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Seasonal Variations of Dissolved Normal Alkanes in the Water Marshes of Iraq

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The distribution and seasonal variations of n-alkanes in the dissolved water of the marshes have been determined by gas-chromatography. Temperature variations, including evaporation, bacterial degradation and adsorption as well as photochemical oxidation, are postulated to produce pronounced seasonal variations of n-alkanes in the water. Higher concentrations of n-alkanes were observed in the winter than in the summer. The n-alkanes showed a regular distribution pattern of the odd and even carbon number compounds between C13 to C34 with additional characteristics associated with biological phenomena; abundance of C17, C19 of algal origin and C25, C27, C29 of terrestrial plant inputs was evident. Pristane and phytane were the most common of the isoprenoids in the water samples, suggesting biological origin, while the presence of Unresolved Complex Mixture (UCM) reflects the anthropogenic (urban and petroleum related) inputs.

Hydrocarbons may enter the aquatic environment by many routes including airborne fall-out, sewage, dredging and industrial outfalls, as well as from natural origins such as living organisms and sediment (Marty & Saliot, 1976).

The marshes of Iraq receive large amounts of organic inputs originating from diverse sources, both biogenic and anthropogenic (Al-Saad & Al-Timari, 1989). These are transported in the form of dissolved and particulate organic matter within the water column, where they undergo intense mixing as well as several transformation processes such as biodegradation or photo-oxidation (Al-Saad & Al-Timari, 1989).

The molecular characterization of the dissolved water phases is of considerable interest from environmental standpoints, so in this paper, we investigated seasonal variations of normal alkanes dissolved in water of Hor Al-Hammar marshes in southern Iraq in order to assess the value of the approach for providing a better understanding of the marshes. The concentration, distribution and sources of n-alkanes in dissolved water of the marshes during three seasons are reported here for the first time.

Description of the Study Area

The marshes consist topographically of an alternation of marshland and lowland plain, divided by sluggish drainage channels, lagoons and ox-bow lakes (Fig. 1). The whole area is extremely flat and a small rise in base level in either river causes extensive flooding. The seasonal flood cycle of both rivers reaches a peak between April and May, while the water recedes and reaches a minimum level in October (Van der Leeden, 1975). The eastern and central marshes draw their water from the Tigris and 80% of the discharge of the river at Baghdad disperses into them. The Euphrates disperses through numerous channels and eventually drains into the large shallow marsh named Hor Al-Hammar. The major part of the discharge of the two rivers is absorbed and stored by these extensive water bodies, where most of the open water eventually evaporates and only part is discharged via the Shatt Al-Arab into the Arabian Gulf (Anon., 1975). The average annual rainfall is less than 200 mm, most of which falls between November and March (Shalash, 1966). Air temperatures frequently exceed 45°C in Summer and fall to near freezing in winter.

Al-Saadi *et al.* (1981) provide some physico-chemical data, total phytoplankton contents and a general vegetation description of the marshes. In these studies they recorded that diatoms were the most dominant phytoplankton, followed by the green, blue green dianoflagellate and the euglenoid species.

Materials and Methods

From our previous experience in the area (Al-Saad & Al-Timari, 1989) seven sampling sites have been selected for the study of dissolved normal alkanes in Hor Al-Hammar marsh (Fig. 1). The sampling programme was carried out seasonally over periods of 9 months (January to July 1987). Water samples (30 l) were obtained from approximately the 1 m of the water column in well-washed glass aspirator bottles from each of these seven stations. The water samples were suction filtered as soon as possible (within 5 h through pre-ignited 450°C) using preweighed 0.45 μm pore size Whatman GF/F glass fibre filters. Materials passing

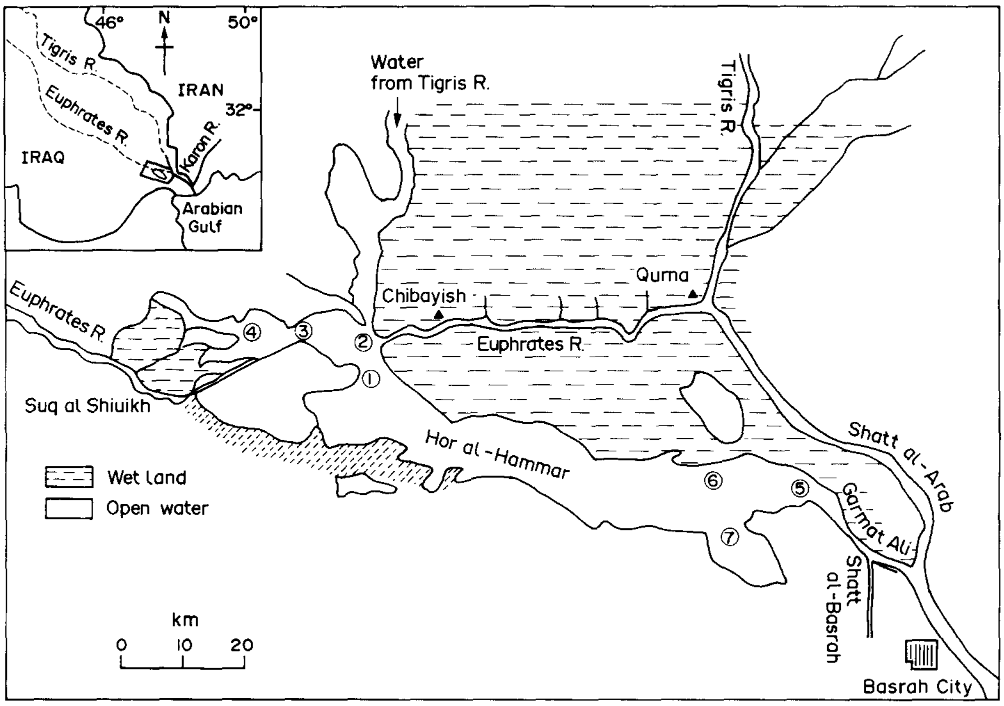

Fig. 1 Map of the marshes of Iraq showing the position of stations.

through the filters were considered as 'dissolved', with the retained as 'particulate'. Dissolved hydrocarbons were extracted by solvent extraction following the procedure of UNESCO (1976). One hundred millilitres of CCl_4 was used in two successive 50 ml extractions and the extracts were combined. To the combined extracts anhydrous sodium sulphate was added to break any emulsion and to remove excess water. The CCl_4 extracts were reduced in volume to less than 10 ml using a rotary evaporator and then carefully pipetted into a precleaned 10 ml volumetric flask in order to make sure that any residual particles of sodium sulphate were excluded and evaporated to dryness by a stream of purified nitrogen. The flask was then rinsed with fresh hexane and the rinsing was used to make the sample volume up to 5 ml. Hydrocarbons were isolated by column chromatography. Twenty milligrams of 5% deactivated florisil was added to the glass column. An extract was then applied to the head of a column and eluted with 50 ml of n-hexane to isolate the n-alkanes.

Strenuous efforts were made to minimize contamination of the samples. Procedural blanks consisting of all reagent and glasswares used during the analysis, were periodically determined. Recoveries calculated by comparing the peak area of internal standards of n-alkanes with reference solution, were always more than 90%. The Unresolved Complex Mixture (UCM) was measured by planimetry.

The analysis of the dissolved n-alkanes was done by a Perkin-Elmer Sigma 300 capillary gas chromatography equipped with Flame Ionization Detector (FID), and a splitless injection port was used. Quantification of peaks and identification of n-alkanes in chromatograms was achieved by a Perkin-Elmer computing integrator (Model LC-100). The fused silica capillary column used was a wall coated open tubular (WCOT) 50 m × 0.25 mm i.d. SE-30 (Methysilicone) Perkin-Elmer. Helium was used as a carrier gas with a linear velocity 1.5 ml min^{-1}. Operating temperatures for detector and injector were 310 and 300°C respectively. The column was operated under temperature programmed condition (4°C min^{-1}) for 60 to 280°C with an isothermal period of 30 min at the end.

Results and Discussion

The composition of n-alkanes extracted from the dissolved water in winter, spring and summer is presented in Tables 1, 2, and 3 respectively, while the seasonal variations of total n-alkanes in the dissolved water for different stations in the marshes are listed in Table 4 and Fig. 2. The total concentration of n-alkanes in dissolved water varied from 0.14 μg l^{-1} in station 5 to 1.42 μg l^{-1} at station 4 in summer, and from 2.72 μg l^{-1} at station 5 to 6.20 μg l^{-1} at station 4 in winter. In general the concentration of n-alkanes were much higher in the winter than in summer season. Hydrocarbon concentrations observed at any time in the water column of the marshes reflect the combined effect of input and removal processes. Several factors, acting either singly or in combination, could produce the seasonal variation observed that is inversely related to water temperature. The water temperature of marshes undergoes seasonal variation. It was reported that the seasonal range encountered at Al-Hammar marsh is 12.4°C in January and 33.9°C in August (Al-Saadi & Al-Mousawi, 1988), thus when the water temperature is higher than 20°C (spring and summer) the n-alkanes residues are lower than when the temperature is less than 20°C (winter), because the temperature is the most important factor determining the removal of hydrocarbons from the water (DouAbul & Al-Saad, 1985; Gordan *et al.*, 1978). Besides the direct effect of temperature on the evaporation of hydrocarbons from water, increase in temperature favours process of bacterial degradation. It is well

TABLE 1

Concentrations of dissolved n-alkanes ($\mu g\ l^{-1}$) in water marshes during winter.

Carbon number	Station 1	2	3	4	5	6	7
C13	0.04	0.04	0.04	0.06	0.02	0.03	0.03
C14	0.05	0.06	0.08	0.09	0.03	0.07	0.06
C15	0.08	0.07	0.09	0.20	0.02	0.08	0.08
C16	0.06	0.08	0.10	0.19	0.04	0.06	0.07
C17	0.30	0.29	0.32	0.43	0.29	0.41	0.38
C18	0.10	0.19	0.25	0.31	0.13	0.38	0.21
C19	0.24	0.27	0.32	0.38	0.27	0.39	0.30
C20	0.18	0.19	0.20	0.23	0.08	0.28	0.11
C21	0.26	0.25	0.28	0.38	0.20	0.28	0.23
C22	0.17	0.15	0.19	0.26	0.19	0.21	0.19
C23	0.19	0.25	0.23	0.26	0.10	0.23	0.29
C24	0.15	0.10	0.17	0.30	0.09	0.26	0.18
C25	0.25	0.29	0.14	0.34	0.24	0.36	0.26
C26	0.13	0.23	0.13	0.28	0.09	0.24	0.20
C27	0.18	0.29	0.38	0.42	0.28	0.34	0.36
C28	0.09	0.18	0.24	0.28	0.10	0.29	0.16
C29	0.18	0.25	0.26	0.48	0.16	0.30	0.29
C30	0.09	0.09	0.15	0.29	0.09	0.28	0.23
C31	0.07	0.13	0.19	0.39	0.10	0.29	0.20
C32	0.06	0.07	0.21	0.25	0.08	0.16	0.10
C33	0.05	0.09	0.10	0.20	0.07	0.18	0.16
C34	0.03	0.08	0.19	0.18	0.05	0.20	0.19

TABLE 2

Concentrations of dissolved n-alkanes ($\mu g\ l^{-1}$) in water marshes during spring.

Carbon number	Station 1	2	3	4	5	6	7
C13	0.05	0.03	0.02	0.03	0.01	0.02	0.01
C14	0.06	0.02	0.03	0.04	0.01	0.03	0.02
C15	0.05	0.02	0.04	0.05	0.02	0.01	0.05
C16	0.03	0.02	0.01	0.04	0.01	0.04	0.04
C17	0.09	0.19	0.11	0.18	0.07	0.18	0.09
C18	0.03	0.05	0.02	0.09	0.03	0.07	0.05
C19	0.08	0.08	0.09	0.10	0.05	0.10	0.07
C20	0.04	0.06	0.06	0.08	0.02	0.08	0.03
C21	0.05	0.05	0.07	0.19	0.06	0.14	0.06
C22	0.02	0.06	0.05	0.09	0.03	0.09	0.05
C23	0.02	0.07	0.09	0.09	0.04	0.08	0.04
C24	0.06	0.03	0.03	0.08	0.01	0.08	0.03
C25	0.09	0.04	0.10	0.16	0.02	0.09	0.01
C26	0.01	0.03	0.07	0.05	0.03	0.07	0.04
C27	0.04	0.09	0.13	0.13	0.06	0.09	0.09
C28	0.04	0.05	0.08	0.07	0.04	0.08	0.06
C29	0.04	0.08	0.09	0.09	0.02	0.13	0.08
C30	0.03	0.05	0.06	0.05	0.01	0.06	0.04
C31	0.02	0.04	0.04	0.06	0.03	0.08	0.03
C32	0.02	0.06	0.02	0.03	0.02	0.06	0.04
C33	0.01	0.03	0.01	0.04	0.01	0.03	0.02
C34	0.01	0.01	0.02	0.02	0.02	0.04	0.01

TABLE 3

Concentrations of dissolved n-alkanes ($\mu g\ l^{-1}$) in water marshes during summer.

Carbon number	Station 1	2	3	4	5	6	7
C13	–	0.01	0.01	0.02	–	0.01	–
C14	–	0.02	0.03	0.03	–	0.02	–
C15	0.01	0.02	0.01	0.03	–	0.03	0.10
C16	0.01	0.01	0.03	0.02	–	0.03	0.03
C17	0.04	0.10	0.09	0.15	0.02	0.10	0.14
C18	0.01	0.04	0.09	0.09	0.01	0.09	0.02
C19	0.02	0.05	0.06	0.06	0.02	0.07	0.01
C20	0.02	0.03	0.09	0.08	–	0.04	0.10
C21	0.03	0.05	0.07	0.06	0.02	0.10	0.03
C22	0.03	0.02	0.05	0.07	0.01	0.08	0.01
C23	0.02	0.06	0.03	0.06	–	0.03	0.04
C24	0.01	0.04	0.02	0.05	0.01	0.04	0.01
C25	0.03	0.07	0.09	0.09	0.01	0.03	0.02
C26	0.01	0.02	0.07	0.07	0.01	0.02	0.01
C27	0.05	0.18	0.06	0.09	0.02	0.13	0.03
C28	0.02	0.02	0.04	0.05	0.01	0.03	0.02
C29	0.01	0.08	0.02	0.13	–	0.05	0.04
C30	0.01	0.03	0.03	0.10	–	0.05	0.01
C31	–	0.01	0.02	0.09	–	0.03	–
C32	–	0.02	0.01	0.08	–	0.02	–

– = Not detected.

TABLE 4

Seasonal variations of the total dissolved n-alkanes in water marshes.

Station number	Total n-alkanes ($\mu g\ l^{-1}$) Winter* January	Spring† March	Summer‡ July
1	2.95	0.89	0.33
2	3.64	1.06	0.88
3	4.26	1.24	0.92
4	6.20	1.76	1.42
5	2.72	0.62	0.14
6	5.32	1.65	1.00
7	4.28	0.96	0.62

*Water temp. = 12°C. †Water temp. = 20°C. ‡Water temp. = 24°C.

documented that the activity of hydrocarbon oxidizing bacteria is controlled by temperature (Cundell & Traxler, 1973) and therefore the rate of microbial breakdown of hydrocarbons will be considerably less in winter when the water temperature is lowest. The same conclusion was arrived at by DouAbul & Al-Saad (1985) in the water of Shatt Al-Arab river and also by Shamshoom *et al.* (1990) who found that oil degrading bacteria was more active in summer than in winter in the North-West Arabian-Gulf.

Photo-oxidation may also degrade the components of oil in water (Lee, 1980). Intensive solar radiation coupled with relatively high water temperature is a characteristic feature of the climate of the subtropical region of Iraq. Thus, rather low levels of n-alkanes encountered in the water marshes are expected to be due to their rapid phytolysis. The water volume of the marshes experiences variations at different season also. Thus the water flow maximum occurs in June while the minimum occurs in January (Van der Leeden, 1975). Al-Hilli (1977) observed pronounced seasonal variations in the average values of suspended matters in the marshes, being at a minimum in summer. Therefore, the lower concentration of n-alkanes observed in the water of the marshes during summer could be caused in part by the increased sedimentation of sorbed hydrocarbons (DouAbul & Al-Saad, 1985). The n-alkanes distribution of dissolved water are characterized by two patterns, the first in the range of C14 to C23 with high C17 and a slight predominance of even carbon n-alkanes, and the second in the range >C23 with predominance of odd carbon n-alkanes (Fig. 3).

An even carbon numbered n-alkanes predominance could be interpreted as a consequence of microbial activity in the area (Bedair & Al-Saad, 1992). The predominance of odd carbon numbered n-alkanes in the range >C23 is generally attributed to inputs from terrestrial higher plants (Wakeham & Farrington, 1980). A mixed diatoms population was found to

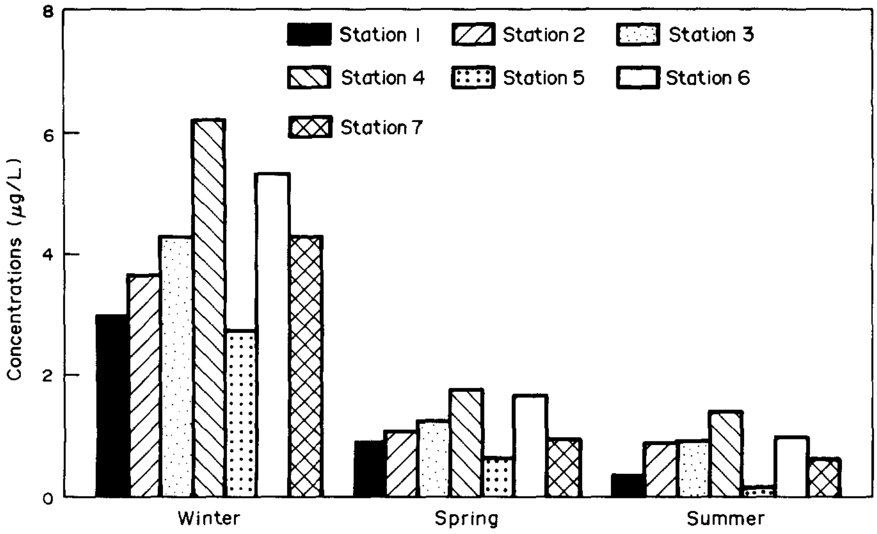

Fig. 2 Seasonal variations of n-alkanes in the water marshes of Iraq.

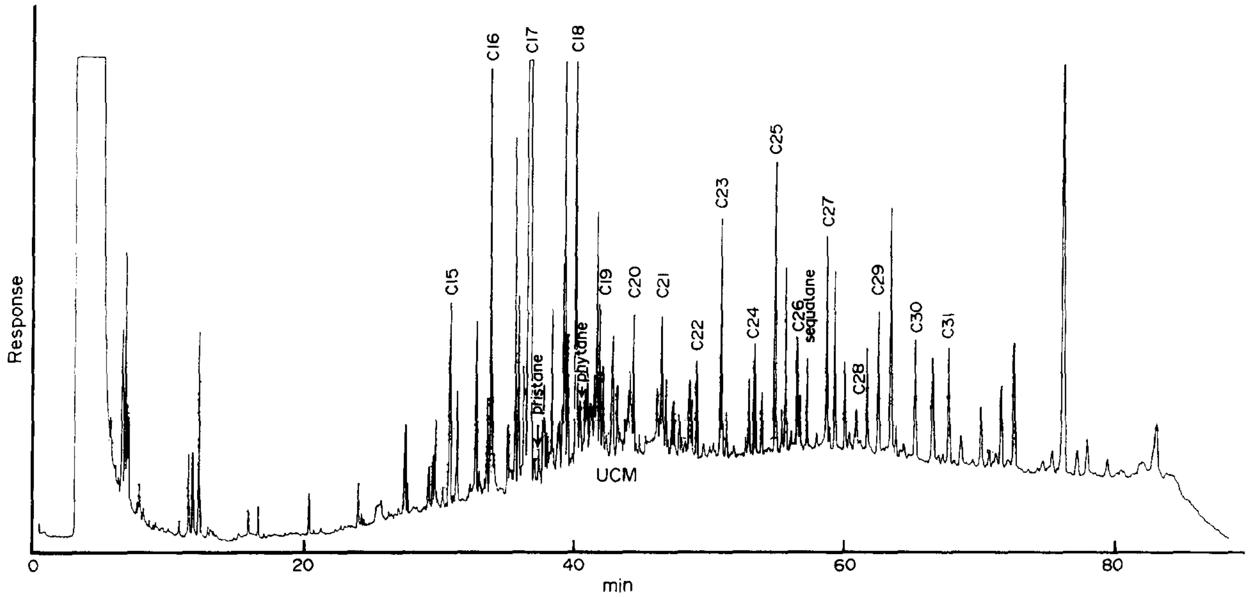

Fig. 3 Chromatograms of n-alkanes in the dissolved water marshes of Iraq.

contain a range of n-alkanes from C15 to C31 with predominance of even range (Saliot, 1981). Diatoms are the most dominant group of phytoplankton in the marshes (Al-Saadi *et al.*, 1981; Al-Zubaidi, 1985), furthermore microscopic examination of sedimentary elements revealed that diatoms are a major and common source of autochthonous organic matter in the region, and this evidence suggests that diatoms are responsible for even carbon n-alkanes in water samples. The same conclusion has been given by Bedair & Al-Saad (1992).

Odd carbon number n-alkanes lower than C21 such as C15, C17 and C19 are commonly found in algae (Goutx & Saliot, 1980). C20 to C28 model n-alkanes, without carbon number preference, maximizing around C23 may be produced by bacterial activity (Grimalt *et al.*, 1985), and C25 to C31 odd carbon numbered n-alkanes are indicative of higher plants (Kennicutt *et al.*, 1987). The marsh waters of Iraq are oligohaline and many aquatic plants were abundant (Al-Hilli, 1977). Such aquatic plants are likely to be the main source of n-alkanes in the water (Bedair & Al-Saad, 1992). The contribution of other sources of n-alkanes in our samples may be due to higher land-based vegetation, reflected by the predominance of alkanes with an odd number of carbon atoms over those with an even number of carbon atoms. This predominance was revealed for the first time by our samples, and encountered in a more pronounced manner in the water probably under the effect of aeoline contributions, and terrestrial inputs derived from plant material.

Al-Saad & Bedair (1989) mentioned that a high percentage of hydrocarbons is associated with high chlorophyll-a concentrations in the water in Shatt Al-Arab estuary. Hence, the dominance of the odd numbered n-alkanes and the high chlorophyll-a concentrations may provide good evidence for the biogenic origin of the n-alkanes in the waters.

The isoprenoids hydrocarbons in the waters of the marshes probably come mainly from aquatic organism either directly, in the case of pristane (Blumer & Snyder, 1963), or indirectly from aquatic biomolecules such as chlorophyll (Didyk *et al.*, 1978). Chlorophyll from land-plant sources providing the high molecular weight n-alkanes could serve as a source for some isoprenoids hydrocarbons. Pristane and Phytane are the most common of the isoprenoids in these samples. The Pristane/Phytane ratio is generally greater than 1 (Table 5) which is an indicator of biogenic hydrocarbons (Shaw *et al.*, 1985).

The presence of squalane during winter and spring in water (Table 5), may originate from either living organisms or from anthropogenic sources (Al-Saad, 1990). The odd/even carbon ratios, or Carbon Preference Index (CPI) of more than 1, indicates that the major source of n-alkanes is terrestrial, mostly aquatic plants, while a CPI aproaching unity indicates greater inputs from aquatic organisms or petroleum hydrocarbons (Simmoneit, 1978). Generally most of the CPI during three seasons are more than 1 (Table 5) indicating the biological origin of n-alkanes in the water of the marshes. On the other hand, the presence of broad Unresolved Complex Mixture (UCM) (Table 5 and Fig. 3) indicates petroleum contamination (Farrington *et al.*, 1977), due to the water flows associated with agricultural activity, and the marshes receive water from both the Tigris and Euphrates rivers which carry tremendous amounts of suspended particulate matter to which organic matter is adsorbed. These materials are mostly deposited in the entrance of the marsh (i.e. station 4 in Fig. 1) as the water velocity drops appreciably. Also the presence of (UCM) in our samples may be due to a large number of small boats using the area. As a consequence, the environment here is constantly subjected to a small spillage of fuel oil as well as direct discharges of engine exhaust. This contention was further supported by the detection of some Polycyclic Aromatic Hydrocarbons which were reported to be present in No. 2 fuel oil used extensively in the region (Al-Saad & Al-Timari, 1989).

In light of the above, the following conclusions may be drawn:

1. Processes brought about by temperature variations including evaporation, bacterial degradation and adsorption as well as photochemical oxidation, produce a pronounced seasonal variation of n-alkanes in dissolved water of the marshes.

2. The present study indicates that the n-alkanes in the dissolved water originate from diverse sources. Biogenic sources such as algal remains, aquatic organisms, and terrigenous plants are all considered to be a source of n-alkanes. The other source is anthropogenic (urban and petroleum related).

TABLE 5

Squalane and ratios of various parameter for dissolved n-alkanes in the water marshes.

Station number	Squalane µg l^{-1}	Pri/Phy	CPI*	UCM† µg l^{-1}
Winter				
1	0.01	0.43	1.62	0.55
2	0.03	1.14	1.56	0.52
3	0.04	1.06	1.23	0.22
4	0.06	1.33	1.08	0.65
5	0.01	0.89	1.33	0.20
6	0.08	1.56	1.81	0.62
7	0.06	1.80	1.51	0.03
Spring				
1	0.01	1.12	1.54	0.01
2	–	1.25	1.40	–
3	0.03	1.13	1.75	0.01
4	0.02	0.69	1.75	0.03
5	–	0.95	1.69	–
6	0.01	1.29	1.35	0.02
7	0.04	1.47	1.34	0.04
Summer				
1	–	0.84	1.75	–
2	–	0.92	2.52	0.05
3	–	1.82	1.00	0.03
4	–	1.77	1.25	0.25
5	–	1.74	1.80	–
6	–	2.42	1.38	–
7	–	1.52	1.95	0.12

*CPI = Carbon perference index.
†UCM = Unresolved complex mixture.
– = Not detected.

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Interaction Between Selenium and Cadmium in *Eledone cirrhosa* of the Northern Tyrrhenian Sea

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The interaction of Se with Cd was studied in *Eledone cirrhosa* in the northern Tyrrhenian Sea. From the results it appeared that in this organism the concentration of the two elements in mantle muscle tissue decreased from the beginning to the end of the life cycle until they were comparable with those of other studied organisms from the same area. The variation of selenium concentration was satisfactorily described by an equation obtained by fitting the experiment set of data and considering the Se concentration related both to that of Cd and to the length of the specimen. The variation of Se was partially explained with the interaction of Cd with a molar ratio of 1:1, hypothesizing a protection mechanism based on the formation and subsequent release from the body of a Cd–Se complex, while the remaining variation of Se concentration, related to that of the length of the specimen, was explained with metabolic and/or physiological variations over the life cycle of *Eledone*.

The interaction of Se with Cd and the protective effects of the former on the toxicity of the latter have been extensively studied in terrestrial mammals, mostly rats and mice, under laboratory conditions (Gasiewicz & Smith, 1976, 1978; Nishiyama *et al.*, 1987; Czauderna & Rochalska, 1989; Yin *et al.*, 1991).

On the contrary, concerning marine organisms, little data and quite divergent results are available. It was seen under laboratory conditions that the Se enhanced the Cd uptake in haemolymph and gills of the shore crab *Carcinus maenas* (Bjerregard, 1982, 1985, 1988), and counteracted the Cd toxicity in the freshwater snail *Lymnaea stagnalis* (Puymbroeck *et al.*, 1982). Bjerregaard (1988) demonstrated that in *Asterias rubens* (sea star) Se increased the Cd uptake in body wall, pyloric caeca and tube feet, while in *Mytilus edulis* (mussel), *Littorina littorea* (strandsnile), and *Arenicola marina* (lugworm) the Cd uptake was not enhanced by Se in any organ or tissue. From research in the field, it was found that in black marlin (*Makaira indica*) muscle tissue the Cd concentrations were not correlated with those of Se (Mackay *et al.*, 1975), while a positive correlation was found in *Mytilus edulis* (Micallef & Tyler, 1989).

Recently, from preliminary research on six marine species, *Merluccius merluccius* (hake), *Trisopterus minutus capelanus* (poor cod), *Solea vulgaris* (sole), *Lepidorhombus boscii* (megrim), *Nephrops norvegicus* (Norway lobster), and *Eledone cirrhosa* (an octopus-like cephalopod), collected in the northern Tyrrhenian Sea, an area contaminated by trace metals of different origins (Majori & Petronio, 1973; Leonzio *et al.*, 1981; Barghigiani *et al.*, 1986), no relation was found between the two elements in muscle tissue in any of the studied species except for *Eledone* (Barghigiani *et al.*, 1991a). For this reason *E. cirrhosa* was chosen in the present