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Geochemistry

Organic contamination identification in sediments from a Mediterranean coastal ecosystem: The case of the Nador lagoon (Eastern Morocco)

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Abstract

The Nador lagoon ecosystem (North-East of Morocco) displays a major socioeconomic interest. In fact, it is essential to evaluate consequences of anthropogenic activities in the lagoon especially by organic matter studies (nature and distribution) in the sedimentary compartment. Surface sediments show variable rates in total organic carbon and in sulfur, high in some cases (7.5 and 1.8% respectively). These high contents are recorded in the center of the lagoon. Their distributions are controlled by the hydrodynamism and the anthropogenic degree. The molecular biomarkers analyses and especially *n*-alkanes distribution reveal: a zone of marine influence; and a zone of continental influence. The occurrence of pentacyclic triterpanes with a typical distribution of a thermally mature organic matter reveals a contamination due to petroleum products in the entire lagoon except for the center. Coprostanol occurrence near cities indicates wastewater effluents inputs and reducing conditions underlined by high values of stanols/sterol ratios. Thus, the organic contamination (petroleum by-products and wastewater effluents) occurs in the vicinity of the cities whereas the littoral edge and center remain weakly affected by these contaminations. ***To cite this article: M. Karim Bloundi et al., C. R. Geoscience 340 (2008).***

Résumé

Identification des contaminations organiques dans les sédiments d'un écosystème côtier méditerranéen : cas de la lagune de Nador (Maroc oriental). La lagune de Nador (Nord-Est du Maroc) est un écosystème présentant un intérêt socioéconomique local majeur. Il est donc important d'évaluer les conséquences des activités anthropiques sur la lagune, notamment en étudiant la matière organique (nature et répartition) du compartiment sédimentaire. Les sédiments superficiels présentent des taux variables en carbone organique total (COT) et en soufre pouvant être importants (7,5 et 1,8 % respectivement). Ces teneurs élevées sont enregistrées essentiellement dans le centre de la lagune. Leurs distributions sont contrôlées par l'hydrodynamisme et le degré d'anthropisation. L'analyse de marqueurs moléculaires et, en particulier, la distribution des *n*-alcanes révèlent une zone à influence marine et une zone à influence continentale. De plus, la présence de triterpanes pentacycliques présentant des distributions typiques de matières organiques thermiquement matures met en évidence une contamination par les produits pétroliers dans toute la lagune, à l'exception du centre. La présence du coprostanol à proximité des villes souligne une

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contamination fécale (contributions d'eaux usées) et des conditions réductrices révélées par des rapports stanols/stérols élevés. Ainsi, les contaminations organiques (produits pétroliers et rejets d'eaux usées) sont prononcées au voisinage des villes, tandis que les sites de la bordure littorale et du centre restent relativement peu affectés par ces contaminations. ***Pour citer cet article : M. Karim Bloundi et al., C. R. Geoscience 340 (2008).***

Keywords: Biomarkers; Extractable organic fraction; *n*-alkanes; Pentacyclic triterpanes; Sterols

Mots clés : Biomarqueurs ; Fraction organique soluble ; *n*-alcanes ; Triterpanes pentacycliques ; Stérols

1. Introduction

The Nador lagoon is the only lagoon ecosystem on the Mediterranean Moroccan coast. It has a 115 km^2 surface area and is separated in two basins by the Attalayoun peninsula. Its water depth is ranging between 5 m in the north and 8 m in the south (Fig. 1).

The lagoon is fed by:

- the waters of the Mediterranean Sea coming through the pass called 'Bokhana';
- the rejections of untreated human activities (agriculture, aquaculture, industries and urban waters);
- wastewater effluents from the treatment plant of Nador.

The hydrosystem constitutes the life unit of three great agglomerations (Fig. 1): Nador (132,000 inhabitants), Beni-Enzar (31,000 inhabitants) and Arekman (18,000 inhabitants). The last two towns reject untreated waters in the lagoon and only a part of Nador city housing is connected with a wastewater treatment plant. This induces a high organic pollution with accumulation of organic carbon in the Nador lagoon sediments and decrease in dissolved oxygen concentrations in its waters [6,9,10,14].

Since the last two decades, several studies were devoted to the Nador lagoon. Some authors have focussed their study on the distribution of clay minerals or organic matter [21,31], others on the physical–chemical quality of waters [9,10,14,19], or on the trace element distribution in sediments [1–3,14] and the influence of anthropogenic pressures leading in some lagoon zones, to living organisms morphological abnormalities as for example nanism in foraminifera and ostracods [15,16,28]. Concerning organic matter

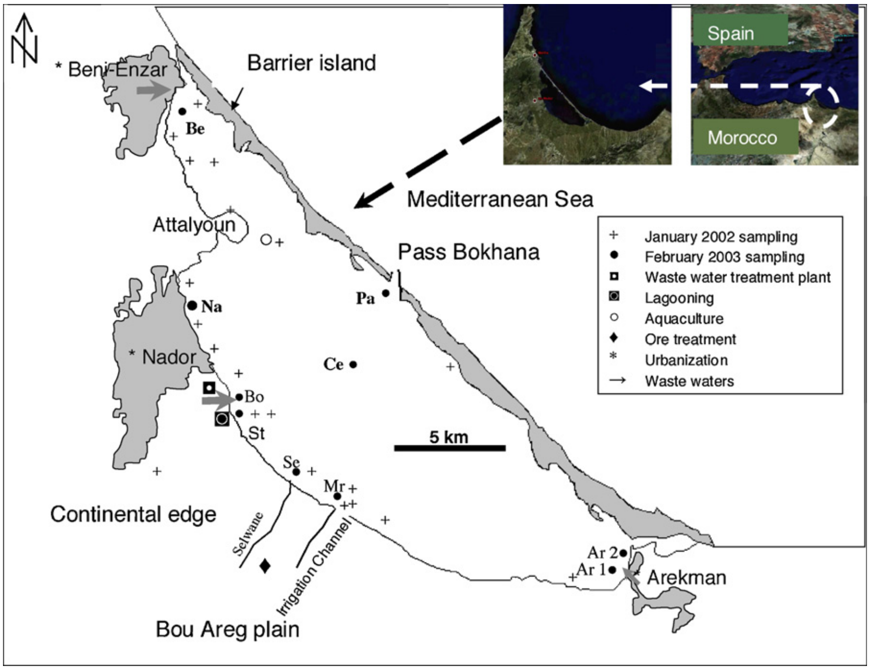

Fig. 1. Nador lagoon geographical setting and sampling sites.

Fig. 1. Situation géographique de la lagune de Nador et points d'échantillonnage.

studies, El Alami et al. [6] in 1998 recorded high total organic carbon (TOC) contents in the central zone of the lagoon and noticed that the organic stock is enriched in aromatic rings on the continental border, showing the contribution of the continental biomass.

The aim of this work is to specify the organic contamination state of sediments taken in various sectors of the lagoon by studying specific ''molecular biomarkers'' [7,17].

First, ''global'' markers, the TOC and sulfur, are studied in order to identify the zones the most sensitive to organic contamination. Second, in the sediments of these identified sites, a molecular characterization is performed specifically for *n*-alkanes, pentacyclic triterpanes and sterols.

These molecular markers are studied in order to obtain information on the origin of the organic matter (anthropogenic or natural) and on the contributing sources (higher plants, wastewater, petroleum...) [7,17,23,26,29,30,34].

2. Material and methods

2.1. Sampling

The location of the sampling sites was made by using GPS (E – map GARMIN) (Table 1). Sediment cores were collected by a diver equipped with a tube (30 cm long and 4.5 cm large). Surface sediments (0.5 cm) were kept in polyethylene plastic bags and maintained at 4 °C and freezed dry before analysis.

TOC and sulfur (S) measurements were carried out on 28 sediments sampled in January 2002 (Fig. 1) in order to obtain a spatial distribution of TOC and S in the lagoon. This first step allowed to choose the most organic contaminated sites and thus to reduce sampling to 10 further sites (sampled on February 2003; Fig. 1, Table 1) for organic molecular analyses, targeting zones located near cities (Be, Na, Bo, Ar1 and Ar2), near fresh water contributions (St and Mr), the lagoon center (Ce) and the pass (Pa).

2.2. Analytical methods

The organic carbon and sulfur analyses were made by dry combustion in an induction furnace at a temperature of 1200 °C (analyzer LECO CS 125). Before analysis, samples were treated to eliminate inorganic carbon (HCl 2N).

The extractable organic fraction (EOF) was separated from the sediment (mineral phases and insoluble organic fraction) by extraction with an organic solvent (dichloromethane) by means of an extractor ASE 200 Dionex (100 bars; 100 °C; static phase: 8 min). To refine the characterization of EOF, organic extracts were separated in three fractions by successive elution on alumina/silica microcolumns (aliphatic hydrocarbons – aromatic hydrocarbons and polar compounds) by liquid chromatography.

For that purpose, the EOF is diluted in dichloromethane, then injected in the microcolumn of alumina. The eluate constituted by aliphatic and aromatic hydrocarbons and a part of the polar compounds is then recovered in a vial. The most polar compounds, trapped at the head of column, are eluted by a mixture of methanol/dichloromethane (50/50, v/v). The hydrocarbon and polar compounds mixture is diluted in *n*-pentane and then injected in a silica microcolumn. The aliphatic fraction is recovered after elution with *n*-pentane, and then aromatic compounds are recovered with a mixture of *n*-pentane and dichloromethane (65/35, v/v). The polar compounds are recovered with a mixture of methanol and dichloromethane (50/50, v/v) in a vial containing the most polar compounds.

The saturated hydrocarbon and polar compounds were analysed by coupled gas chromatography (HP 5890 series II) and mass spectrometry (HP 5971A). The chromatographic separation was performed with a silica capillary column DB-5 J&W Scientific (length: 60 m; diameter: 0.25 mm; film thickness: 0.1 µm) with nonpolar phase (5% phenylmethylpolysiloxane) according to the following temperature steps: 60–130 °C at 15 °C/min, 130–300 °C at

Table 1
Geographical coordinates of the samples from February 2003 sampling campaign.
Tableau 1
Coordonnées géographiques des échantillons de la mission février 2003.

	Sample	Latitude (DMS)	Longitude (DMS)		Sample	Latitude (DMS)	Longitude (DMS)
Beni-Enzar	Be	35°15′ 6.4″N	2°55′ 50.0″W	Mrader	Mr	35° 7′ 40.4″N	2° 51′ 37.4″W
Nador	Na	35°11′ 21.9″N	2°55′ 34.9″W	Arekman	Ar1	35° 6′ 22.8″N	2° 45′ 6.6″W
Bouaroug	Bo	35°10′ 2.2″N	2°54′ 24.4″W	Arekman	Ar2	35° 6′ 44.3″N	2° 44′ 37.7″W
Epuration	St	35°9′ 32.1″N	2°54′ 11.6″W	Centre	Ce	35° 9′ 30.8″ N	2° 50′ 27.7″W
Selwane	Se	35°8′ 7.3″N	2°52′ 59.6″W	Passe	Pa	35° 11′ 53.9″N	2° 50′ 43.9″W

3 °C/min, step of 15 mn at 300 °C, the helium flow being kept constant at 1.4 ml/min. [7,17,20].

For polar compounds analysis, a preliminary silylation was done using BSTFA [35] before injection in the chromatograph.

3. Results and discussion

3.1. Spatial distribution of organic carbon and sulfur contents

TOC and sulfur contents in surface sediments vary, respectively, between 0.22 to 7.59% and 0.02 to 1.79% of sediment dry weight (Fig. 2). The higher percentages of these elements are recorded in the center of the lagoon where water depths are maximum (5 and 8 m). In the lagoon winds create two major currents near the north and south borders [13] (Fig. 3); in the center currents and hydrodynamism are lower and facies characterised by clays and silts. These are the best conditions for organic matter accumulation and lower dissolved oxygen concentrations (Table 3) also favour its preservation [6].

High TOC and S contents are also recorded near the residential areas where treated (Na: Nador) or untreated (Ar: Arekman and Be: Beni-Enzar) wastewaters are discharged. These high concentrations are related to high anthropogenic contributions in nutritive elements (nitrogen and phosphorus) in these wastewaters [12]. Bloundi [3] also noticed that S contents are well correlated with Fe contents in these sites, which is in agreement with the presence of pyrite and suggests reducing conditions.

Elevated TOC and S contents in the immediate vicinity of an aquaculture area (breeding of sea-bream) are probably related to the fish faecal products and also to non consummate granulated food.

On the other hand, low TOC and sulfur rates are recorded in the littoral border zones (Fig. 2), characterized by a sandy facies and a strong hydrodynamism where sediment particles remain in suspension. These conditions do not favour the accumulation and the conservation of the organic matter.

These results show that TOC and S distributions are controlled by:

- hydrodynamism on which depend the conditions of organic matter conservation;
- the anthropization degree.

The TOC contents in the Nador lagoon surface sediments are higher than those generally recorded in other Mediterranean lagoon ecosystems as for example the Thau pond (5.36%) [24] or the Salses-Leucate pond (3%) [4]. Moreover, TOC rates recorded in our study (up to 7.59%) are slightly higher than those recorded by El Alami et al. [6] in Nador lagoon (6.3%). Our higher values are probably related to a strong increase of the population in this region implying an intensification of wastewater discharges. As an example, the number of Nador inhabitants was 62,000 in 1982, 126,000 in 2004 and 132,000 in 2006.

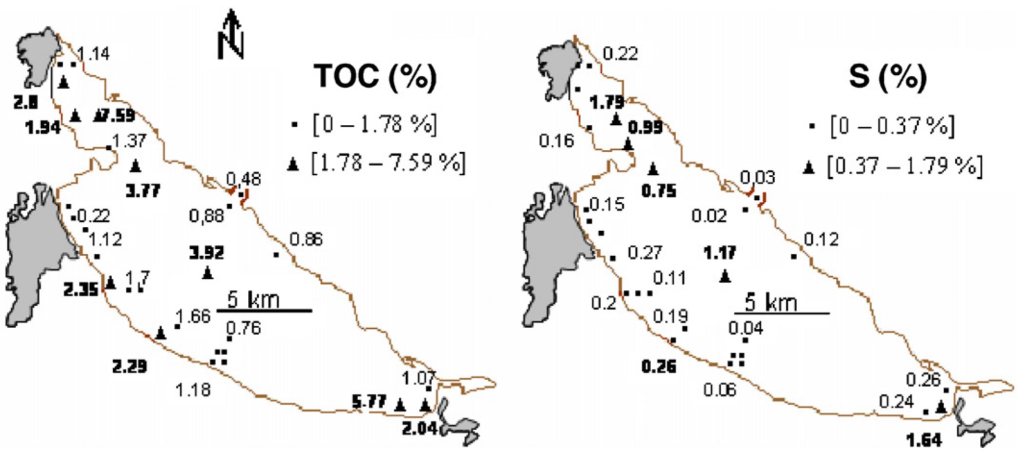

Fig. 2. Carbon and sulfur rates distributions in the surface sediments of Nador lagoon (■: sites where rates are lower than the average, ▲: sites where rates are higher than the average).

Fig. 2. Répartition des pourcentages en carbone et en soufre dans les sédiments superficiels de la lagune de Nador (■ : stations dont les pourcentages sont inférieurs à la moyenne, ▲ : stations dont les pourcentages sont supérieurs à la moyenne).

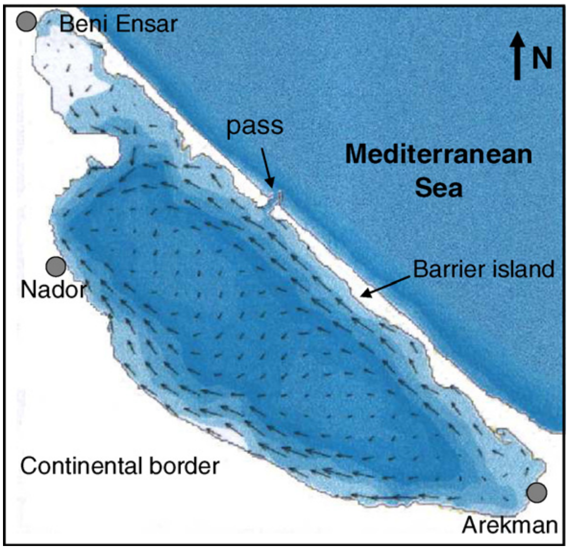

Fig. 3. Map of Nador lagoon currents according to Hilmi [13].

Fig. 3. Carte des courants dans la lagune de Nador d'après Hilmi [13].

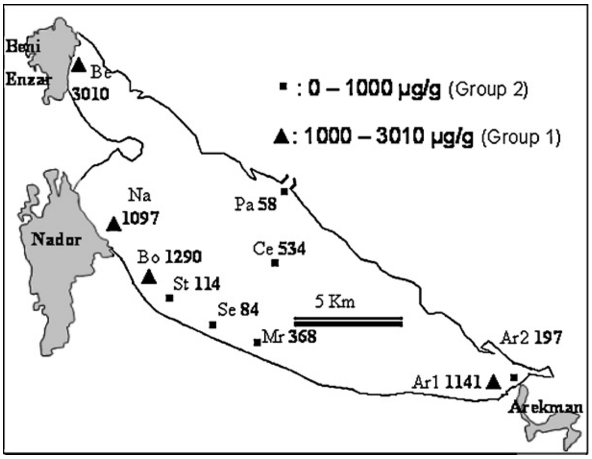

Fig. 4. Extractable organic fraction (EOF) content (µg/g) in the sediments of the studied samples.

Fig. 4. Teneur de la fraction organique soluble (FOS) (µg/g) de sédiment des échantillons étudiés.

3.2. Organic matter molecular signatures and distribution

3.2.1. EOF distribution

EOF contents vary between 56 and 3000 µg/g of dry sediment. The most important content is recorded in the station bordering the city of Beni-Enzar (Be) and is 50 times higher than in the transition zone between lagoon and Mediterranean Sea (Pa) (Fig. 4). EOF spatial distribution is consistent with TOC distribution and allows defining two groups:

- sites located near the cities (Beni-Enzar [Be], Oued Bouaroug [Bo], Arekman [Ar1] and Nador [Na]) where the EOF content exceeds the average value of 1000 µg/g;
- other sites (St, Mr, Ar2, Ce and Pa) characterized by an EOF content lower than 1000 µg/g (Fig. 4).

3.2.2. EOF molecular signature characteristics and distribution

Generally, two types of contributions are in the origin of natural organic matter in aquatic sediments:

- autochthonous (plankton and macrophyte);
- allochtonous (higher plants, soil alteration products ...) [20].

These organic contributions (parents), characterized by a specific organic identity, undergo diverse biochemical damages during their diagenesis, which produce other secondary organic compounds. These compounds called ''sons'' keep a part of the initial information of the parent compounds (molecular skeleton). They are therefore defined as molecular biomarkers [25].

Besides, anthropogenic contributions from fossil organic matter (notably oil products) are added to the natural contributions; the former are also related to urban wastewater discharges. These sources generate special organic compounds with specific molecular signatures.

Three families of biomarkers were considered within the framework of this work: *n*-alkanes, pentacyclic triterpanes and sterols. These compounds are highly interesting not only for studying the origin of the organic matter (continental or marine) and the anthropogenic influence, but also to draw the biochemical processes undergone by organic matter during its transfer through the water column till deposit and diagenesis.

3.2.2.1. n*-alkanes.* *n*-alkanes are synthesized by living organisms in the aquatic ecosystems, but can also result from anthropogenic contributions (industrial discharges, wastewaters, oil products). Among aliphatic hydrocarbons, *n*-alkanes are the predominant molecular families in the studied sediments. The analysis of their distribution allows distinguishing the various sources of organic matter: anthropogenic (oil products) and natural autochtonous (plankton and bacteria) and allochtonous (higher plants) [27].

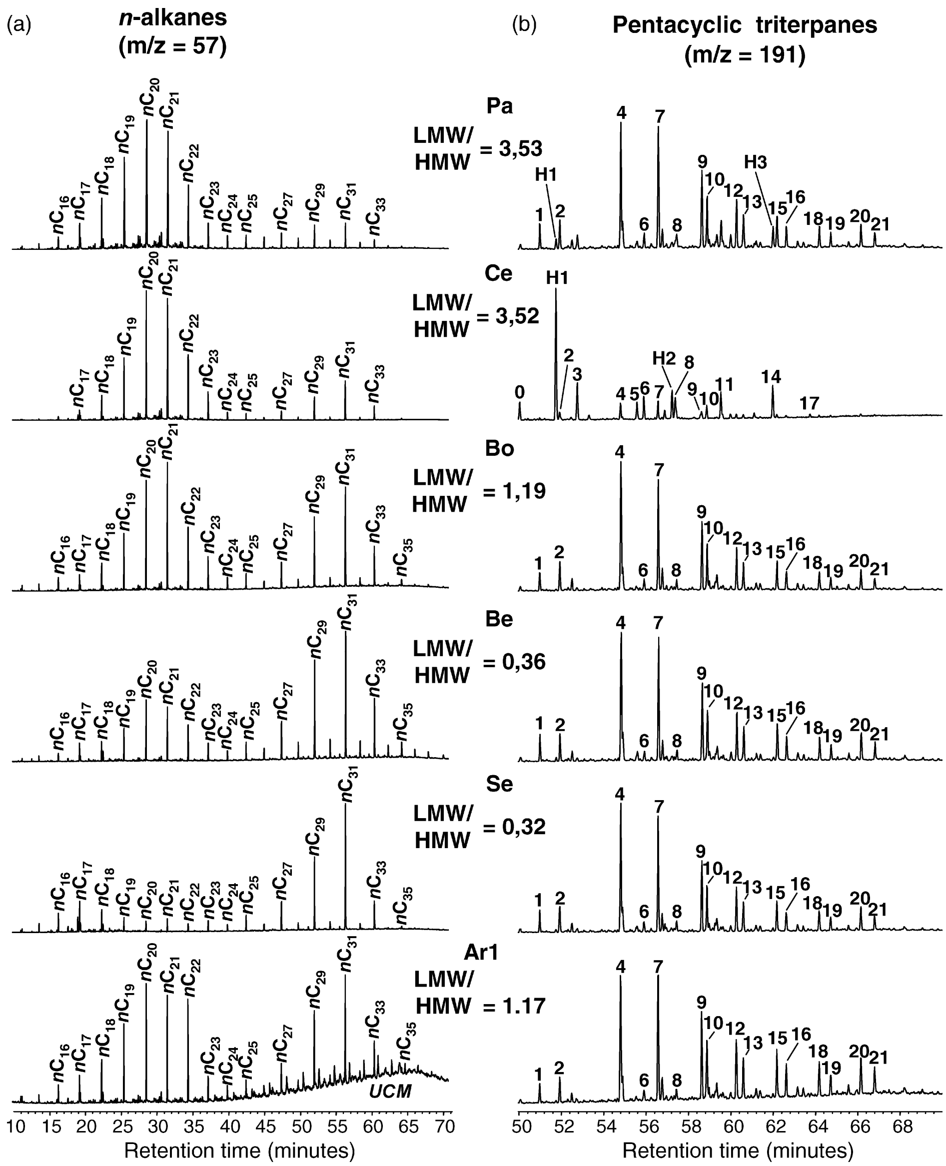

Fig. 5. a: *n*-alkanes ($m/z = 57$) and b: pentacyclic triterpanes ($m/z = 191$) chromatograms for the sediments of Nador lagoon (LMW/HMW: low molecular weight *n*-alkanes/heavy molecular weight *n*-alkanes ratio and pentacyclic triterpanes identification in Table 2).

Fig. 5. a : chromatogrammes des n-alcanes (m/z = 57) et b : des triterpanes pentacycliques (m/z = 191) des sédiments de la lagune de Nador (avec LMW/HMW : rapport des n-alcanes légers/n-alcanes lourds, identification des triterpanes pentacycliques dans le (Tableau 2).

Fig. 5a shows representative single ion chromatograms ($m/z = 57$) of the aliphatic hydrocarbons of the various studied samples. These partial chromatograms show that *n*-alkanes have aliphatic chains constituted by 14 to 37 atoms of carbon.

Littoral edge samples are characterized by a strong preponderance of low molecular mass *n*-alkanes (C_{17} to C_{23}), probably emphasizing an important algae contribution [33]. On the contrary, sediments sampled on the continental edge are characterized by a majority of high molecular mass *n*-alkanes with an odd carbon numbers predominance (C_{29}—C_{31}—C_{33}), typical of higher plants inputs [29,33] (Fig. 5a).

Samples from the lagoon center show an intermediate signature (both algae and higher plants contributions).

The ratio of the peak areas of low molecular weights *n*-alkanes (C_{14}—C_{23}) on those of high molecular weights (C_{24}—C_{37}) (ratio LMW/HMW) is a good indicator to distinguish marine from continental organic matter relative contributions. The ratio calculation results show that the influence is clearly marine (ratio LMW/HMW > 3 – Fig. 5a) on the littoral edge (sample Pa) and in the centre (sample Ce). Other samples show lower ratios emphasizing a more marked contribution of continental organic matter (ratio LMW/HMW < 1.5).

An "unresolved complex mixture" (UCM) is observed on sample Ar1 in the aliphatic hydrocarbon chromatogram (Fig. 5a). This UCM corresponds to a mixture of i*so*- and *cyclo*-alkanes which cannot be resolved with traditional chromatographic columns [8]; they are generally associated with distillated petroleum products (lubricants, road asphalts) [17]. The sample Ar1 taken in the neighborhood of Arekman city where human activity is intense and where wastewater discharges are not treated may be contaminated by oil by-products.

3.2.2.2. Pentacyclic triterpanes: hopanes. The pentacyclic triterpanes distribution (m/z = 191) in the studied sediment samples is given in Table 2 and Fig. 5b. These compounds are usually used by petroleum geochemists to estimate the degree of organic matter thermal maturity. Studying their molecular distribution, enables to determine if organic matter reached the degree of maturation required for oil and/or gas generation [33]. The occurrence in sediment samples of pentacyclic triterpanes presenting a distribution of thermal mature organic matter is generally revealing an anthropogenic contamination due to usage of fossil products (petroleum, coal) [26].

A majority of samples (Ar1, Be, Bo, Fig. 5b) contains pentacyclic triterpanes with a distribution dominated by isomers in configuration βα and 22S (peaks 5,8,10,11,13,14,16,17,19,20,22,23). Besides, isomers in configuration 22S (peaks 9, 12, 15, 18, 20) are more abundant than those in configuration 22R (peaks 10, 13, 16, 19, 21) confirming the thermal maturity of organic matter probably inherited in the lagoon from fossil hydrocarbons contamination [20].

Nevertheless, three samples show different pentacyclic triterpanes distributions (Ce, Pa – Fig. 5b and Ar2). Especially, Ce sample distribution is characterized by the occurrence of unsaturated pentacyclic triterpanes (H1, H2) and pentacyclic triterpanes in biological configuration ββ underlining recent organic matter inputs.

Samples Pa and Ar2 show intermediate distributions compared to the latter sample and to those with thermal mature triterpanes distributions.

Thus, on the basis of the pentacyclic triterpanes distribution, the lagoon centre (sample Ce) seems to be the only location preserved from thermal mature organic matter contribution. The other samples are strongly affected by an anthropogenic contribution; the lagoon – Mediterranean Sea exchange zone (Pa) as well as Ar2 are also affected but in a lesser extent. These samples are contaminated by fossil hydrocarbons (road asphalts, atmospheric deposition, intra lagoon maritime traffic...).

However, in the case of the preserved site (Ce), the intense contribution of the triterpanes of natural origin may mask a possible anthropogenic contribution.

3.2.2.3. Sterols. Sterols play an essential role in the aquatic medium; they are part of cellular membrane composition of many living organisms and thus participate in their reproduction and growth. In the marine medium, sterols result mainly from planktonic or benthic seaweeds, from zooplankton and in a lesser measure fungi [30].

Table 2
Identification of pentacyclic triterpanes from Fig. 5b.
Tableau 2
Identification des triterpanes pentacycliques de la Fig. 5b.

N	Name	Carbon number	*N*	Name	Carbon number
0	22,29,30-Trisnorhop-13(18)-ene	C_{27}	11	17β(H), 21β(H)-hopane	C_{30}
1	18α(H)-trisnorhopane (Ts)	C_{27}	H_3	Hop-22(29)ene	C_{30}
H_1	22,29,30-Trisnorhop-17(21)-ene	C_{27}	12	22S-17α(H), 21β(H)-30 bishomohopane	C_{32}
2	17α(H)-22,29,30-Trisnorhopane (Tm)	C_{27}	13	22R-17α(H), 21β(H)-30 bishomohopane	C_{32}
3	17β(H)-22,29,30-Trisnorhopane	C_{27}	14	17β(H), 21β(H)-30 homohopane	C_{31}
4	17α(H), 21β(H)-30-Norhopane	C_{29}	15	22S-17α(H), 21β(H)-30 trishomohopane	C_{33}
5	Hop(17)21ene	C_{30}	16	22R-17α(H), 21β(H)-30 trishomohopane	C_{33}
6	17β(H), 21α(H)-30 normoretane	C_{29}	17	17β(H), 21β(H)-30 bishomohopane	C_{32}
7	17α(H), 21β(H)-Hopane	C_{30}	18	22S-17α(H), 21β(H)-tetrakishomohopane	C_{34}
H_2	Neohop-13(18)-ene	C_{30}	19	22R-17α(H), 21β(H)-tetrakishomohopane	C_{34}
8	17β(H), 21β(H)-30 norhopane	C_{29}	20	22S-17α(H), 21β(H)-pentakishomohopane	C_{35}
9	22S-17α(H), 21β(H)-30 homohopane	C_{31}	21	22R-17α(H), 21β(H)-pentakishomohopane	C_{35}
10	22R-17α(H), 21β(H)-30 homohopane	C_{31}			

Sterols in the coastal zones may come from higher plants and soils, but also from anthropogenic activities (especially wastewater discharges) [34]. In particular coprostanol, which is a specific sterol characteristic of human faeces (produced by cholesterol degradation in the human digestive system), is frequently used as indicator of pollution by wastewater [32].

Sterols studied in this work are: coprostanol (5β, cholestan-3βol), cholesterol (cholest-5-en-3β-ol), cholestanol (5α, cholestan-3β-ol), stigmasterol (stigmast-5-en-3β-ol) and stigmastanol (5β, stigmastan-3β-ol).

The use of ratios between selected sterols has been proposed to enhance the reliability of contamination assessments based on sterol markers. One commonly used ratio in sediments is the percentage of coprostanol versus total sterols [5,18]; the ratio stanol/sterol ([cholestanol + stigmastanol]/[cholesterol + stigmasterol], Fig. 6) is used as indicator of redox conditions [11,22].

The ratio values of coprostanol on the sum of the other sterols are systematically higher for samples previously classed as under strong anthropogenic influence (group 1 – Fig. 6).

Coprostanol is often proposed as tracer of human faeces [32,34] but may also have a natural origin according to Pocklington et al. [26]; these authors showed that the concentrations of coprostanol can be similar to those of some natural sterols reflecting the primary production.

Our results concerning coprostanol show that there are maxima values (coprostanol/$\sum$sterols > 0.17 – Fig. 6) in the vicinity of cities which feed the lagoon with untreated wastewaters (Fig. 7). The minima values (coprostanol/$\sum$sterols < 0.05 – Fig. 6) are recorded close to the littoral edge (Fig. 7). Thus, samples located near big cities (Fig. 7) are particularly contaminated by discharges of wastewater (high coprostanol/$\sum$sterols ratio) whereas samples located in more preserved zones (the center of the lagoon and near the pass) are little affected by urban waters discharges. These results

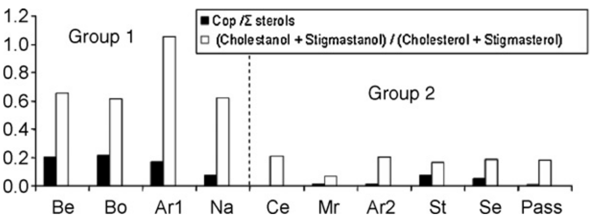

Fig. 6. Coprostanol/$\sum$sterols ratio and (cholestanol + stigmastanol)/(cholesterol + stigmasterol) ratios for the studied sediment samples.

Fig. 6. Rapports coprostanol/$\sum$ stérols et (cholestanol + stigmastanol)/(cholestérol + stigmastérol) des échantillons de sédiment étudiés.

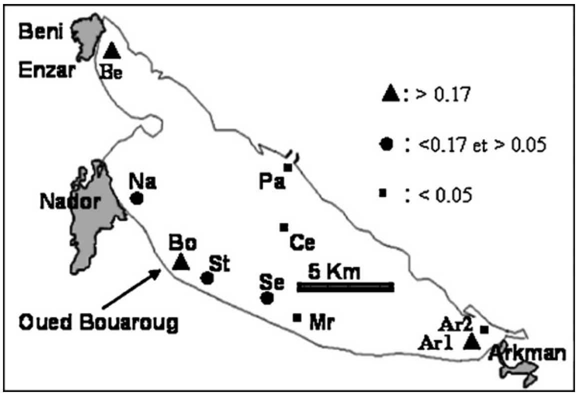

Fig. 7. Distribution of values of the coprostanol/Σsterols ratio for the studied sediment samples.

Fig. 7. Répartition des valeurs du rapport coprostanol/Σstérols dans les échantillons de sédiment étudiés.

enable to map the sites where the faecal contamination is pronounced (Fig. 6).

Near the cities, values of another ratio (stanols/sterols) are definitely higher (> 0.6) compared to the marine edge (< 0.25). The stanol/sterol ratio values higher than one are generally considered as indicator of reducing conditions [11,22]. Indeed, the sediments sampled near the cities show lower hydrodynamism and dissolved oxygen content (Fig. 3, Table 3), and thus are in reducing conditions. This is in good agreement with the good correlation between S and Fe and the presence in these zones of pyrite stable in reducing conditions [3]. Indeed, these conditions, the low thickness of water section, and especially the continuous contribution and the large amount of organic matter related to the

Table 3
Dissolved oxygen concentrations in lagoon surface waters sampled on February 2003.
Tableau 3
Concentrations en oxygène dissous dans les eaux de surface de lagune, échantillonnées en février 2003.

Sampling site	Dissolved O_2 (mg/l)
Oued Afelioun mouth (Ar1)	6.3
Beni-Ensar city (Be)	6.6
Arekman city Ar2	7
Lagooning (St)	7.1
Lagooning (St)	7.12
Nador city (Na)	7.2
Center near Nador city	7.2
Oued Bouaroug mouth (Bo)	7.2
Oued Selwane mouth (Se)	7.5
Centre near the pass	7.6
Irrigation channel (Mr)	7.87
Pass (Pa)	8.3
Oued Saleh mouth	8.73

wastewater discharges, do not favour the biodegradation and particularly the reduction of the double bonds C_5—C_6 leading to the transformation of sterols into stanols.

4. Conclusions

This work concerns surface sediments of Nador lagoon sampled on representative sites. Zones close to potential organic pollution sources (cities, wastewater treatment plant and fish farming) were also targeted. The study of TOC and sulfur distributions shows that two major factors control their distribution:

- the sedimentary facies strongly related to hydrodynamism;
- the organic contributions (anthropogenic or natural).

Our study shows that the recorded organic content is above average in sites located near cities [Beni-Enzar (Be), Oued Bouaroug (Bo), Arekman (Ar1) and Nador (Na)], whereas the sites on the littoral border present organic contents lower than the average.

Two sectors within the lagoon can be distinguished according to the distribution of biomarkers (*n*-alkanes, pentacyclic triterpanes and sterols): a marine sector with dominant *n*-alkanes of low molecular weights associated with two specific sterols (cholesterol and stigmasterol) giving evidence of an algal influence (biological origin) and a sector under continental influence where the odd *n*-alkanes of high weight (signature typical of cuticular waxes from higher plants) dominate, associated with three sterols (cholestanol, coprostanol and stigmastanol). Besides, in all lagoon sites except in the centre, petroleum byproducts contributions are identified by the presence of pentacyclic triterpanes with a molecular distribution typical of thermal matured organic matter.

The presence of coprostanol near Beni-Enzar and Arekman cities and Oued Bouaroug underlines a pronounced faecal contamination; the site located near Nador city seems less contaminated, which is in relation with the occurence of Nador city wastewater treatment plant. The rest of the lagoon seems less affected by the wastewater discharges. Besides, it seems that the organic contributions from wastewater discharges partially control the redox conditions of sediments. Indeed, zones which are the most contaminated by wastewater (close to cities) show reducing conditions highlighted by high values of stanols/sterols ratios, higher values of S contents and occurrence of pyrite.

Thus the organic contamination is particularly marked in the vicinity of Nador, Beni-Enzar and Arekman cities. Moreover, aquaculture also contributes to the lagoon sediments enrichment in organic matter in the western sector. On the contrary, the littoral edge and the lagoon centre seem still preserved from organic pollution.

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