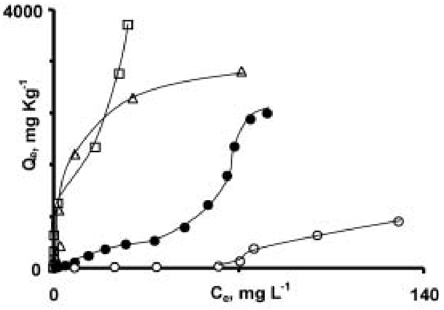

Figure 1. Sorption Isotherms, Q_e (mg kg^{-1}) *versus* C_e (mg L^{-1}) for phenanthrene (open circles), pyridine (open squares), phenol (open triangles) and crude oil (black circles)

The determined sorption isotherms are shown in Fig. 1. The curve for pyridine shows that this solute has very high affinity and it is completely sorbed in dilute solutions. The curve for phenanthrene shows opposite behavior in dilute solutions, while the curve for phenol is similar to the pyridine for dilute solutions, but saturation of the soil sorption capacity occurs when the concentration increases. It is known that the rates and enthalpies of activation of sorption and desorption of organic compounds are strongly dependent on the structural characteristics of the compounds; the curves for phenanthrene, pyridine, and phenol clearly show that different sorption mechanisms are operating. Table 1 shows the best fitting parameters found by application of the Eqns (1) and (2) for phenanthrene, pyridine, phenol, and crude oil. More simple models (linear, Freundlich, and Langmuir) were tested, but they did not account for the experimental behavior of all sorbates. It can be observed that K_1^{app} constant was in the range of 0.0044–0.7272 L mg^{-1} ('app' is used to indicate that total interactions are taken into account). In BET theory, K_1 is related to the average heat of sorption in the first sorbed layer, the phenanthrene takes the lower values ($K_1^{\mathrm{app}} = 0.0044$ L mg^{-1}). Pyridine is the more polar organic molecule tested, the interaction with the mineral matrix is the stronger ($K_1^{\mathrm{app}} = 0.7272$ L mg^{-1}).[29] The errors in the isotherms predicted by the model were: 6, 13, 16, and 24% for phenanthrene, crude oil, pyridine, and phenol, respectively. This indicates that multilayer sorption is a good model for phenanthrene, but it is not so good for phenol.

The second part of Table 1 shows the best fitting parameters found by application of the Eqns (1) and (2) to each one of the fractions of the crude oil, previously obtained by column chromatography.[6] It can be observed that K_1^{app} constant was in the range of 0.0194–0.0786 L mg^{-1}. If K_1^{app} is related to the average heat of sorption of the first sorbed layer, the order found is: phenanthrene $\ll$ crude oil $\approx$ aliphatic fraction $<$ aromatic fraction $<$ phenol $<$ polar fraction $\ll$ pyridine, respectively. This is the same order that the polarity of the compunds and fractions of the crude oil tested, increases. It is known that the sorbate polarity is main point in the sorbate/sorbent interactions.[1,4] This is in agreement with the finding of relationships between the chemical and structural characteristics and the sorption and desorption behavior that have been recently described.[5,6] It has been reported that in the layered mixture of clays, with most of the sorption sites (80%) located between the clay layers, it is important to consider the role of sorbate size in the sorption process.[30,31]

Distribution coefficients

In Patagonian soils, the distribution coefficient of oil residuals between water and soil under equilibrium conditions (K_d) is strongly dependent on the ionic aqueous phase and soil characteristics. The dependence of adsorption on salt content is given by the Setschenow equation.[1] As observed in some sorption isotherms, the environmental exposure time, also affects the interactions between both phases. Table 2 summarizes some characteristics of the soil samples contaminated by oil spills in eight different sites near Comodoro Rivadavia's city. The content of organic matter in the Patagonian soils is in the range of 0.02–1% wt/wt.

To untangle the simultaneous dependence of multiple variables on the estimation of the distribution coefficients, an equation derived from the Rao's solvophobic theory was used[5]

$$\log(K_{d\,2}/K_{d\,1}) = p(\mathrm{INP}_2 - \mathrm{INP}_1) \qquad (3)$$

$K_{d\,2}$ and $K_{d\,1}$ are the distribution coefficients in two solvents of different polarity, INP_1 and INP_2 are polarity indexes of the solvent 1 and 2, respectively, (see below) and p is the slope. Equation (3) can be rewritten as the following equation:

$$\log K_{d\,1} + p\,\mathrm{INP}_1 = \log K_{d\,2} + p\,\mathrm{INP}_2 = \text{constant} \qquad (4)$$

If K_d is known in two solvents (e.g., methanol and hexane), then the slope 'p' and K_{d,H_2O} can be calculated, using $\mathrm{INP}_1 = \mathrm{INP}_{H_2O}$. This parameter represents the distribution coefficient in the

Table 1. Sorption model fitting parameters

Sorbate	$K_1^{\mathrm{app}}\ 10^2$	$K_2^{r\ \mathrm{app}\,b}$	R^{2c}	10^2a	$10b$	R^{2c}	Error%
Phenanthrene	0.44 ± 0.01	1	0.997	0.45 ± 0.02	11.44 ± 0.40	0.999	6
Crude oil	1.31 ± 0.10	5.13	0.996	0.64 ± 0.03	11.18 ± 1.01	0.998	13
Aliph fraction^a	1.94 ± 0.34	2.89	0.996	1.0 ± 0.07	10.8 ± 0.24	0.997	17
Aro fraction^a	3.08 ± 0.62	3.55	0.995	1.1 ± 0.09	10.9 ± 0.31	0.995	18
Phenol	4.76 ± 0.15	10.3	0.997	0.01 ± 0.00	9.5 ± 0.25	0.996	24
Pol fraction^a	7.8 ± 1.6	2.54	0.973	2.4 ± 0.07	10.8 ± 0.23	0.996	24
Pyridine	72.7 ± 6.6	11.5	0.997	0.20 ± 0.01	15.97 ± 0.54	0.965	16

[a] Aliph, aliphatic; Aro, aromatic; Pol, polar fractions of the crude oil.
[b] $K_2^{r\ \mathrm{app}} = K_2^{\mathrm{sorbate\ app}}/K_2^{\mathrm{phe\ app}}$, app, apparent.
[c] R, correlation coefficient.

Table 2. Characteristic of the oil spills residue samples

Soil					Percentage of oil fractions[e]					
No.	Site[a]	Conductivity (μmhos/cm)[bc]	pH clays wt%[c]	Percentage of oil[d]	Ali	Aro	Pol	Asph	Age (years)	$K_{d\,H_2O}$ (L kg^{-1})
1	CS	9364	7.6 33	25.8	32.2	31.1	36.7	0.0	20[f]	406
2	CO	1633	7.4 22	16.6	33.1	39.0	28.0	0.0	10[g]	416
3	CS	618	7.4 8	8.6	21.0	19.7	58.7	0.6	3[g]	144
4	BV	426	6.8 16	16.1	28.2	27.8	43.0	1.0	2	85
5	DA[h]	610	6.9 13	11.4	35.1	32.3	32.5	0.1	57	569
6	DA[h]	700	6.5 8	6.5	37.3	29.5	25.8	7.4	22	530
7	DA[h]	530	7.4 11	8.6	46.1	29.5	19.4	5.0	10	432
8	DA[h]	1500	7.2 24	10.0	35.0	33.0	28.0	4.0	7	238

[a] BV Bella Vista, CS Cañadón Seco, CO Caleta Olivia, DA Diadema Argentina.
[b] Soil extract 1/5 wt/wt.
[c] Uncontaminated soil.
[d] %wt/wt.
[e] Ali, aliphatic; Aro, aromatic; Pol, polar; Asph, asphaltene fraction, %wt/wt.
[f] A 20 cm deep sample (subsurface).
[g] Biostimulation.
[h] Different sites in the Diadema (DA) region.

aqueous phase, without the interference of the ionic content of the soil and water phase. For the definition of the polarity indexes (INPs), we have taken into account the work previously developed by Katritzky *et al.*[32] Multiple linear regression was employed to correlate the observed K_d in different solvents with their polarity properties. The selection of the indexes by group, based on the correlation of the experimental data and the weight of the different Katritzky's groups to the definition of the INPs, is shown in the Table 3. To obtain the best correlation coefficients, the residues should be separated into two groups (approx. 2–10 years and 20–57 years age, respectively). Although a complex problem, this behavior suggests that the magnitude and type of interactions change with exposure time, likely due to the modification of the chemical composition.

Table 2 shows the K_{d,H_2O} for the oil residues, calculated by Eqn (4). In spite of the multiple variables that can be involved, it can be observed that the values increase with the environmental exposure time. It has been shown, that the chemical extractability and bioavailability of hydrophobic organic contaminants from soils, decrease with increasing contact time.[33] Therefore, the observed increase in K_{d,H_2O} shown in Table 2, should be mainly due to the change in chemical composition and the physical sequestration, which is related to the exposure time and it

Table 3. Selected scale by Katritzky's definition groups of interactions

Parameters[b]				Parameters		
Group[a]	Scale	Author[c]	Age of the residues (2–10 years[d], age wt%)	Scale	Author[c]	Age of the residues (20–57 years[e], age wt%)
I	S'	Drago[45]	15.3	d	Fowler and Katritzky[46]	37.5
II	$E_{CT(A)}$	Davis[47]	12.4	E_T^{SO}	Walter and Bauer[48]	29.1
III	BB	Swain[49]	40.8	BB	Swain[49]	9.84
IV	D_π	Oshima[50]	23.6	$\pi^*{}_{aso}$	Buncel and Rajagopal[51]	15.3
V	SB	Catalan[52]	3.2	SB	Catalan[52]	5.83
VI	P	Kopel and Palm[53]	4.3	$\Delta\nu_{Cl}$	Laurence *et al.*[54]	2.23

The numbers in 4th and 7th columns give the contribution to the polarity index (INP).
[a] Group is defined on the basis of the measured property: I, dielectric constant; II, charge transfer in the UV/vis; III, ability of the solvent to change UV absorption maxima; IV, basicity; V, UV/Vis spectra of 5-nitroindoline and 1-Me-5-nitroindoline; VI, refractive index.
[b] See definition of each solvent parameter scale in the given references.
[c] Only the main authors are given.
[d] Correlation coefficient 0.893 (five samples).
[e] Correlation coefficient 0.950 (three samples).

suggests a decrease in the bioavailability of the remaining residues caused by the decrease in its water solubility.

NMR determinations

The application of the ^1H NMR technique to the study of petroleum samples is relatively recent, and the assignments of the different kinds of hydrogen atoms are rather difficult. The ^1H NMR spectra of crude oil can be divided into major regions, according to the different types of protons, four types of aliphatic hydrogen were recently distinguished.[17,21,27] In the present study, the shapes of the ^1H-NMR spectra of the sample residues were similar to that of the crude oil, but the percentages of each type of hydrogen were different.

Table 4 summarizes the concentration of the four aliphatic (H_1, H_2, H_3, H_4) and the aromatic (H_A) proton types of crude oil and of the residues. (The actual NMR spectra are provided as Supplementary Materials). For this crude the main hydrogen type is aliphatic. As it is known, because of overlapping, most of the regions are not structurally pure, and the cut-off points might change depending on the nature of the sample.[25,26] Additional details of the compositional changes were found by analysis of the spectra of the aliphatic, aromatic, and polar fractions of crude oil for samples 4 and 7. The presence of aromatic hydrogens was observed also in the aliphatic fraction. It is known, that the *n*-hexane fraction of crude oil and residues contain saturated compounds, but recently, it was found that it could also contain long-side-chain alkylaromatics.[34] A previous GC–MS analysis reported the presence of a homologous series of *n*-alkylaromatics, namely mono-, di-, and tri-*n*-alkylbenzenes in the C_7–C_{27} range (the subscript indicates the total number of carbon atoms in the alkyl side chain) and di- and tri-*n*-alkylbenzothiophenes, with alkyl chains in the C_3–C_{22} range.[17] This is in agreement with our observation that the *n*-hexane fractions of the crude oil and the residues show absorptions between 245 and 345 nm, in the UV–Visible spectrum (not shown).

The mayor differences in the ^1H NMR spectra, were observed for the polar fractions of crude oil and for samples 4 and 7. In the region 0.5–1.5 ppm, the intensity of the signals, slightly decrease with the addition of D_2O. In contrast, the significant decrease in the intensity of the signals between 4.0 and 4.5 ppm observed by the addition of D_2O, indicates the presence of hydroxyl groups. In the 6.6–8.2 ppm region, only 10% of the signal intensity is affected by D_2O, suggesting that the polar substituents in aromatic rings are mainly not exchangeable protons. In addition, in the spectra of polar fraction of crude oil and of sample 4, signals were detected at 10–11 ppm, that corresponded to the chemical shift for carboxylic hydrogen (H_{COOH} protons). Consequently, a significant decrease in the signals intensity was observed upon addition of D_2O, 85% for crude oil and 100% for the sample 4. The presence of free fatty acids in the C_{14}–C_{26} range has been reported recently.[35,36] An increase in the acid content has been reported to correspond to evidence of (bio)-degradation.[37] In the present paper, the areas of the H_{OH} protons were 3.94 (crude oil), 8.18 (sample 4), and 0.00 (sample 7), while the areas for the H_{COOH} protons were 0.56, 0.13, and 0.00, respectively. These results suggest that the hydrophilicity of the younger residue increase in the first years, mainly due to the increase in OHs, and then decreases.

The environmental evolution of the polar fraction residues shows first the formation of the more oxidative species by biodegradation and photodegradation and then the continuous removal of the remaining species by the processes of water washing and sorption in mineral surfaces.[5,37] When the degradation process decreases, the polar species, such as the *n*-alkanols and acids, disappear, likely due to the loss in the water-soluble fraction, or by sequestration by the soil mineral components.[15,38] This rationale is in agreement with the null content of H_{OH} and H_{COOH} observed in sample 7.

Principal component analysis (PCA)

Table 5 provides some relevant GC data that are used in this paper, full details on the GC analyses will be given elsewhere.[39] (Some representative GCs are provided as Supplementary Materials). Table 5 shows some ratios calculated from the GC data for crude oil and residues. The data show that the indexes for residues decrease, compared with oil, except in the case of sample 1 that was the only subsurface sample (see Subsection 'Oil Spill Samples' in the Experimental Section). Residues with stimulated biodegradation, samples 2 and 3, show lower indexes than the non-assisted residues (samples 5, 6, and 7). The ART

Table 4. ^1H NMR percentage area of five types of protons in crude oil and in residues

Chemical shift (ppm)	Assignment	Percentage of area crude oil	Percentage of area aged spills[a]					
			2(4)	3(3)	7(8)	10(7)	22(6)	57(5)
0.5–1.0[b]	H_1	34.4	30.1	16.7	12.9	25.0	28.9	28.2
1.0–1.5	H_2	57.4	54.0	48.4	43.3	60.2	58.9	56.7
1.5–2	H_3	4.2	8.3	18.4	24.2	11.1	8.1	11.9
2.0–3.0	H_4	1.3	3.9	11.7	17.9	2.0	2.4	2.7
6.6–8.5	H_A	2.7	3.7	4.8	1.7	1.7	1.6	0.4
3.0–5.0[c]	H_{OH}	3.9	8.2	—[d]	—	0.0	—	—
10–11	H_{COOH}	0.56	0.13	—	—	0.0	—	—

[a] Each column shows the age of the spill in years. (The number in brackets is the sample number of Table 2).
[b] Whole crude (H_1, H_2, H_3, H_4, and H_A).
[c] Polar fractions show also carboxyl (H_{COOH}), and hydroxyl (H_{OH}) protons.
[d] —, Not analyzed.

Table 5. Gas chromatography parameters of some selected samples and of crude oil[a]

Sample no.	n-C_{17}/ Pristane	n-C_{18}/ Phytane	TRH/ TEH[b] 10^2	ART[c]
1	2.3	0.97	0.42	25.6
2	0.06	0.17	0.49	25.5
3	0.15	0.55	0.60	24.0
5	0.31	0.48	0.50	27.4
6	0.64	0.95	0.80	24.8
7	0.56	0.93	0.85	25.3
Crude oil	1.2	1.5	1.1	21.1

[a] Sample number refers to the labeled samples in Table 2.

[b] TRH, total resolvable hydrocarbons; TEH, total extractable hydrocarbons.

[c] ART, average retention time.

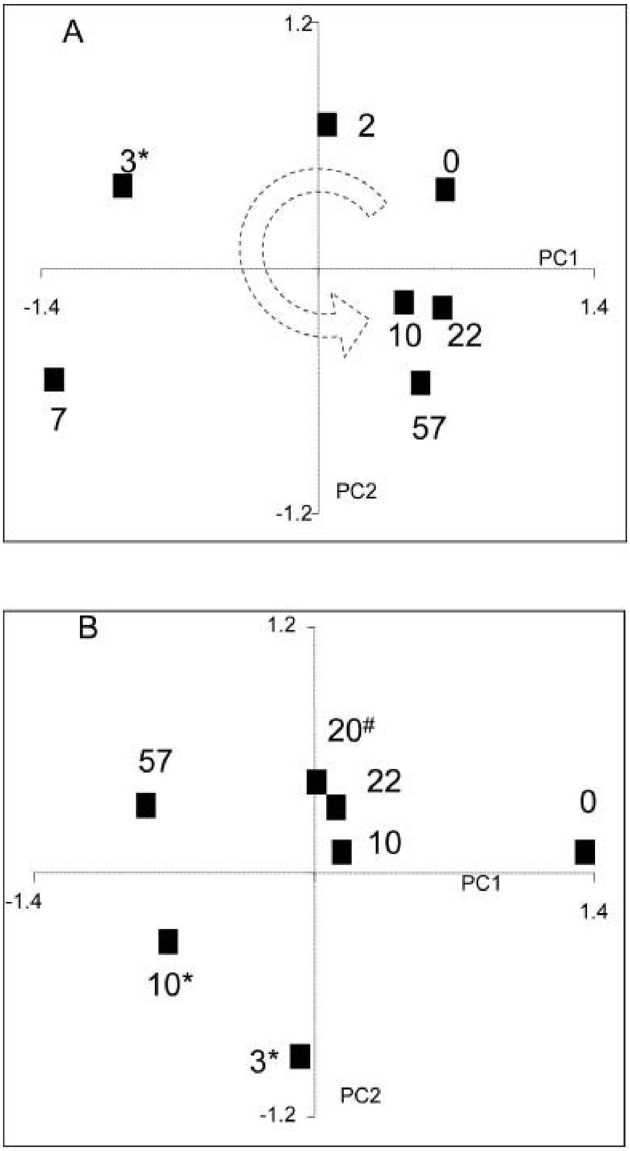

Figure 2. PC factor score plot (first *vs.* second PC). (A) PCA with $K_{d\ H_2O}$ and NMR parameters. (B) PCA with $K_{d\ H_2O}$ and GC indexes. Labels show the age of the spill. The dashed arrow shows the environmental evolution of the oil residues. Points for bio-stimulated degraded and subsurface samples are shown by * and #, respectively

(Table 5) values are between 21 and 27 min. The increase in ART with time is consistent with the loss of the more degradable hydrocarbons (microorganisms prefers small molecules).

The following parameters: (i) the NMR data (Table 4), and (ii) the GC indexes shown in Table 5 were used in the PCA. In its basic form, PCA is a transformation of a set of variables into a new set of variables which are uncorrelated with each other. Thus, a large number of correlated variables are transformed into a small number of uncorrelated variables that describe the most important trends in the original set of data. These new variables are called 'principal components' (PC).[40] The PCs are linear combinations of all the original variables located in the directions explaining most of the variation in the data set. The explanatory importance of a PC is measured through the ratio of its variance to the total variance contained in the original variables. If the original variables are highly correlated the first few PCs explain most of the total variance. The utility of PCA as a data analysis tool is that it provides an unbiased comparison and a simple (*xy*) graphical interpretation of a complex data set. Graphical representation of these values, the 'scores' plot for the samples and the 'loadings' plot for the characteristics, provide pictures that allow recognition of systematic patters that is otherwise difficult to deduce from the original data matrix.

Two PCA determinations were carried out: one using $K_{d\ H_2O}$ and NMR parameters and the second with $K_{d\ H_2O}$ and GC indexes. In both cases, no pre-classification of the residues was performed. Each parameter was previously normalized to eliminate the influence of their varying magnitudes. The first and second PC were used to generate the factor score plots. (Fig. 2A, B, the labels show the age of the spill). The symbol * is used for surface samples with stimulated degradation, while subsurface samples are shown by the # symbol.

In the PCA with $K_{d\ H_2O}$ and NMR parameters, the first two PC (first and second), account for more than 95% of variance. The factor score plot is shown in Fig. 2A, first and second PC represent 70 and 25%, respectively, of the total variance among the residue samples. The Euclidean distances between the samples in the plot represent real differences in the parameters indexes. First PC is largely influenced by H_2 (20%), H_4 (20%), H_1 (19%), and H_3 (19%) in this order, while second PC is influenced by H_A (35%) and $K_{d\ H_2O}$ (28%), respectively. In the PCA with $K_{d\ H_2O}$ and GC indexes the first two PC (first and second), accounted for more than 81% of variance. In Fig. 2B, first and second PC represented 52 and 29%, respectively, of the total variance. First PC is largely influenced by n-C_{17}/Pristane (28%), n-C_{18}/Phytane (27%), and ratios TRH/TEH (25%) in this order, while second PC is influenced by K_{dH_2O} (39%), and ART (22%), respectively.

In Fig. 2B, the first PC, show that the most positive values represent crude oil or younger oil residues (high C_{17}/Pris, C_{18}/Phy, TRH/TEH, and low ART), while the most negative values are older oil residues (low C_{17}/Pris, C_{18}/Phy, TRH/TEH, and high ART). In Fig. 2A, the samples show distribution into groups: (i) those with positive first PC and second PC, are crude oil or younger oil residues (high H_1 and H_2 and low H_4), suggesting a high aliphatic compounds concentration; (ii) positive first PC and negative second PC, these samples are oil residues with intermediate age (low H_1 and H_2, high H_4 and H_A); (iii) negative first PC and second PC, these samples are older oil residues (high H_2, low H_1, H_4, and H_A), suggesting the transformation of aromatic compounds and the increase in polycyclic aromatic hydrocarbons (PAHs). This hypothesis is in agreement with the changes in the maximum absorbance wavelengths observed in the UV–Visible spectrum ($\lambda = 220$ nm in crude oil and $\lambda = 300$ nm in the oldest residue).

The fact that the samples show distribution into groups and that the total amount of the variance accounted by the first analysis was the 95% while in the second analysis was the 81%, suggests that, in the present study, the NMR parameters (H_1–H_4 and H_A) would be better indicators to account for the compositional changes than the parameters obtained by GC (n-C_{17}/Pristane, n-C_{18}/Phytane, ART, and TRH/TEH). It is usually assumed, that the major transformations occur in the first years of the environmental exposure, as can be observed in the PCA analysis. This conclusion is related not only to the biodegradation of the *n*-alkanes observed by GC analysis, but also to the other indexes, (K_d) and NMR parameters, shown in this study.

The fate oil spills in soils and sediments in the Patagonian environment are usually evaluated employing GC–FID and/or GC–MS. Nevertheless, conventional GC methods can mainly detect volatile components,[37] which are, generally, sensitive to biodegradation. In other words, the global alterations of the crude oil components that are resistant to biodegradation cannot be characterized by direct GC, derivatization, or other treatments are usually needed. Moreover, sometimes GC or gas chromatography–mass spectroscopy (GC–MS) gives poor resolution due to severe overlap among the numerous peaks.

In the last few decades, NMR spectroscopy has been established as a very powerful and highly useful technique for the structural elucidation of various petroleum distillate fractions, starting from light naphtha to heavier products like bitumen and asphaltenes.[41] The NMR spectra of oil samples contain, comparatively, fewer peaks. Since the major components in crude oil are made up of rather few molecular fragments, ^{1}H NMR and ^{13}C NMR spectroscopies produce spectra with well-resolved parts even from fractions containing a large amount of compounds. The limitation imposed on the interpretation of the NMR spectra, using molecular substructures rather than individual components, turns out to be an advantage in the present context, since NMR spectroscopy usually provides an understanding of the average molecular structure of complex hydrocarbon mixtures in terms of various structural parameters.[41] Extensive research in the last years reflects the growing need of rapid and quantitative methods for characterization of a large amount of environmental samples. The observed results indicate that ^{1}H NMR would be a useful technique to evaluate the degree of transformation of crude oil spilled in soils.

The comparison of the environmental evolution of the oil residues show that the combined analysis of different indexes could be useful to estimate the structural changes that oil spills undergo in Patagonian soils, and to select potentially more efficient remediation strategies. Nevertheless, extrapolation of these results to other environments is not straightforward because the changes depend strongly on the crude oil source and the variable exposure conditions along the time (soil type, temperature, pluvial precipitation, etc.). The environmental evolution of the samples reported, does not represent a time series of a sample collection of a field; it is like an instantaneous view of some weathered oil spills from Central Patagonia, Argentina. Regrettably, information on the chemical composition of the released oils was usually not available; therefore, comparisons were made by analogy with actual samples of crude oil. More investigation is needed for a full understanding of how the environmental exposition modifies the physical and chemical properties of the crude oils in the particular Patagonian environment.

EXPERIMENTAL

Materials

Soil for sorption isotherms

Surface samples of soil were taken from Diadema, (a site on the north of Comodoro Rivadavia City in Patagonian). The mineralogical composition is: sand (quartz, lithics, feldspars, and gypsum of eolian origin) and clay (montmorillonite and illite). Properties of the soils are (extract 1:1 wt/wt): pH 7.4; conductivity 600 μS cm^{-1}; Na^+ 3.25 meq L^{-1}; K^+ 0.11 meq L^{-1}; Ca^{+2} and $Mg^{+2} <$ 0.01 meq L^{-1}; clay (montmorillonite and illite) including silt: organic matter 0.02 wt% (dry); Fe^{+3} 2.5 g kg^{-1} and Fe^{+2} 0.4 g kg^{-1} (extract 1: 200 wt/wt); montmorillonite total surface 600–800 cm^2 g^{-1}; illite total surface 65–100 cm^2 g^{-1}, total water retention capacity 43 wt% (dry). The soil was air-dried, ground, and sieved with a 1.7 mm sieve. Then, it was oven dried at 140°C for 48 h and placed in a desiccator for 2 h at room temperature before loading.

Crude oil

The crude oil came from the Golfo San Jorge basin, located in central Patagonia, southern Argentina, between 44 and 47° of south latitude and between 66 and 71° of west longitude. It is the most prolific basin in Argentina: oil was discovered in 1907. Oils from the Golfo San Jorge Basin range between 15 and 30° API; in general, they have low sulfur content.[42] Lacustrine shales of the Pozo D-129 Formation, are the source rocks of the oil bearing sandstones of the middle to late Cretaceous. Overall compositions of the crude oils (six samples) are: aliphatic fraction (41 ± 8%), aromatic fraction (39 ± 6%), polar fraction (19 ± 6%), and asphatene fraction (5 ± 4). The isoprenoids (Pristane and Phytane) are less abundant than the corresponding *n*-alkane (n-C_{17} and n-C_{18}). Typically, n-C_{17}/Pristane and n-C_{18}/Phytane are 1–2 and 2–3, respectively, in crude oils.[43,44]

A sample of fresh crude oil was analyzed by column chromatography with silica gel. The eluents were: hexane (30 ml), benzene (30 mL), and methanol/chloroform (1:1) (30 ml). Three fractions of different chemical nature were separated: aliphatic (41%), aromatic (35%), and polar (17%) fractions. The numbers in brackets give the wt% composition of the crude oil. The portion remaining in the column is the 'asphaltenes' fraction, nearly 7%. The API gravity was 25.

Sorption experiments

Four different stock solutions were prepared in hexane with crude oil and the three fractions obtained by column chromatography. Three stock solutions of pure compounds were prepared by dissolving, appropriate amounts of phenanthrene (>96%, Sigma), pyridine (>98%, Aldrich), and phenol (>98%, Aldrich) in hexane. Sorption experiments were carried out at room temperature (23 ± 2°C) using periodically shaken flask reactors, containing 10 g of sorbent (soil) and 100 ml of organic solution. After the required time, the supernatant was immediately withdrawn and the solute concentration was analyzed by UV–Visible spectrophotometry.[5]

Oil spill samples (residues)

Soil samples contaminated by oil spills in the surroundings of Comodoro Rivadavia's city, were analyzed. Table 2 summarizes some characteristics of the samples. As it can be observed, they exhibit different clay content, a wide range of conductivity mainly due to the different salinity in the sites and different ages; the organic matter (not shown) is <1% in all samples. In samples 2 and 3, fertilization of the affected areas was carried out, this process is known as biostimulation.[1,44] All samples were extracted from the surface, except in the case of sample 1 that was extracted to a depth of 20 cm to evaluate the most aged residuals, since more recent oil residuals were overturned. This sample was called subsurface residue. The total hydrocarbon determination in each sample was carried out by Soxhlet extraction using methylene chloride as solvent, during 24–48 h, depending on the sample.

Desorption experiments

Aliquots of approximately 0.1 g of each soil sample were placed in 15 ml test tubes (at least by duplicate). To each tube, 10 ml of solvent (methanol or hexane) was added. The tubes containing the soil–solvent slurries were periodically shaken during 7 days. The soil/solution ratio and the total contact time were selected on the basis of previous studies. The tubes were sealed and covered by aluminum foil to avoid light exposure and prevent photooxidation. Desorption determinations were carried out at ambient temperature (22 ± 3°C). After the required time the oil concentration in the liquid phase was analyzed using UV–Visible spectrophotometry in the range of 200–400 nm. The overall estimated error was $<15 \pm 4$%.

Gas chromatography

GC was determined on a Konic 3000 Gas Chromatograph, equipped with a J & W DB1 fused-silica column (30 m × 0.25 mm i.d.; film thickness, 0.25 μm). Resolved aliphatic hydrocarbons and unresolved complex mixtures (UCM) were calculated using the mean response factors for *n*-alkanes. Procedural blanks and standards were run in association with samples. Recovery assays were made by spiking a pristine sample. The results were 95% ($n = 5$) for C_{20}–C_{28} *n*-alkanes.[44] Prior to GC analysis, the asphaltene fraction of each residue was separated by extraction with *n*-pentane.[25] In some cases, *n*-heptane was used as well. The differences in weight between the asphaltene fractions precipitated with *n*-pentane, those from column chromatography and some measured by extraction with *n*-heptane were always <20%.

NMR spectrometry

^{1}H-NMR spectra were recorded by a Bruker 500 MHz spectrometer, using internal tetramethylsilane (TMS) in $CDCl_3$ (99.8%, Aldrich). The automated phase and base line corrections were applied in order to get reproducible integral values. The spectra were integrated three times; average values were considered in the calculations. To assess the repeatability of ^{1}H chemical shift at 500 MHz, some samples were independently determined several times, a standard deviation of ±0.003 ppm was obtained.

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