Sudanese Coastal Water- Composition and Some Environmental Aspects

by

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Supervisors: Professor Leiv K. Sydnes
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To

my dear wife Mona and

our first son, Musa :)

UNIVERSITY OF BERGEN

Abstract

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Red Sea water samples were collected from four stations in the Sudanese coast at depth of 10 m during July 2011 and analyzed for major ions and trace metals in order to determine their insitu concentration, their distribution patterns, and level of heavy metals contamination in the Sudanese coastal water. The data of the analysis was used in the preparation of the Red Sea artificial water which was used to study how salinity affects the photooxidation of 1,8-dimethylnaphthalene (1,8-DMN) and the water-soluble fraction (WSF) from Norwegian crude oil.

The results show a small range of spatial variation for Na^+, Mg^{2+}, Ca^{2+}, Cl^-, K^+, and SO_4^{2-}. Also, the concentration of Na^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} in the Sudanese coastal water is high compared to all other water basins and average seawater. The reason of this is the high evaporation and low precipitation in Red Sea.

The concentrations of the major ions Na^+, Mg^{2+}, Ca^{2+}, and K^+ at the coastal stations are some what lower than at the other stations. This might be due to the adsorption of these ions by the suspended particles.

Cu, Ti, As, Co, Cr, La, and Eu did not give any instrumental response, which means either that their concentrations in the Sudanese coastal water are below the detection limit of the instrument or the elements do not occur in the Sudanese coastal water. Thus, in order to detect their concentrations, preconcentration should be done or another more sensitive method should be used.

The results show a low concentration of Sr (7.6 mg/L) compared to the concentration of Sr in average seawater (8 mg/L) and this decrease in Sr concentration may be due to the presence of Acantharians. Also, concentration of B is low compared to the concentration of B in average seawater and the reason for this is that

boron is partly present in seawater as the neutral compound $B(OH)_3$ which can be distilled from surface water in the tropics during evaporation process.

Unfiltered seawater samples were collected from five stations in the Sudanese coastal water. The extractable organic matter (EOM) ranged from 1.3 to 10 mg/L with an average of 4.46 mg/L. The highest concentration of EOM was observed at the closest station to the coast. The dissolved/dispersed petroleum hydrocarbons (DDPHs) concentration equivalent to Sudanese heavy crude oil ranged between 15.84 and 95.92 μg/L with an average of 40.95 μg/L. The level of DDPHs at Sudanese coastal water does not affect the planktonic ecosystem.

Photooxidation experiments of 1,8-dimethylnaphthalene (1,8-DMN) under artificial sunlight and natural sunlight in deionized water, Red Sea natural water, and Red Sea artificial water, revealed that the oxidation of 1,8-DMN in a dark environment is dependent on temperature. The results show that salinity has no effect on the photooxidation of 1,8-DMN. But it might affect the kinetic of the reaction. The results show that the nature of the oil affects the photooxidation of 1,8-DMN.

The WSF from Norwegian crude oil consists of low molecular weight aromatic hydrocarbons. These compounds had disappeared after two days of irradiation. This reinforce photodegradation as an effective weathering process for the transformation of dissolved crude oil fraction, particularly in high solar radiation environments such as the Red Sea.

Acknowledgements

This thesis would have remained a dream until I met my supervisor, professor Leiv K. Sydnes, who welcomed me while I was reading a paper in front of his office. I consider it an honor to work with you Leiv, I share the credit of my work with you, and it gives me great pleasure in acknowledging your support and help.

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Contents

Chapter 1

Introduction

1.1 Inorganic composition of seawater

Most naturally occurring elements exist in seawater but only chloride (Cl^-), sodium (Na^+), sulfate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), bicarbonate (HCO_3^-), bromide (Br^-), strontium (Sr^{2+}), borate (BO_3^{3-}), and fluoride (F^-) occur in so high concentrations to be called major ions (Culkin and Cox, 1976). These elements make up above 99.4% of the mass of dissolved solids in seawater (Emerson and Hedges, 2008).

Salinity defines the saltiness of the seawater. Salinity is the total mass in grams of salts dissolved in 1 kg of seawater. It is composed entirely of elements that do not measurably change concentration geographically due to chemical reactivity (Emerson and Hedges, 2008).

The Red Sea is one of the saltiest water bodies in the world because of the high evaporation and low precipitation (Sakshaug et al., 2009).

As discussed by Emerson and Hedges (2008), elements in seawater are classified into four groups: *conservative elements*, *bioactive elements*, *adsorbed elements*, and *gases*. This is based on the vertical distribution of the chemicals as reflected by their concentrations.

Conservative elements have a constant concentration relative to salinity. As a result, their concentrations are not very much altered by processes other than evaporation and precipitation, the same processes that affect the salinity (Emerson and Hedges, 2008). This definition is operational since the ability to detect the influence of chemical and biological processes on concentration depends on the analytical method(s) (Emerson and Hedges, 2008).

The constancy in chemical composition of seawater is due to longer residence time than 10^7 years of the major ions and the mixing of the seawater. Residence time is the average time an element spends in seawater once it reaches it (Goldberg, 1963).

Ca^{2+}, Mg^{2+} and Sr^{2+} are not firmly conservative, since changes in the order of 1% in their ratios of concentration to salinity have been observed (Emerson and Hedges, 2008). This observation was discovered by making very accurate titration and mass spectrometric analysis (Emerson and Hedges, 2008).

Bioactive elements have a non uniform vertical distribution, characterized by surface water depletion caused by plant consumption and deep water enrichment caused by remineralization (Emerson and Hedges, 2008). Examples of bioactive elements are nutrients required for phytoplankton growth (PO_4^{3-}, NO_3^-), oxygen is used during respiration, constituents of shells made by some plankton species (e.g. Ca), and trace metals necessary for plankton growth (e.g. Fe) or incorporated into the plankton for unknown reasons (e.g. Cd) (Emerson and Hedges, 2008).

Adsorbed elements characterized by depth profiles that are overturned from those in the bioactive elements (Emerson and Hedges, 2008).

Dissolved gasses in seawater can be chemically unreactive (noble gases) or bioactive (such as O_2 and CO_2) (Emerson and Hedges, 2008).

The first investigation of some of the major ions in seawater was carried out by Marcet (1819) who analyzed water samples from some of the major oceans. He found that all samples contain the same constituents all over the world in spite of the effect of the present day standards and the approximate atomic weights on the accuracy and the precision of his method (Culkin and Cox, 1976).

Forchhammer (1865) examined several hundred water samples from all over the world for the constituents of seawater. He found that the ionic ratios showed only very small variations, if some seas were neglected (Culkin and Cox, 1976).

Dittmar (1965) carried out the most famous investigation of seawater composition. He analyzed 77 samples from different depths in some of the major oceans during the world-wide cruise of H.M.S. Challenger, he examined the precision of his methods and was able to assess the significance of any determined variations in ionic ratios. He detected some variations in the ratios of Mg^{2+}, K^+, SO_4^{2-}, Br^- and K^+ to Cl^- and total salt (Culkin and Cox, 1976).

The results of the investigation usually being expressed as ratio of concentration to chlorinlty at that time (Culkin and Cox, 1976). Chlorinity is defined as the weight in grams of the chlorides obtained in 1 kg of seawater when all the halogens (bromides and iodides) have been replaced by chlorides (Barnes, 1954), see Table 1.1 (Morris and Riley, 1966; Culkin and Cox, 1976).

Table 1.1: Major ion/chlorinity ratios in average seawater.

Major ion	Major ion/chlorinity ratio
Na^+	0.5555 ± 0.0007
K^+	0.0206 ± 0.0002
Mg^{2+}	0.0669 ± 0.00004
Ca^{2+}	0.0669 ± 0.00004
SO_4^{2-}	0.14000 ± 0.00023
Br^-	0.003473 ± 0.000012

The concentrations of major ions and trace metals in seawater and their variance are shown in Table1.2. The data were taken from Grasshoff et al. (1999); Morris and Riley (1966).

Table 1.2: The concentrations of elements in seawater

Element	Concentration mg/L (ppm)	Element	Concentration μg/L (ppb)
Cl^-	19700	Zn	0.01–11
Na^+	10900	V	1.2–3.2
SO_4^{2-}	2779.0015	As	1.29
Mg^{2+}	1290	Mn	0.004–2.8
Ca^{2+}	420	Cu	0.03–1.9
K^+	400	Ni	0.12–1.4
Sr^{2+}	8	Fe	0.001–1.3
Br^-	68	Cr	0.09–0.26
C	27	Se	0.018–0.18
S	920	Cd	0.0001–0.11
B	4.6	Co	0.0002–0.06
Mo	0.005–0.012	Pb	0.0006–0.05
U	0.0018–0.0028	–	–

The inorganic composition of Sudanese coastal water has been investigated in this study.

1.1.1 Heavy metals and their effects on the marine environment

Metals exist in seawater as dissolved ions and bound to organic molecules or complexes (Kennish, 1992). For example, all of the iron in seawater is organically complexed (Rue and Bruland, 1995). The distribution of trace metals can be affected by humic materials which are abundant in seawater (Miller, 2000). The interaction of dissolved trace metals with particles suspended in seawater is the main mechanism of the observed concentration and distribution patterns (Grasshoff et al., 1999).

Heavy metals have density higher than 3.8 g/cm^3; e.g. Fe, Zn, Mn, Cr, Pb, and Hg (Ismail, 2002). The source of these metals in seawater is mining, volcanism, burning of waste and industrial production (Sakshaug et al., 2009). Trace metals are heavy metals necessary for life in small concentration (μg/L) (Sadiq, 1992).

Many metals have no known biological functions, but are toxic to some living organisims and therefore the term heavy metals is used to refer to these. Heavy metals may be toxic when their concentration is greater than their concentration found in nature. Elevated metal concentrations may cause a several of sublethal effects in marine organisms: changed tissue morphology, changed physiology (e.g. suppression of growth), changed biochemistry (e.g. enzymes activity), changed behavior, and changed reproduction (Connell and Miller, 1984). Marine invertebrates consume and accumulate trace metals whether essential or non-essential, all of which have the potential to cause toxic effects (Hare, 1992).

The increase of trace metal concentrations in seawater is a common problem and the productivity can be reduced by the discharge of these metal waste (Shriadah et al., 2004).

Although the population density along the coasts of the Red Sea is low, metal pollution can take place because of oil industry, transportation by ships, stainless steel industry, power stations, and cement industries (Shriadah et al., 2004).

1.2 Area of Study

The Red Sea is a long narrow sea extending from the straits Bab el Mandab to the southern tip of Sinai Peniusla. As discussed by (Schroeder, 1982), coastal lagoons, fringing reefs, barrier reefs, and atolls are the major features of the coast. Fringing reefs, with a typical width of 1 to 3 km, line most of the coast, and depth of 5 m. Barrier reefs with width of 1-14 km, are parallel to the coast. A ship cannel with depth of 100–400 m and width of 2.5 km, separates the barrier reefs from the fringing reefs. Sanganeb Reef which is situated about 30 km northeast of Port-Sudan, is the best common example for atolls that arise with steep flanks from depths of 400- 800 m (Schroeder, 1982).

Air temperature at Port-Sudan range from 15–47.5 °C; the winds in general from the northerly quarter, but in July and August come from all directions, while in September and October the northerly winds are dominant; rainfall which occurs in November and December is 111 mm/yr (Schroeder, 1982). The temperature of the surface coastal water range from 26.2°C– 30.5°C (Robinson, 1973). Salinity of surface water ranges from 38 to 42 in the Sudanese coastal water, which makes this one of the saltiest water bodies in the world. Salinity of the deep brines is more

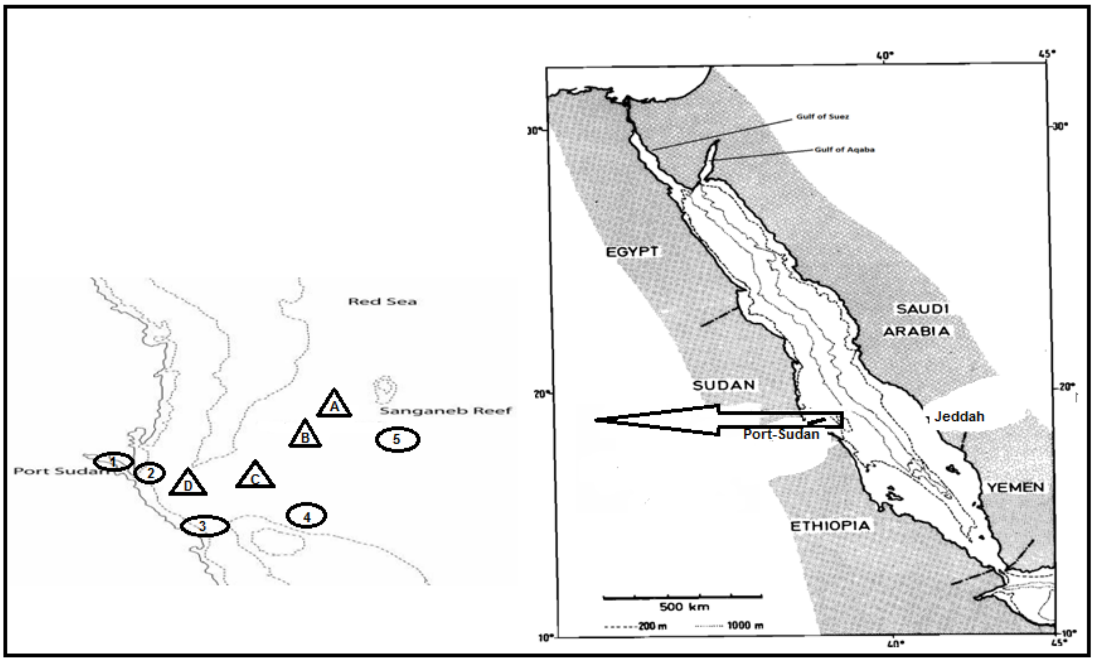

FIGURE 1.1: Map of the study area showing the position of stations, A, B, C, and D and stations 1, 2, 3, 4, and 5. Gulf of Suez and Aqaba are seen in the north.

than 250 (Ross, 1972). The temperature and salinity of water at 10 m in the area of study in July 2011 are 31°C and 39 respectively. The overall circulation pattern of the Red Sea is govern by monsoon winds (Patzert, 1974). Surface currents flow northward from November to April and southward for the others months. In general, coastal surface currents follow the local wind pattern (Schroeder, 1982). The average UV radiation for October and November 2011 in Port- Sudan is 330.8 W/m^2 (Saadia, 2013). The transparency of the Red Sea water ranges between 20–30 m in open waters, but in coastal water, it may be less than 1 m (Schroeder, 1982). In general, production of organic matters by photosynthesis is low in the Red Sea (Schroeder, 1982). Of the 92 genera and subgenera of scleractinian corals (an important reef formation animals), 59 occur in the area of Port-Sudan and Sawakin (close to Port-Sudan) (Mastaller, 1978). The microscopic planktonic algae is abundant in the Red Sea which gives the water a red appearance and hence the name *Red Sea*.

In this study the focus has been on the coastal water off Port-Sudan in the western Red Sea, and surface water from stations between Sanganeb atolls and the coast have been analyzed (see Figure 1.1).

TABLE 1.3: Concentrations ppb (μg/L) of trace metals in surface water samples from different regions at the Red Sea.

Trace metal	Gulf of Suez[1]	Gulf of Aqaba and Northern Red Sea[2]	Jeddah coast[3]	Egypt coast[4]
Cu	1.45-9.75	0.07-0.29	3.5-4.0	5.1
Zn	6.79-25.19	0.13-1.17	6.0- 14	–
Pb	0.56-3.17	0.02-0.68	1.1-27	–
Cd	0.04-0.27	0.02-0.78	0.3	–
Cr	0.33-1.21	–	–	–
Ni	1.36-3.65	0.05-0.52	–	–
Fe	1.36-3.65	0.56-4.44	–	16.2
Mn	1.28-4.56	0.06-0.21	–	0.83

[1] Hamed and Emara (2006), [2] Shriadah et al. (2004)
[3] Hamza and Amierh (1992), [4] Saad and Kandeel (1988)

1.2.1 Inorganic composition of Red Sea water

Very little is known about the concentrations and distributions of major ions and trace metals in Rea Sea water. Table 1.3 shows the concentrations of trace metals in surface water samples from different locations in the Red Sea; northern Red Sea, the Gulf of Aqaba, and Gulf of Suez (see Figure 1.1).

The concentrations of Mn, Fe, Ni, Cu, Zn and Pb in sediments of two harbours along the Sudanese Coast determined by Idris et al. (2007) and their study revealed that some sites in Port-Sudan harbour and one site in Sawakin harbour are contaminated by heavy metals due to ships and industrial activities.

In this study, trace metals has been determined in Sudanese coastal water.

1.3 Oil spills in the marine environment

The pollution of the environment can arise from natural processes as well as man-made pollution. In the case of oil pollution, natural processes (Landes, 1973) and man-made pollution (Jeffery, 1972) contribute to the problem, and the latter is the probable source of most marine pollution (Blumer, 1972).

Approximately 320 million tonnes of oil per year is being released into the ocean by accidental spills and as the result of human activities (Etkin et al., 1998). At least 114,000 tonnes per year are due to accidental spills from tankers for the period 1990-1999 (ITOPF, 2009). The number of accidents involving large spills decreases with time, this caused a reduction of the total oil spilled in the ocean related to tankers (see Figure 1.2) during the last four decades ((ITOPF, 2009).

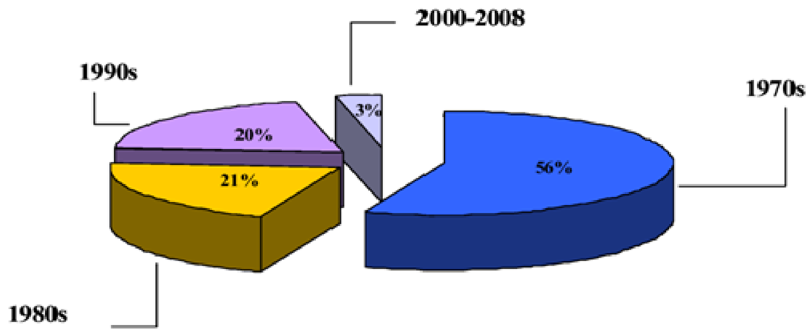

Figure 1.2: Percentage of decadal oil spill in the world compared to the total, for the period 1970-2008. Data source: (ITOPF, 2009).

Spilled oil as the result of human activities represents one of the most important sources of pollution in the marine environment (Serret et al., 2003).

Sea-based activities make up between 9% (ITOPF, 2009) (period 1900-1999) and 37% (Boehmer-Christiansen, 2008) (period 1987-1997) of the total oil contribution to the ocean. According to Boehmer-Christiansen (2008), the average amount of oil entering the marine environment from sea-based activities was 1.25 million tonnes per year for the period between 1988-1997. This quantity may vary between 0.47 and 8.4 million tonnes per year when land-based activities and atmospheric sources are included, as estimated by the National Research Council Committee on Oil in the Sea (2003) for the period 1990-1999.

Although estimates differ, approximately half of the spilled oil may come from natural seeps in the seabed and from erosion processes (Committee on Oil in the Sea, 2003; Boehmer-Christiansen, 2008).

1.3.1 Oil spills in the Red Sea

According to Maillard and Soliman (1986), the Red Sea particularly vulnerable to pollution build-up due to the slow water turnover times and the small size, and this requiring careful consideration of any activities in the coastal zone. Because coastal waters take up much of the impacts of human activities, they are the most threatened by contamination from industrial activities (Gerges, 2002). The population density along the coast, with the exception of Jeddah (1.25 million people) and Port-Sudan (300,000 people) is relatively low and as a result, the Red Sea remains overall an extremely pristine environment with the largest diversity of aquatic life of any body of water in the world (Coakly and Rasul, 2001).

As argued by PERSGA (1998), although the Red Sea has remained relatively free of pollution, it is now under increasing threat from a wide range of land activities because of the increasing industrial development in oil industry and manufacturing industries (fertilizers, chemicals, cement). Also, unlike other oceans where pollution is mostly due to land-based activities, sea-based activities such as shipping and oil exploitation are the most important source of pollution in the Red Sea (PERSGA, 1998). Although approximately 11% of the world seaborne oil is transported through the Red Sea and Gulf of Aden, there have been no major oil spills (> 5,000 tones) due to shipping accidents, hence, most oil spills in the Red Sea have been as the result of operational discharges, equipment failures, and groundings (PERSGA, 1998). This chronic pollution increases rapidly more than any regional sea (ITOPF, 2003).

1.3.2 The fate of oil spill in the marine environment

A complete understanding of the fate of the spilled oil is important to predict the extension of the environmental damage and to develop successful restoration strategies (González et al., 2006). When crude oil comes into the marine environment, it becomes subject to several physical, biological, and chemical processes that change its nature.

Crude oil has a typical density of 0.85 g/cm^3, and this factor combined with wind, currents, and wave action spread the spilled oil on the sea surface (Dutta and Harayama, 2000). Evaporation and emulsification appear to be the dominant processes after spreading (wol, 1977). These processes depend on temperature, wind, and waves in addition to the chemical composition of crude oil (Jordan and Payne, 1980). Crude oil forms a thin film on the surface water which increases the surface area of the oil and this increases the rate of evaporation of the volatile components. About 35% of the crude oil components are removed by this process (Abelson, 1977), and subsequently the surface becomes enriched in high molecular-weight constituents (Tjessem and Aaberg, 1983).

From a physical point of view, dispersion results in the formation of small oil droplets with so low buoyancy that they are kept in the water column for quite long time. Dispersion is directly proportional to wave breaking (Sydnes, 1991).

The composition of the spilled oil is further changed by biodegradation, photooxidation, and dissolution into water column (Dutta and Harayama, 2000). Biodegradation has been studied in great details. It has been shown that the lighter fractions such as normal alkanes and aromatic compounds with small molecular weight (1-3 rings) are biodegraded more rapidly than the heavier ones (Forstner et al., 1997). Solar radiation has no significant effect on biodegradation of crude oil (Delille et al., 1997). But Ni'matuzahroh et al. (1999) found that the biodegradation of the aromatics compounds such as 2-methyl naphthalene was found to be enhanced by photooxidation. The photooxidation is discussed in details below.

1.3.3 Photooxidation of crude oil on seawater

Crude oil is a mixture of tens of thousands of different hydrocarbon compounds and heterocyclic compounds (Sydnes, 1991). It contains small amounts of nitrogen, sulfur, and metal Ni and V (Speight and Ebrary, 1999). About 90% of most crude oil are pure hydrocarbon compounds but in extreme cases this quantity may be less than 50% (Sydnes, 1991). Sydnes (1991) argued that, the composition of an oil depends on the type of biogenic material from which it has been formed. This affects the relative abundance of aromatic hydrocarbons, saturated hydrocarbons, and asphaltenes/resins. The saturated hydrocarbons contain normal and branched alkanes (paraffins) and cycloalkanes (naphthenes), the aromatic hydrocarbons include pure aromatics, cycloalkanoaromatic compounds, and unsaturated sulfur compounds. The asphaltene and resin fraction include high molecular weight polycyclic compounds (Sydnes, 1991).

Photooxidation removes crude oil from the marine environment, especially in tropical and subtropical regions under conditions of intensive solar radiation (Ali et al., 1995). Thus, photooxidation of chemical compounds in Red Sea natural waters is of interest because of the high intensity of solar irradiation.

Ultraviolet (UV) region of the electromagnetic radiation can penetrate as deep as 50 m into the water column depending on the concentration of absorbing materials (Jerlov, 1968). Therefore, the photochemical reactions induced by UV light are not restricted to the surface waters (Jerlov, 1968). Sunlight is necessary for the degradation of many types of chemical compounds in nature (Ross and Crosby, 1975; Zepp et al., 1984).

As discussed by Sydnes (1991), since the solar irradiation is filtered by ozone before reaching the earth, the photochemical reactions involved in natural sunlight are limited to those reactions that do not require light with a wavelength shorter than approximately 300 nm. So, photooxidation by direct irradiation in nature is restricted to molecules that contain molecular orbitals that interact extensively (conjugated systems) such as, aromatic hydrocarbons (Sydnes, 1991). When light absorption occurs, an excitation follows, and an electron is transferred to an antibonding orbital (high energy orbital) without changing its spin. As a result, the molecule becomes in a *singlet* excited state from which it undergoes physical processes and/or chemical changes (Sydnes, 1991).

Sensitization is defined as a process in which energy is transferred from an excited molecule to another molecule in ground state (Turro, 1967; Calvert and Pitts Jr, 1966).

Dissolved organic matter (DOM) which absorbs a large portion of solar radiation, can be considered as a potential photosensitizer (Vialaton and Richard, 2002; Zepp et al., 1985). The rate of photosensitization reactions that include humic substances as a photosensitizer depend strongly on the concentration of dissolved oxygen indicating that humic substances transfer energy to *triplet* molecular oxygen to form singlet oxygen (Zepp et al., 1985).

Most crude oil contain a number of compounds considered as sensitizers toward triplet oxygen such as, polycyclic aromatic compounds and asphaltene constituents (Larson and Hunt, 1978; Sydnes et al., 1985a).

Crude oil includes a significant number of unpaired electrons which are able to form aryloxy radical and superoxide (Mill, 1989). These are considered as oxidants under both aqueous and non aqueous condition (Sotiriou et al., 1990). As a result, some of the oil constituents may to some extent be oxidized in the dark as oxygen is available (Sydnes, 1991).

Irradiation of oil layered on water by either solar irradiation or artificial sunlight increases the oil solubility in water (Scheier and Gominger, 1976; Ducreux et al., 1986), and this increase can be in the range of 30-40 ppm for light crudes (Gordon Jr et al., 1976; Sydnes et al., 1985a). This increase is mainly due to the formation of polar derivatives (Nicodem et al., 1997).

To investigate the potential of crude oil in this respect we have carried out a photochemical study of 1,8-dimethylnaphthalene (1,8-DMN) to examine the phototransformation of alkylnaphthalenes which are common constituents in crude oil (Petrov, 1987) and which have a relatively high solubility in water (Ehrhardt et al., 1997). Also, the water-soluble fraction (WSF) of Norwegian crude oil has been used.

D'Auria et al. (2009) showed that the irradiation of crude oil as the whole causes a 9% reduction of linear alkanes, a 5% reduction of branched alkanes, and a decrease of as much as 54% of cyclic alkanes, while aromatic hydrocarbons were reduced by 37% (see Figure 1.3).

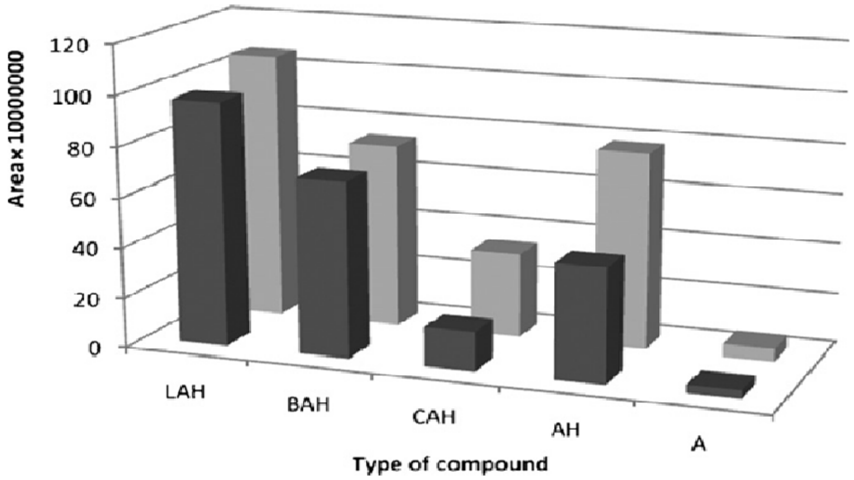

FIGURE 1.3: Solid-phase microextraction (SPME) analysis of crude oil before (light grey) and after UV irradiation (dark grey). LAH: linear aliphatic hydrocarbons; BAH: branched aliphatic hydrocarbons; CAH: cyclic aliphatic hydrocarbons; AH: aromatic hydrocarbons; A: alkenes. Figure from D'Auria et al. (2009).

Sydnes et al. (1985b) showed that the photooxidation of 1,8-DMN is inefficient in the absence of oil and the oxidation occurs in the benzylic positions (see Figure 1.4 (A)), while in the presence of oil it occurs in the naphthalene moiety. This is due to the abundant formation of singlet oxygen as shown in Figure 1.4 (B) and proved by the chromatogram C and D. 1,8-dimethylnaphthalene-1,4-endoperoxide (1,8-DMN-O_2) is the product of addition of singlet oxygen to 1,8-DMN.

Also Sydnes et al. (1985b) showed that the silylation process, addition of N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMCS) increases the ability of GC-MS to detect the water soluble products of photooxidation of 1,8-DMN (see Figure 1.5).

The solubility of different kinds of substances in water decreases in the presence of inorganic salts; this is called the salting-out effect (Görgényi et al., 2006). Aromatic hydrocarbons which are some of the crude oil constituents, decrease their solubility with increasing concentrations of inorganic salts in the media. At salinity of 35, the solubility of naphthalene and phenanthrene is 22.0 and 0.71 ppm respectively, while solubilities ranged from 31.3 ppm for naphthalene to 1.07 ppm for phenanthrene at salinity of 0 (Eganhouse and Calder, 1976; Gold and Rodriguez, 1989).

As shown by Hamam et al. (1988), the solubility of the crude oil in water increases as the API° (The American Petroleum Institute gravity) of the crude oil increases. The solubility of crude oil in distilled water is higher than its solubility in saline water.The solubility decreases in saline water due to the salting out effect. Heavy

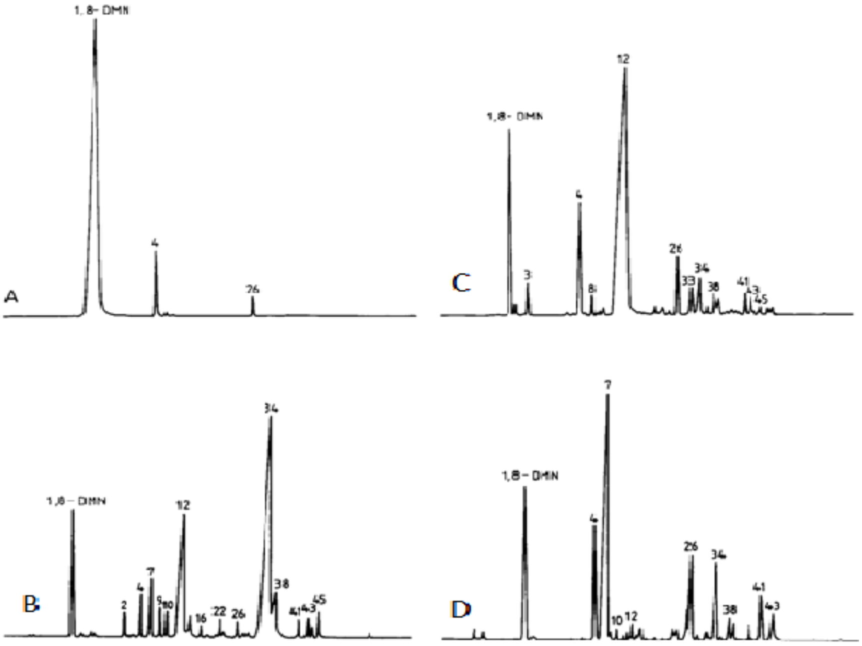

FIGURE 1.4: GC traces of the organic material dissolved in the aqueous phase during the following reactions. A: 1,8-DMN/distilled water/hν, B: 1,8-DMN/oil/distilled water/hν, C: 1,8-DMN-O2/distilled water/heat, D: 1,8-DMN-O2/distilled water/hν . Figure from Sydnes et al. (1985b).

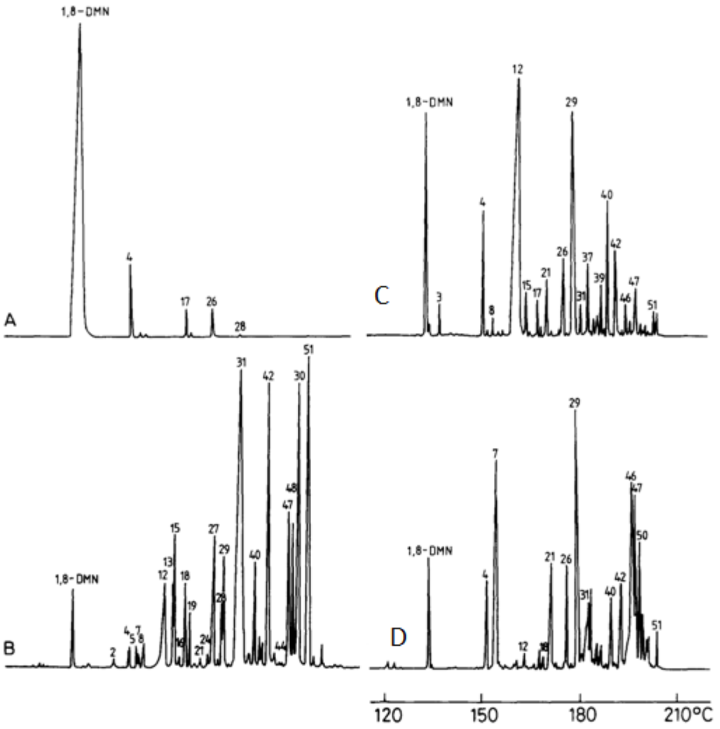

FIGURE 1.5: GC traces of silylated samples of the organic material dissolved in the aqueous phase during the following reactions. A: 1,8-DMN/distilled water/hν, B : 1,8-DMN/oil/distilled water/hν, C: 1,8-DMN-O2/distilled water/heat, D : 1,8-DMN-O2/distilled water/hν . Figure from Sydnes et al. (1985b).

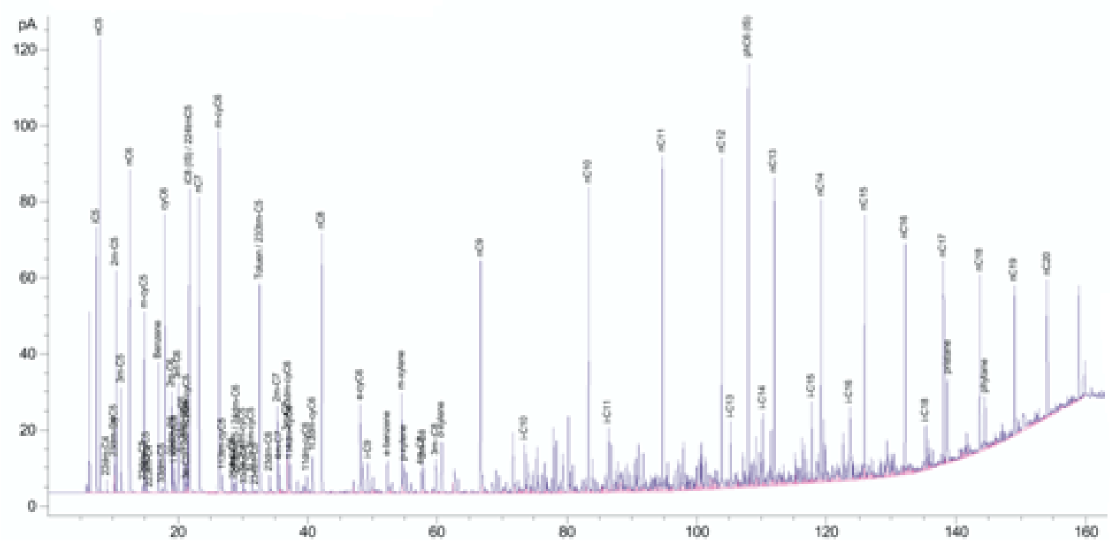

Figure 1.6: Gas chromatogram of the Norwegian oil sample. Taken from NIGOGA (2000)

oils have API° gravities of 20 or less, super-heavy oils have API° gravities of 10 or less, and a typical light marine non-biodegraded oil has an API° gravity around 36-38 (Head et al., 2003).

Sudanese crude oil has a low API° and aromatic content compared to Norwegian crude oil. In this context, the latter with API° of 33.3 and aromatic content of 37% (NIGOGA, 2000) was used to investigate the effect of the irradiation on the water-soluble fraction of this oil. Figure 1.6 shows the gas chromatogram of the Norwegian oil used in this study.

Salinity may affect the effectiveness of chemical dispersants, and the binding characteristics of the residual oil fractions onto suspended particles (Ramachandran et al., 2006). As shown by Sydnes et al. (1985b), salinity of the aqueous phase may influence the photooxidation of dimethylnaphthalenes layered on seawater. The rate of photooxidation in a saline water containing increasing amount of salt, remained practically constant in spite of the decrease in the concentration of singlet oxygen and this might be due to a compensation between the mentioned decrease in oxygen solubility and an increase in the photooxidation rate due to the solvent polarity effect (Gutiérrez et al., 1994).

Also Fukuda et al. (1988) showed that the rate of photolysis of naphthalene in a solution containing increasing amount of salt was increased several times over that in distilled water. NaCl, the main component of seawater was estimated to be the cause of this increase since the rate increased nearly proportional to the concentration of NaCl.

Photooxidation was found to be favored in nutrient-depletion seawater, and under intense sunlight (Ehrhardt et al., 1992). The concentrations of nutrients in the Red Sea are found to be low (Weikert, 1987).

The salinity and the nature of dissolved metals influence the photooxidation of oil in a given seawater body. In this context, the Red Sea is an interesting water body because the salinity is high and the composition of the oil produced in the region is very different from those oils being studied in other water. Thus, the salinity effect on the photooxidation of one of the petroleum constituents (1,8-dimethylnaphthalene) has been investigated in this study, as well as the effect of the salts on the water-soluble fraction of crude oil.

1.3.4 The effect of crude oil on the marine environment

Marine phytoplankton is the most important species in the biological primary production, it offers food to zooplankton, larvae, and juvenile fish (Behrenfeld et al., 2006). Thus, plankton community can be changed by crude oil pollution and this may change the structure, function, and stability of the marine ecological system (Duffy and Stachowicz, 2006).

Crude oil has toxic effect on marine phytoplankton (Hsiao, 1978) as it inhibits the growth of unialgal cultures of marine phytoplankton (Prouse et al., 1976). Crude oil also has toxic effects on seabirds (Peakall et al., 1982), on larval marine fish (Couillard et al., 2005), and some components appear to be toxic to young Coho salmon (Morrow et al., 1975). Alkylnaphthalenes, an important aromatic water soluble fraction of crude oil, are considered to be one of the most toxic groups of hydrocarbons to marine life (Anderson et al., 1974). These compounds showed a toxic effect on marine copepods (Ott et al., 1978). Calbet et al. (2007) has shown that naphthalene and 1,2-dimethylnaphthalene has toxic effect on the marine copepod Paracartia grani. As shown by Saethre et al. (1984), the toxic effect of naphthalene and mono and disubstituted methylnaphthalene on newly fertilized sea urchin and fish eggs were dependent on the number and position of methyl groups.

Most of the polycyclic aromatic hydrocarbons (PAHs) are not water soluble and therefore not toxic to marine organisms. When such PAHs are oxidized and dissolved, their concentration will therefore not change quickly. Thus, it is not surprising that such components (O-PAH) of petroleum hydrocarbons, have been suggested to be included in the monitoring of organic pollutants in seawater (Burns, 1993; Ehrhardt and Bums, 1990).

The oxidation products of petroleum hydrocarbons are more water soluble than the parent hydrocarbons. Some of them have been shown to be quite toxic to marine organisms (Larson et al., 1977).

1.3.5 Petroleum hydrocarbons and oxidation products in Sudanese coastal water

Aromatic hydrocarbons with low molecular weight are of special concern since they exhibit higher solubility in water and toxicity in the aquatic environment (González et al., 2006).

Oil refineries and oil transportation are considered as a major source of pollution along the Sudanese coast and may contribute to most of the oil contaminants to the seawater. Measurements of polycyclic aromatic hydrocarbons (PAHs) are usually used to assess the oil contamination in the marine environments (Al-Lihaibi, 2003), and the main sources of oil pollution in the study area are the refineries and the activities related to oil transportation.

Al-Lihaibi (2003) found that the average concentration of extractable organic matter (EOM) and the total concentration of dissolved and dispersed petroleum hydrocarbons (DDPHs) in Red Sea coastal area of Jeddah are 3.8 mgl^{-1} and 4.7 μg/L respectively. According to Al-Lihaibi and Al-Ghamdy (1997), the concentration of the total petroleum hydrocarbons in surface water from the Red Sea coastal area of Jeddah (Saudi Arabia), ranged between 1.79 and 17.9 μg/L light Arabian oil equivalents.

The products of the photooxidation reactions have been determined experimentally by several researchers using crude oils, fuel oil and also individual PAHs under artificial and natural solar radiation (Burwood and Speers, 1974; Ehrhardt et al., 1992; Larson et al., 1977; Sydnes et al., 1985b). They have found that the major products were peroxides, phenols, acids, carbonyls and lactones. Some of these products have been detected in the Eastern Red Sea coastal waters (Jeddah coast) (Al-Lihaibi, 2003).

1.4 Objectives of the thesis

Very little is known about the levels and distributions of major ions and trace metals in Sudanese coastal water, therefore, the determination of metals and anions carried out here are important and fill a gap in the present knowledge of this area.

In the present study, sodium (Na^+), potassium (K^+), strontium (Sr^{2+}), magnesium (Mg^{2+}), calcium (Ca^{2+}), boron (B), iron (Fe), zinc (Zn), manganese (Mn), nickel (Ni), copper (Cu), cadmium (Cd), cobalt (Co), lead (Pb), arsenic (As), barium (Ba), chromium (Cr), europium (Eu), lanthanum (La), silicon (Si), and titanium (Ti) were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES). Sulfate (SO_4^{2-}), chloride (Cl^-), and bromide (Br^-) were analyzed using ion chromatography (IC). The purpose of the analysis of these constituents is to determine their insitu concentration, their distribution patterns, and to assess the metal pollution in the area of study. The results of the analyses are used to prepare artificial Red Sea water which would subsequently be used to study how salinity affects the photooxidation of 1,8-dimethylnaphthalene (1,8-DMN) and the water-soluble fraction (WSF) from Norwegian crude oil.

No study has been reported on the estimation of petroleum hydrocarbons in this area. So the available information concerning the concentrations of petroleum hydrocarbons in the marine environment of the Sudanese Red Sea coast is limited. This study aims at assessing the level of oil contamination as results of the refineries and oil transportation.

Photooxidation of WSF of Norwegian crude oil and 1,8-DMN was studied in order to understand the photooxidation as a weathering process of crude oil in Res Sea water and to investigate the salt effects on this process.

Chapter 2

Experimental part

2.1 Analysis of seawater for inorganic composition

Analysis of seawater for the inorganic composition is one of the most challenging analytical tasks since it requires detection of extremely low concentrations of some elements and very high concentrations of others (Rodushkin and Ruth, 1997).

Inductively coupled plasma optical emission spectroscopy (ICP-OES) has been used for the determination of metals in this study, while ion chromatography (IC) has been used for the determination of inorganic anions.

2.1.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Boss and Fredeen (1999) argued that, in optical emission spectroscopy (OES), atoms of the element of interest are excited (and ionized) by thermal sources and when these excited atoms decay to the ground state through radiative transitions, the intensity of the emitted radiation is directly proportional to their concentration. The high temperature sources which can excite many elements at the same time, represent one of the most important advantages of OES (Boss and Fredeen, 1999). And thus, more than one element can be analyzed instantaneously. Discharging by plasma is used for atomization, ionization, and excitation of atoms in OES (Boss and Fredeen, 1999). A plasma is a form of matter that consists of fraction of electrons, positive ions, and neutral atoms (Greenfield et al., 1964).

The emitted wavelengths by the excited atoms contain the qualitative and quantitative information about the elements in the sample (Boss and Fredeen, 1999).

Seventy elements can be determined using inductively coupled plasma optical emission spectrometry (ICP-OES) at levels of concentration below 1 mg/L (Boss and Fredeen, 1999). But as the number of emitted wavelengths (number of elements) increases, the probability of the interferences of these wavelengths also increases and this is the disadvantage of the OES (Boss and Fredeen, 1999) (see Appendix A.1).

2.1.1.1 Reagents and procedure

All reagents used (listed below) were of analytical grade, and pre-tested for possible trace metal contamination.

- Concentrated nitric acid (68 % w/v)
- Multi-element primary standard solution (sps-sw2)
- A solution of 2% (w/v) nitric acid prepared from the concentrated nitric acid, serving as a calibration blank
- Scandium used as an internal reference standard (see Appendix A: Internal reference standard).

Procedure: Standard solutions were prepared from independent primary standard solutions. The ICP-OES instrument was started, brought to operation conditions and let stabilized. The sample introduction system was checked and the wavelengths were tuned (see Table A.3). Seawater samples were diluted 100 times for major metals by 2% nitric acid (w/v). Calibration was done with five external calibration solutions (included calibration blank). Sc was used as internal standard. Dilution factor correction as well as normalization to the internal standard were done by the software.

Seawater samples were collected in previously acid-washed polyethelene bottles from 4 stations representing the Sudanese coastal water at 10 m depth by using water sampler during July 2011 (see Figure 1.1A, 1.1B, 1.1C 1.1D). The unfiltered seawater samples were acidified with extremely pure nitric acid until the concentration of nitric acid in the stabilized water samples had become 2%.

2.1.2 Ion Chromatography (IC)

There are two phases; stationary and mobile phase in ion chromatography (IC). Anions interact with the acidic sites of ion-exchange of the stationary phase. The retention time of the anions depends on the strength of this interaction (ion exchange equilibrium constants). Different ion exchange equilibrium constants lead to different retention times of the respective anions and that means separation of the anions. Then the area under the peak is used for the quantitative analysis.

The interferences in IC from other anions are avoided since all anions elute at different times which is the advantage of IC (Strickland, 1972). The use of single column ion chromatography has become more common and it has been applied for the analyses of ppm levels (mg/L) of inorganic anions in a variety of aqueous solutions (Yamamoto et al., 1984). Ion chromatographs are usually fitted with a conductivity detector, which is often supplemented with a UV-visible absorbance detector (Haddad et al., 1999) (see Appendix A.2).

2.2 Analysis of seawater for crude oil

Crude oil is a complex mixture of tens of thousands of chemical compounds. The composition varies from one location to the other, and may also vary from and the same reservoir. This means that no simple chemical method exists for a quantitative or qualitative analysis of oil in seawater (Gunnar and Ostvedt, 1984).

2.2.1 Fluorescence spectroscopy

Fluorescence spectroscopy is confirmed to be a suitable method for the determination of petroleum residue in seawater when large numbers of samples must be analyzed (Keizer and Gordon Jr, 1973). It is a main method for estimating petroleum hydrocarbons in seawater, namely using UV-fluorescence for the analysis of total hydrocarbons (Grasshoff et al., 1999).

As discussed by Christian (2004), when a molecule absorbs electromagnetic radiation, it loses absorbed energy of the electromagnetic radiation via collisional processes. But some molecules lose this energy via emission of light. The intensity of the emitted light is proportional to the intensity of the incident radiation. Only those molecules that absorb UV light, can fluoresce, and only about 5 to 10% of them fluoresce. This decreases the interferences in fluorescence (see Appendix B.1). Fluorescence spectroscopic method has extremely high sensitivity (Christian, 2004).

2.2.1.1 Reagents and procedure

Dichloromethane and n-hexane used were HPLC grade.

The unfiltered seawater samples were analyzed by LS50B Perkin Elmer luminescence spectrometer for dissolved/dispersed petroleum hydrocarbons according to the MARPOLMON protocol (Commission, 1984) with some modification.

The unfiltered seawater samples (1 m depth) were collected from five stations in Sudanese coastal water. Station 1 is very close to the coast and subject to different types of pollution; station 2 located at the centre of Port-Sudan harbour; station 3 is close to Port Bashair used for oil transportation; station 4 is in the middle between the coast of Port-Sudan and Sanganeb, and station 5 is close to Sanganeb coast (see Figure 1.1).

Pre-cleaned amber glass bottles were used for the collection, and they were closed with Teflon stopper after water sampling. The collected samples were preserved by adding aliquots of organic solvent (dichloromethane), then shaken, and transported to the laboratory for extraction and analysis.

1.0 L of seawater was extracted with dichloromethane (4 X 100 mL). The organic extracts were combined, dried over anhydrous $MgSO_4$, concentrated by vacuum evaporation on a rotary evaporator and then kept under a gentle stream of pure nitrogen. The extractable organic matter (EOM) was weighed and re-dissolved in n-hexane.The dissolving quantity of the n-hexane (ca. 25 mL) was sufficient to avoid the quenching during measurement (see Appendix B.1). The concentration of petroleum hydrocarbons equivalent to Sudanese heavy crude oil were determined by the intensity of their fluorescence (310 nm excitation, 360 nm emission wavelengths) and quantification was at 360 nm using an ultraviolet fluorescence(UVF) Spectrofluorophotometer. The procedural blank was determined as water extracts and the equivalent value to heavy Sudanese crude oil equivalents was subtracted from the sample concentrations.

The calibration curve was made with n-hexane solutions of Sudanese heavy crude oil (between 0.1 and 7 mg/L).

2.2.2 Gas chromatography-mass spectroscopy (GC-MS)

The combination of gas chromatography (GC) for separation and mass spectrometry (MS) for detection and identification of the components of a mixture of constituents is rapidly becoming the definitive analytical tool in the research and commercial analytical laboratory (McMaster and McMaster, 1998), and among the analytical techniques available for the determination of structures of the oil components, combination of GC with MS (GC-MS) has been the best choice so far and most widely used (Dutta and Harayama, 2000) (see Appendix B.1).

2.3 Photooxidation experiments

All glassware was washed with hot tap water, followed by distilled water. They were oven-dried and subsequently washed with dichloromethane.

The dimethylnaphthalene used was 1,8-dimethylnaphthalene (1,8-DMN) which was commercially available with a purity of better than 98% (see Figure 3.2). Sudanese heavy crude oil and Norwegian crude oil were used. The organic solvents were of reagent grade quality. Red Sea water was taken from a depth of 10 m off the Sudanese coast station B (see Figure 1.1). The salts used for the preparation of Red Sea artificial water were of reagent grade quality. Red Sea artificial was prepared by addition of calculated weights from these salts to distilled water.

2.3.1 Photooxidation of 1,8-dimethylnaphthalene

The experiments were performed in a beaker (18.5 cm x 3 cm), containing 500 mL of water. Irradiation was performed for 72 hours without stirring using a low pressure mercury lamp (LPML) which was situated 15 cm above the water surface. The light was filtered through glass which filters wavelengths below 290 nm (cut-off 290 nm) placed 5 cm below the lamp. Irradiation with natural sunlight (NSL) was performed for 15 days in Khartoum (32°35'E /15°31'N) in January 2012. The reaction mixture were worked up and analyzed as described below. Each experiment was carried out twice and turned out to be reproducible. Table 2.1 gives an overview of the reactants and irradiation.

TABLE 2.1: Photooxidation experiments

Container	Reactants	Radiation source
1	1,8-DMN in distilled water at 8°C	Darkness
2	1,8-DMN in distilled water at 8°C	LPML
3	1,8-DMN in Red Sea natural water at 8°C	LPML
4	1,8-DMN in artificial Red Sea water at 8°C	LPML
5	1,8-DMN + SHCO in distilled water at 8°C	LPML
6	1,8-DMN in distilled water at 35°C	Darkness
7	1,8-DMN in distilled water at 35°C	NSL
8	1,8-DMN + SHCO in distilled water at 35°C	NSL

LPML: low pressure mercury lamp. NSL: natural sunlight. SHCO :Sudanese heavy crude oil

For container 1, 2, 3, 4, 6, and 7 (Table 2.1), 1,8-DMN (0.025 g) was dissolved in 2 mL of ethanol and added to 500 mL water, the mixture was stirred vigorously for 2 hours and then irradiated.

For container 5 and 8, a solution of 1,8-DMN (0.5 g) in a 3:1 (weight) mixture of Sudanese oil and ether was layered on the surface of distilled water. The film

Table 2.2: Temperature program of Trace GC altera

Rate (°C/min)	Temp(°C)	Time
	70	2.00
40	100	2.00
8	300	1.00

of oil and DMN left after the evaporation of ether was irradiated as described in Table 2.1. Sudanese heavy crude oil layered on distilled water was irradiated representing the reference samples.

The organic materials dissolved in the aqueous phase were extracted four times with 100 mL of diethyl ether, the organic extracts were combined, dried over anhydrous $MgSO_4$, concentrated via vacuum evaporation on a rotary evaporator and then kept under a gentle stream of pure nitrogen. The dried extractable was re-dissolved in methanol and analyzed by gas chromatography coupled to mass spectrometry (GC-MS).

2.3.2 Photochemical transformations of water-soluble fraction (WSF) of crude oil

Pyrex flasks (750 ml) were filled with 500 ml of water. Norwegian crude oil was added at the ratio of 1:20 (v/v), and the solution was magnetically stirred gently for two days. The solutions were then kept in the dark at room temperature to reach equilibrium for 8 hours. The Pyrex flasks remained stoppered for the entire period, except when water samples were drawn, without disturbing of the oil/sea-water surface. Samples (about 400 ml) were irradiated for 3 days as described above. The samples were extracted four times with 100 mL of diethyl ether, the organic extracts were combined, dried over anhydrous $MgSO_4$, concentrated via vacuum evaporation on a rotary evaporator and then kept under a gentle stream of pure nitrogen. The dried extractable was re-dissolved in methanol and analyzed by GC-MS and GC. Table 2.2 shows the temperature program used of the Trace GC altera with methyle siloxane column.

Chapter 3

Results and Discussion

3.1 Inorganic composition of Sudanese coastal surface water

3.1.1 Major ions in Sudanese surface coastal water

To our knowledge, there is no available information about major ions in the Sudanese coastal water. The concentration (ppm) of the major ions in Sudanese surface coastal water at the four stations, A, B, C, and D between the Sudanese coast and Sanganeb atolls (see Figure 1.1) is displayed in Table 3.1. Each station is divided into five locations; number 1–5 which are approximately 10 m apart from one another. Station A is closest to Sanganeb atolls and D is closest to the Sudanese coast. Cations were determined by ICP-OES while anions were determined by ion chromatography (IC). The averages concentrations of the five locations within each station are shown in Table 3.2.

The results revealed a small range of spatial variation. It also show a high concentrations of Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} compared to their concentration in Table 1.2, and this explains the high salinity of the Red Sea water compared to average open ocean water. The reason of the high concentration of Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} is the high evaporation and low precipitation in Red Sea. The dissolution of $CaCO_3$ particles secreted by corals might be additional reason for the high concentration of Ca^{2+} in the area of study.

The concentrations of the metal ions Na^+, Mg^{2+}, Ca^{2+}, and K^+ at station A and D are some what lower than at the other stations. This might be because both of station A and D are close to the coast where the sedimentary suspended particles can adsorb these metals and reduce their concentration.

Table 3.1: Concentration of major ions (ppm) the Sudanese coastal water

Station	Na^+	Mg^{2+}	Ca^{2+}	K^+	Cl^-	SO_4^{2-}	Br^-
A1	11810	1449	466.7	387.3	23023.8	3176.2	68.3
A2	11910	1459	468.6	396.6	23842.1	3143.1	68.2
A3	11990	1462	470.8	392.6	23494.5	3185.6	70.3
A4	9445.0	1068	405.1	320.8	23771.0	3156.8	69.5
A5	12090	1472	473.2	398.3	23795.8	3178.3	?
B1	12100	1474	472.2	394.7	23468.2	3183.4	69.3
B2	12120	1474	472.4	394.7	22446.0	3196.5	69.9
B3	12050	1472	472.4	398.9	20922.0	3115.2	68.4
B4	12140	1488	477.2	401.3	24211.9	3174.1	69.9
B5	12130	1474	473.7	398.4	23344.7	3171.5	67.9
C1	12090	1480	475.9	395.6	23866.5	3165.3	69.0
C2	12060	1480	474.9	396.9	23669.2	3159.5	69.0
C3	11990	1468	471.6	392.6	24120.6	2960.8	?
C4	12010	1475	475.0	394.1	23464.9	2993.8	67.4
C5	11900	1464	471.5	393.6	21401.6	3064.7	65.4
D1	11890	1466	472.2	386.5	24262.2	3100.8	65.7
D2	11896	1458	470.7	385.0	21445.9	3143.6	70.1
D3	11920	1465	471.5	386.2	23481.7	3168.9	70.1
D4	11764	1451	466.4	373.8	23528.0	3151.9	68.4
D5	12100	1485	477.3	391.2	23549.7	3175.1	69.1

Note that the average for station A is calculated without the results from location A4.

?: Not able to calculate the integration of the peak.

Table 3.2: Average concentration of major ions (ppm) in the Sudanese coastal water

Element	St. A	St. B	St. C	St. D
Na^+	11950	12108	12010	11914
RSD	0.003	0.003	0.006	0.010
Mg^{2+}	1460.5	1476.4	1473.4	1465
RSD	0.009	0.004	0.005	0.009
Ca^{2+}	456.88	473.58	473.78	471.628
RSD	0.008	0.004	0.004	0.008
K^+	393.7	397.6	394.56	384.54
RSD	0.004	0.007	0.004	0.017
Cl^-	23525.44	22878.56	23304.56	23253.50
RSD	0.01	0.05	0.04	0.04
SO_4^{2-}	3168.00	3168.14	3068.82	3148.081
RSD	0.005	0.009	0.030	0.009
Br^-	55.26	69.08	54.16	68.68
RSD	0.018	0.010	0.031	0.026

Table 3.3 shows the ratios between some major ions to chlorinity in the Sudanese coastal water compared to the average seawater which were calculated by Knudsen (1900) empirical relationship

$$S = 1.805Cl + 0.030 \tag{3.1}$$

where Cl is the chlorinity. The values of the ratios of Mg^{2+}/Cl, Ca^{2+}/Cl, and SO_4^{2-}/Cl in the coastal water of this study are greater than the values of average seawater. Dissolution of CaCO_3 particles secreted by corals might be a reason for high Ca/Cl ratio. The values of the ratios of Na^+/Cl, K^+/Cl, and Br^-/Cl are less than that calculated by Morris and Riley (1966); Culkin and Cox (1976). However, the variations found can be attributed to differences in the analytical methods used. The abundance of the bacteria that use SO_4^{2-} as a source of O_2 leading to lower values, is low in the Sudanese coastal water. This can be additional reason for the high value of SO_4^{2-}/Cl.

TABLE 3.3: Comparison between the ratios of element/chlorinity in Sudanese Coastal water and average seawater

Element/Cl	Average seawater values	Mean values in SCW
Na^+/Cl	0.5555± 0.0007	0.5498
Mg^{2+}/Cl	0.0669± 0.0002	0.0671
K^+/Cl	0.0206± 0.00004	0.01802
Ca^{2+}/Cl	0.02126± 0.00004	0.02172
SO_4^{2-}/Cl	0.14000 ± 0.00023	0.14536
Br^-/Cl	0.003473 ± 0.000012	0.002862

SCW: Sudanese Coastal water.
Average seawater values data were taken from Morris and Riley (1966); Culkin and Cox (1976).

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3.1.2 Trace metals in Sudanese coastal surface water

Table 3.4 shows the concentration of trace metals, determined by ICP-OES, from the four stations (A-D) in the Sudanese coastal water. The average concentrations of the five locations within each station are shown in Table 3.5.

The results show that there is no significant spatial variation. Cu and Ti did not give any instrumental response, which means either that their concentrations in the Sudanese coastal water are below the detection limit of the instrument or the elements do not occur in the Sudanese coastal water. This is also the fact for As, Co, Cr, La, and Eu (not shown). So, the detection power of ICP-OES does not permits direct determination of some trace metals at their levels in seawater. Thus, in order to detect their concentrations, preconcentration should be done as carried out by Shriadah et al. (2004), or a more sensitive method should be used.

Table 3.4: Concentration of trace metals (ppm) in Sudanese coastal water

St.	B	Ba	Cu	Fe	Li	Mn	Si	Sr	Ti	Zn
A1	4.208	0.0053	ND	0.0118	0.255	ND	0.0550	7.592	ND	ND
A2	4.205	0.0054	ND	0.0176	0.256	ND	0.0683	7.562	ND	ND
A3	4.188	0.0053	ND	0.0213	0.253	ND	0.0864	7.562	ND	ND
A4	4.160	0.0052	ND	0.0158	0.253	ND	0.0586	7.619	ND	ND
A5	4.199	0.0078	ND	0.0291	0.252	ND	0.0722	7.776	ND	0.045
B1	4.243	0.0052	ND	0.0267	0.253	ND	0.0725	7.681	ND	ND
B2	4.200	0.0052	ND	0.0148	0.251	ND	0.0741	7.580	ND	ND
B3	4.144	0.0051	ND	0.0155	0.247	ND	0.0657	7.638	ND	ND
B4	4.145	0.0052	ND	0.0300	0.246	ND	0.0698	7.596	ND	ND
B5	4.214	0.0054	ND	0.0192	0.252	ND	0.0570	7.660	ND	0.045
C1	4.127	0.0051	ND	0.0154	0.244	ND	0.0657	7.526	ND	ND
C2	4.209	0.0078	ND	0.0129	0.252	ND	0.0538	7.519	ND	ND
C3	4.147	0.0050	ND	0.0162	0.242	ND	0.0605	7.508	ND	ND
C4	4.150	0.0057	ND	0.0184	0.249	ND	0.0676	7.505	ND	ND
C5	4.215	0.0053	ND	0.0261	0.248	ND	0.0615	7.543	ND	ND
D1	4.203	0.0052	ND	0.0211	0.249	ND	0.0686	7.586	ND	0.045
D2	4.283	0.0052	ND	0.0117	0.253	ND	0.0530	7.536	ND	ND
D3	4.259	0.0052	ND	0.0176	0.252	ND	0.0616	7.626	ND	ND
D4	4.153	0.0051	ND	0.0202	0.246	ND	0.0627	7.589	ND	ND
D5	4.218	0.0056	ND	0.0371	0.250	0.0017	0.0774	7.749	ND	0.051

ND: Notdetected, below the detection limit.

Table 3.5: Average concentration of trace metals (ppm) in Sudanese coastal water

Element	St. A	St. B	St. C	St. D
B	4.192	4.189	4.170	4.223
RSD	0.00464	0.01042	0.00953	0.01196
Ba	0.0058	0.0052	0.0058	0.0053
RSD	0.1931	0.0209	0.2007	0.0370
Fe	0.01912	0.02124	0.01780	0.02154
RSD	0.3422	0.3202	0.2831	0.4382
Li	0.2544	0.2503	0.2476	0.2505
RSD	0.0076	0.0124	0.0157	0.0121
Mn	ND	ND	ND	0.00034
RSD	-	-	-	2.23606
Si	0.06810	0.06782	0.06182	0.06466
RSD	0.18187	0.10077	0.08659	0.13983
Sr	7.622	7.631	7.520	7.617
RSD	0.01170	0.00556	0.01528	0.01054
Zn	0.00906	0.00904	ND	0.00906
RSD	2.23606	2.23606	-	2.92602

ND: Not detected, below the detection limit.

The concentration of Sr is lower than that shown in Table 1.1 and this might be connected to the presence of Acantharians. Acantharians are marine planktonic protozoans that use Sr as a major structural component (Bernstein et al., 1992). Measurements done near the detection limit are not considered to be quantitative measurements. For accurate quantitative analysis, the concentration must be 100 times greater than the detection limit (Boss and Fredeen, 1999). Thus, the precision of the analysis of Si, Zn, and Fe is low (high RSD) compared to the analysis results of other elements because their concentration not greater enough than the detection limit of the instrument (see Table A.1). So, the concentration of these metals does not represent their insitu concentration in the Sudanese coastal water.

The results also show that the concentration of B in Sudanese coastal water (4.193 ppm) is lower compared to its concentrations in Table 1.2 (4.6 ppm). Boron is partly present in seawater as the neutral compound $B(OH)_3$, boric acid, and it has been hypothesized that this compound can be distilled from surface water in the tropics during evaporation and transported to high latitudes through the atmosphere (Martens and Harriss, 1976), and this might be the reason for the low concentration of B in Sudanese coastal water.

3.2 Extractable organic matter and petroleum hydrocarbons in the Sudanese coastal water

Any organic material in seawater which can be dissolved in the extraction solvent (dichloromethane) contributes to the extractable organic matter (EOM) concentration; photosynthetic pigments, dissolved humic substances, in addition to organic pollutants such as crude oil. The EOM concentrations in surface seawater samples from the Sudanese coast ranged from 1.3 to 10 mg/L (see Table 3.6) with 4.46 mg/L as the average concentration. This is slightly higher than in the eastern Red Sea coastal water, where Al-Lihaibi (2003) found EOM values between 0.8 and 6.1 mg/L (average 3.8 mg/L).

It is noteworthy that the highest concentration of EOM was observed at station 1 which is the closest station to the coast. This is most likely due to the continuous discharge of several pollutants (e.g.fossil-fuel) from the coast and/or high concentration of dissolved organic matter. The concentration of EOM in seawater near the port (Station 2) is 6 mg/L whereas in the zone close to Port Bashair, where oil is transported (Station 3), the EOM is 1.3 mg/L, i.e. 4.7 mg/L lower than what is measured near the port. The high level in the port is due to the continuous discharge of oil from the ships. It is noteworthy that the concentration of EOM was not detected at station 4 because this station is quite far from the coast. The concentration of EOM in seawater near Sanganeb (Station 5) is 5 mg/L. This might be due to the discharge from the boats that regularly visit Sanganeb and the high production of organic matter near its coast.

TABLE 3.6: Concentrations of extractable organic matter (EOM) and dissolved and dispersed petroleum hydrocarbons (DDPHs) from the Sudanese coastal water

Station no.	EOM mg/L	DDPHs μg/L
1	10	15.84
2	6	95.92
3	1.3	41.92
4	n.d.	19.26
5	5	31.79
Average	4.46	40.95

n.d: not detected.

The fluorescence based concentrations of dispersed petroleum hydrocarbons (DDPHs) equivalent to Sudanese heavy crude oil in seawater from the Sudanese coastal water (at 310 nm excitation, 360 nm emission wavelengths) are also presented in Table 3.6. In spite of the high sensitivity of the fluorescence spectroscopy ; only DDPHs can fluoresce at these wave lengths, some dissolved organic substances such as chlorophyll can interact. The concentrations ranged between 15.84 and 95.92 μg/L with an average of 40.95 μg/L . This range is much larger than the range measured by Al-Lihaibi (2003) which was between 0.9 and 18.0 μg/L with an average of 4.7 μg/L. It is noteworthy that Stations 2 and 3 have the highest petroleum hydrocarbon concentrations and consequently these locations are considered polluted. Thus, the influence of the ships in station 2 and oil transportation in station 3 is obvious. The level of DDPHs in station 4 and 5 can be attributed to the dissolved organic matter such as and chlorophyll pigments and humic substances which can fluoresce the same wave lengths. Thus, individual aromatic hydrocarbons should be determined using GC-MS in order to investigate the oil residue.

We observe that in spite of the highest concentration of EOM in station 1, the concentration of DDPHs is the lowest. That that means EOM at this station consists of organic materials other than DDPHs.

According to Keizer and Gordon Jr (1973), who defined a concentration of 2 μg/L of petroleum hydrocarbons as the threshold between oil polluted and unpolluted waters, all the stations in this study are polluted. But the level of DDPHs in the Sudanese coastal water (the average) does not affect the planktonic ecosystem because the threshold value for effects from oil lies in the range 50-100 μg/L (Gunnar and Ostvedt, 1984).

Figure 3.1 represents the calibration curve which has been made by standard solutions of Sudanese crude heavy oil using hexane as solvent. Good linearity was achieved (R^2=0.998). The calibration curve was used in the determination of dissolved/dispersed petroleum hydrocarbons (DDPHs) as Sudanese heavy crude oil equivalent.

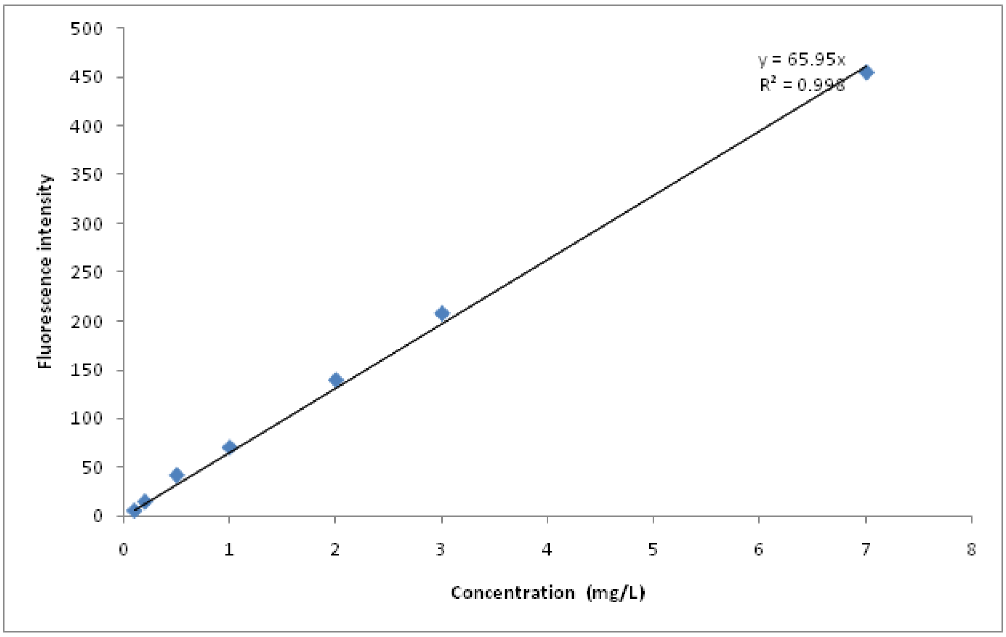

Figure 3.1: Calibration curve by standard solutions of Sudanese crude oil using hexane as solvent

3.3 Photooxidation of 1,8-dimethylnaphthalene

The photooxidation of petroleum spilled on seawater, has been studied. 1,8-dimethylnaphthalene (1,8-DMN) which is one of the petroleum constituents that are photochemically reactive, was used as a model of crude oil.

The photooxidation reaction was carried out in distilled water, and Red Sea artificial water in order to study how salinity affect the photooxidation of 1,8-DMN. Sudanese heavy crude oil was mixed with 1,8-DMN to study the influence of this oil on the photooxidation.

Figure 3.2 shows the GC-MS result of 1,8-DMN used in this study. Notice that the figure shows only one peak (upper panel) with a retention time of 20.5 min, and this indicates the high purity of the compound. The bottom panel shows the MS of 1,8-DMN.

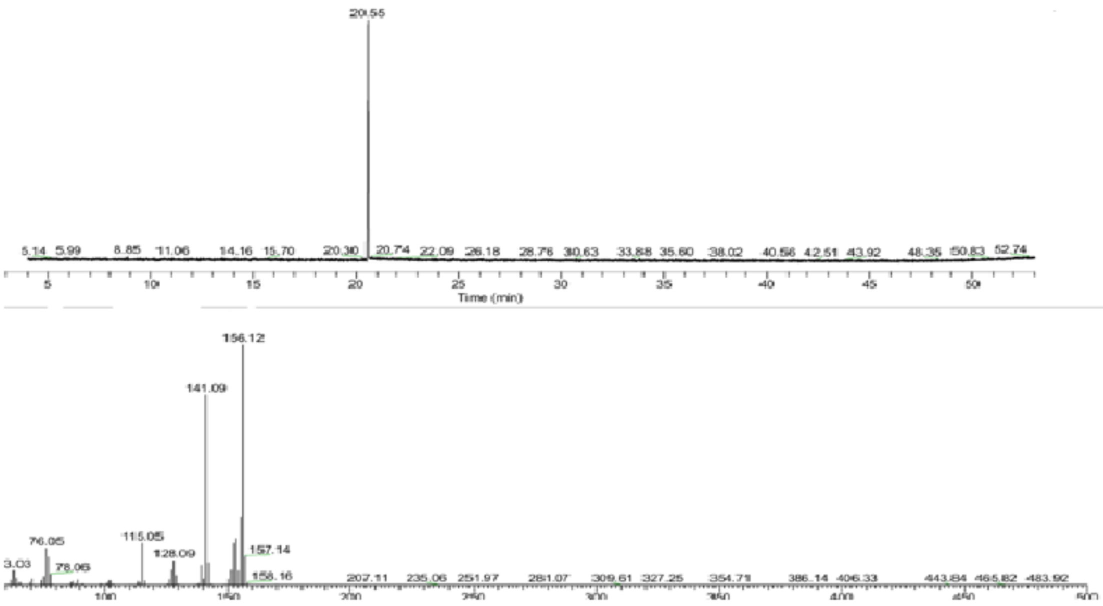

Figure 3.2: Gas chromatogram (upper panel) and mass spectrum (lower panel) for 1,8-DMN used in the study.

Figure 3.3 shows the gas chromatograms of the organic material dissolved in the aqueous phase after the dissolution of 1,8-DMN in distilled water kept at completely dark environment at 8°C (container 1 in Table 2.1). The appearance of only one tiny peak with a retention time of 21.75 which was identified as 2,6-(t-butyle)-2,5-cyclohexadiene-1,4-dione which is the diethyl ether stabilizer (the extraction solvent), indicates that the photooxidation of 1,8-DMN does not occur in the absence of light.

The gas chromatograms of organic material dissolved in the aqueous phase after the irradiation (by low pressure mercury lamp) of 1,8-DMN in distilled water, in Red Sea natural water, and in artificial Red Sea water at 8°C (containers 2-4 in Table 2.1) are shown in Figure 3.4, Figure 3.5, and Figure 3.6 respectively.

These figures show a peak of starting material, 1,8-DMN at retention time of 20.41 min and a tiny peak at retention time of 24.59 which was identified as 8-methyl-1- naphthaldehyde (one of the photooxidation products) by comparing its mass spectrum with that of authentic samples. The peak at retention time of 21.66 min was identified as 2,6-(t-butyle)-2,5-cyclohexadiene-1,4-dione which was present originally in the extraction solvent (diethyl ether) as stabilizer.

Irradiation (by low pressure mercury lamp) of 1,8-DMN in distilled water, in Red Sea natural water, and in artificial Red Sea water at 8°C (containers 2-4 in Table 2.1) result in the same chromatogram. This indicates that salts have no obvious effect on the photooxidation of 1,8-DMN but it might affect the reaction kinetics. The low efficiency (small number of peaks) of these reactions compared to

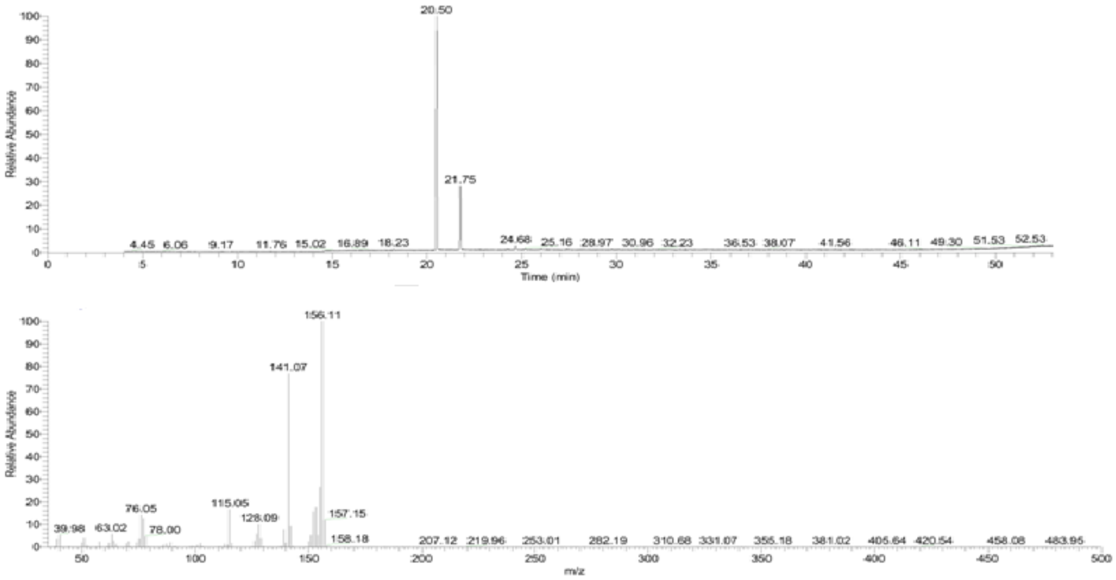

FIGURE 3.3: GC (upper panel) and MS (lower panel) for the organic material dissolved in the aqueous phase for 1,8-DMN mixed in distilled water stored in completely dark environment at 8°C

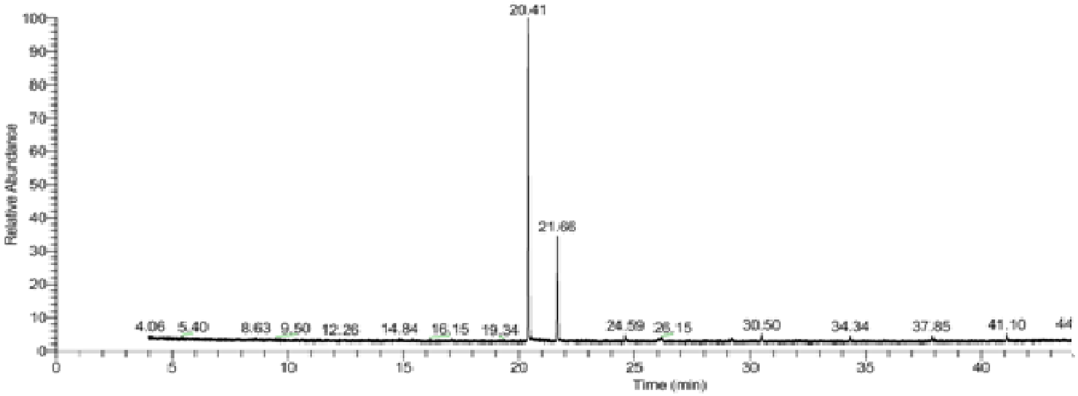

FIGURE 3.4: Gas chromatogram of the organic material dissolved in the aqueous phase after the irradiation of 1,8-DMN in distilled water

that in Figure 1.5 in which more than four products appeared, might be due to the low efficiency of the lamp (LPML) used in this study. Silylation or addition of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMCS) which was done in the reaction of Figure 1.5 increases the volatilization of the products and then the ability of their detection by GC-MS. Silylation of the extracted organic materials was not carried out, because unfortunately, the silylating agent, BSTFA and TMCS was not available when the experiments were performed and the analysis carried out. This might be a reason for the low efficiency.

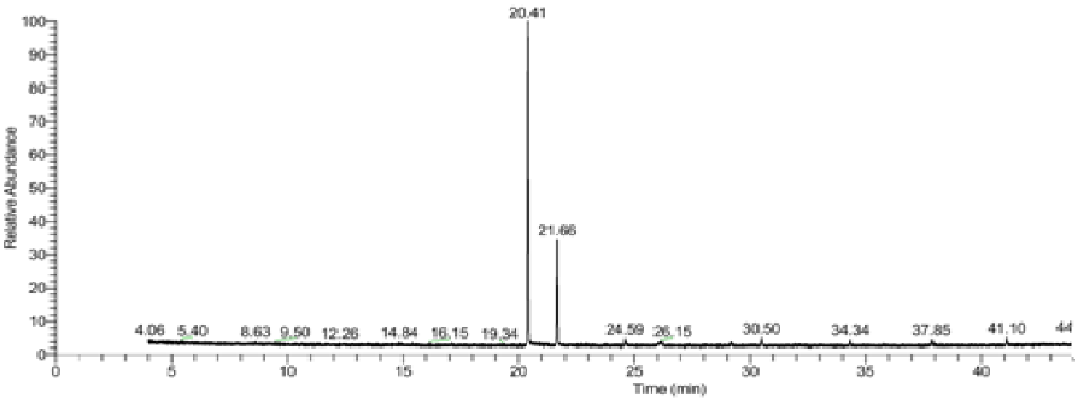

FIGURE 3.5: Gas chromatogram of the organic material dissolved in the aqueous phase after the irradiation of 1,8-DMN in Red Sea natural water

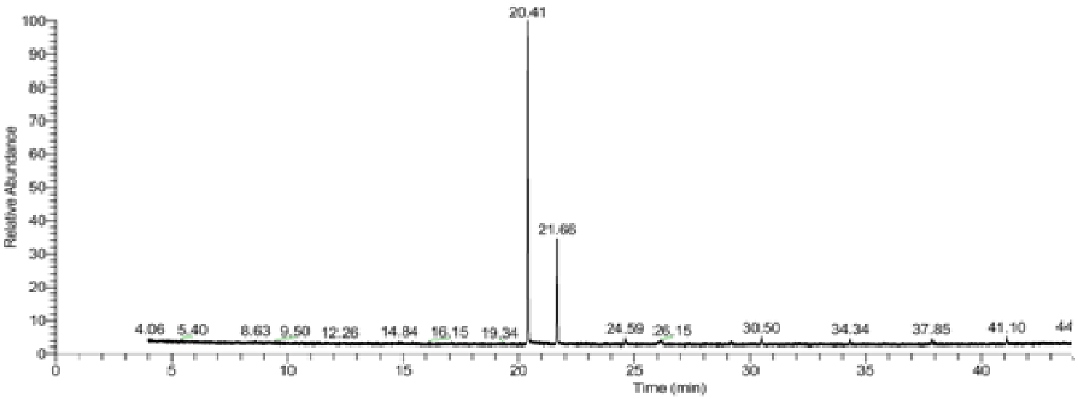

FIGURE 3.6: Gas chromatogram of the organic material dissolved in the aqueous phase after the irradiation of 1,8-DMN in Red Sea artificial water

A third explanation might be connected to the extraction solvent used in this study, which has low efficiency since the weight of the extract was much less than the weight of the starting material (the extraction solvent used in the reaction in Figure 1.5 was ethyl acetate). Some of the starting material probable evaporated during the irradiation.

The gas chromatogram of organic material dissolved in the aqueous phase after the irradiation (by low pressure mercury lamp) of 1,8-DMN mixed with Sudanese heavy crude oil in distilled water at 8°C (container 5 in Table 2.1) are shown in Figure 3.7.

Figure 3.7 show a peak of starting material (1,8-DMN) with a retention time of 19.45 min and a tiny peak at retention time of 23.46 which was identified as 8-methyl-1- naphthaldehyde (one of the photooxidation products) by comparing its mass spectrum with that of the an authentic sample. The peak with a retention

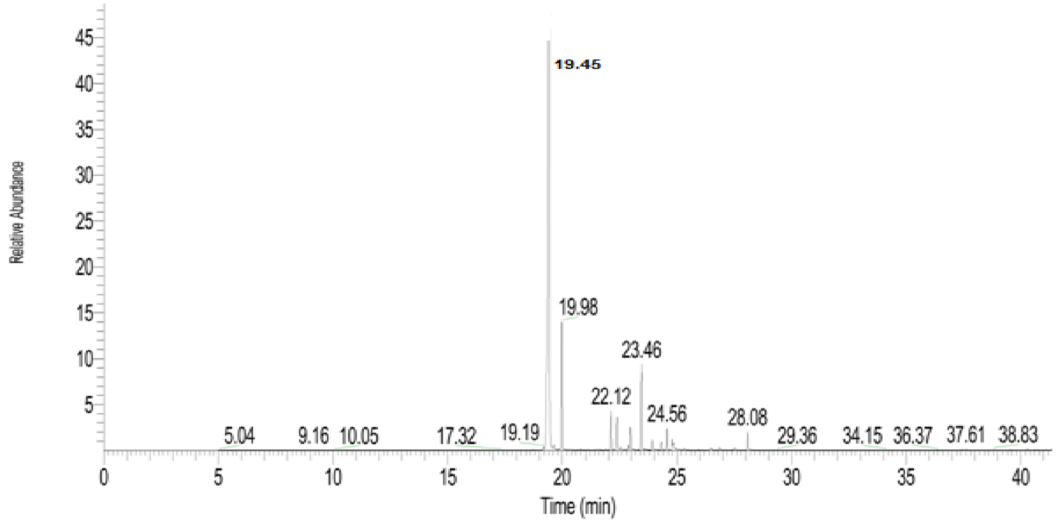

Figure 3.7: Gas chromatogram of organic material dissolved in the aqueous phase after the irradiation (by low pressure mercury lamp) of 1,8-DMN mixed with Sudanese heavy crude oil in distilled water

time of 19.98 min was identified as the extraction solvent (diethyl ether) stabilizer. The figure also shows a small several peaks due to undefined products. The effect of the oil on the photooxidation is obvious from this figure since the number of peaks was increased. This because the oil contains a several sensitizers. The difference between this figure and Figure 1.4 (B) is due to the difference in the oil. The oil in this study was very thick compared to that in Figure 1.4 (B).

Figure 3.8 shows the GC-MS for the organic material dissolved in the aqueous phase after the dissolution of 1,8-DMN in distilled water at completely dark environment at 35°C (container 6, Table 2.1). The chromatogramshows that the oxidation of 1,8-DMN can occur in the darkness but with very low efficiency, since only a tiny peak identified as 8-methyl-1-naphthaldehyde appears with a retention time of 30.02. The peak with a retention time of 27.0 was identified as the diethyl ether stabilizer. The occurrence of the oxidation reaction might be due to the ambient high temperature compared to the temperature of the reaction in container 1 (see Table 2.1). So, the high temperature can induce the formation of the reactive species such as peroxides and these species oxidize the 1,8-DMN.

Figure 3.9 shows the gas chromatogram of the organic material extracted from the aqueous phase after the irradiation (by natural sunlight) of 1,8-DMN in distilled water at 35°C (container 7 in Table 2.1).

The figure shows a tiny peak of starting material, 1,8-DMN at retention time of 26.55 min, a small peak at retention time of 26.97 which was identified as the diethyl ether stabilizer, and two unidentified peaks at retention time of 30.18 and 35.59. According to Figure 3.9 we can say that the photooxidation of 1,8-DMN

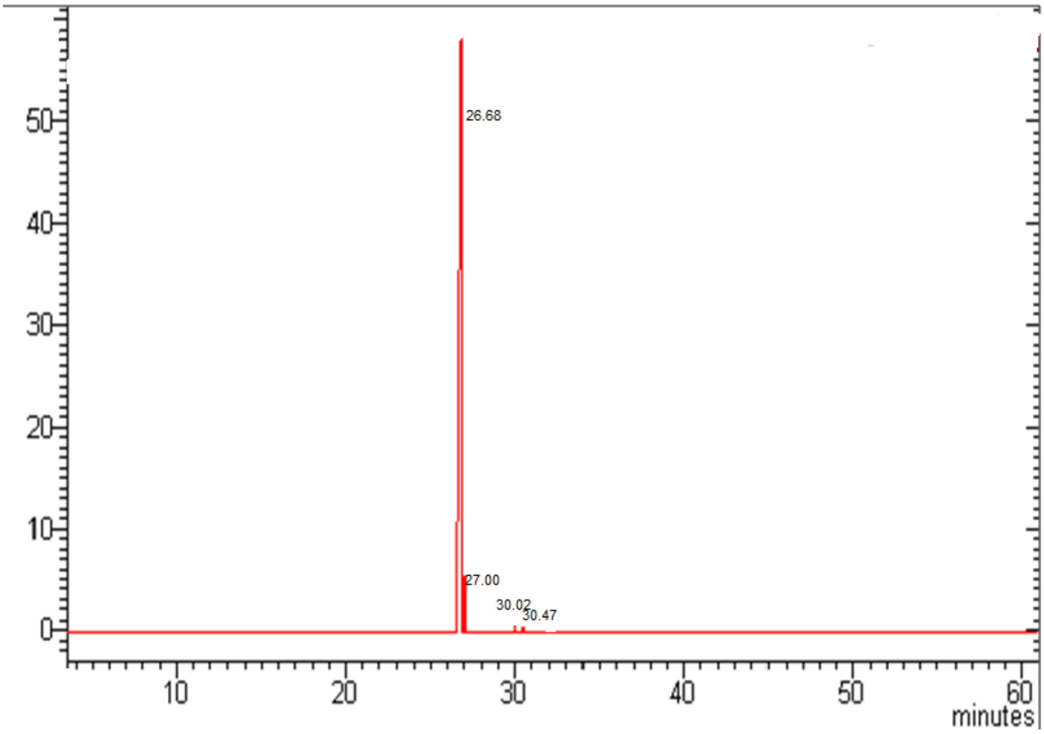

FIGURE 3.8: Gas chromatogram of the organic material dissolved in the aqueous phase for 1,8-DMN mixed in distilled water stored in completely dark environment at 35°C

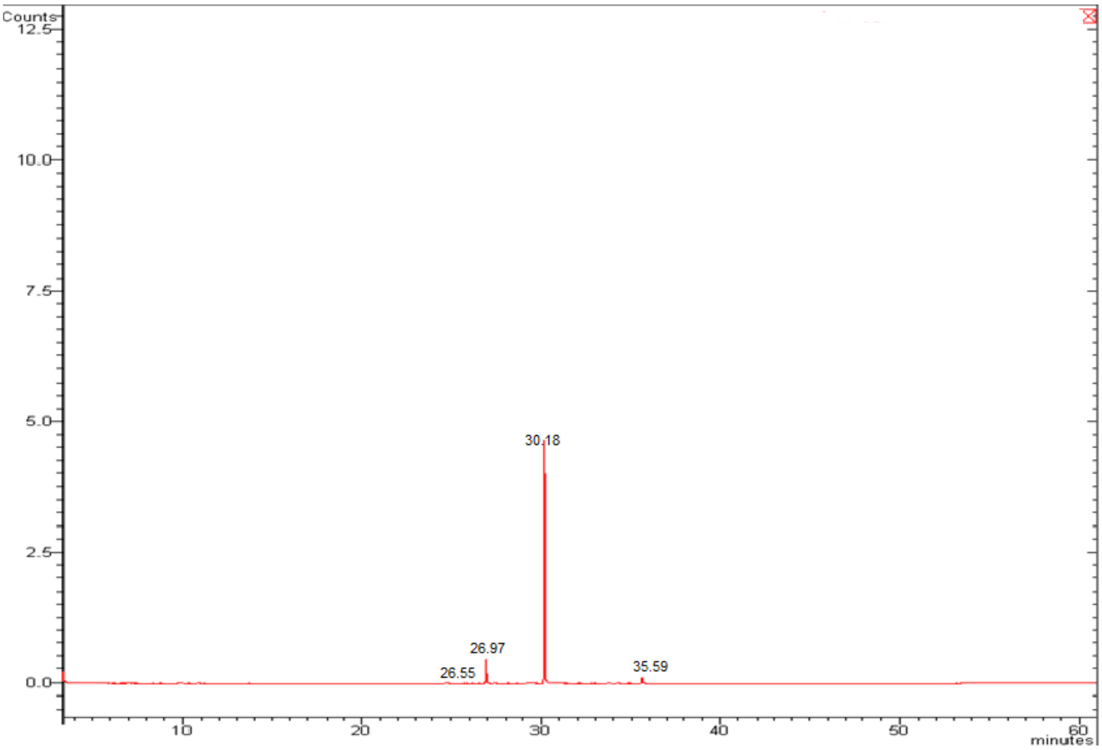

FIGURE 3.9: Gas chromatogram of the organic material extracted from the aqueous phase after the irradiation (natural sunlight) of 1,8-DMN in distilled water at 35°C (container 7 in Table 2.1)

occurs under natural sunlight with low efficiency because of the small number of peaks. Most of the starting material has disappeared due to the evaporation.

Figure 3.10 shows the gas chromatogram for the organic material extracted from the aqueous phase after the irradiation (natural sunlight) of 1,8-DMN mixed with Sudanese heavy crude oil in distilled water at 35°C (container 8 in Table 2.1). The figure shows a small peak of starting material (1,8-DMN) at retention time of 26.55 min, a small peak at retention time of 27.23 which was identified as the diethyl ether stabilizer, and an undefined peak at retention time of 30.53. According to Figure 3.10, the oil increases the efficiency of the photooxidation of 1,8-DMN under natural sunlight since the number of peak is greater than the number of peaks in Figure 3.9. Since the the peak of the starting material (1,8-DMN) in Figure 3.10 is tall compared to its height in Figure 3.9, the oil decreases the rate of the evaporation of 1,8-DMN.

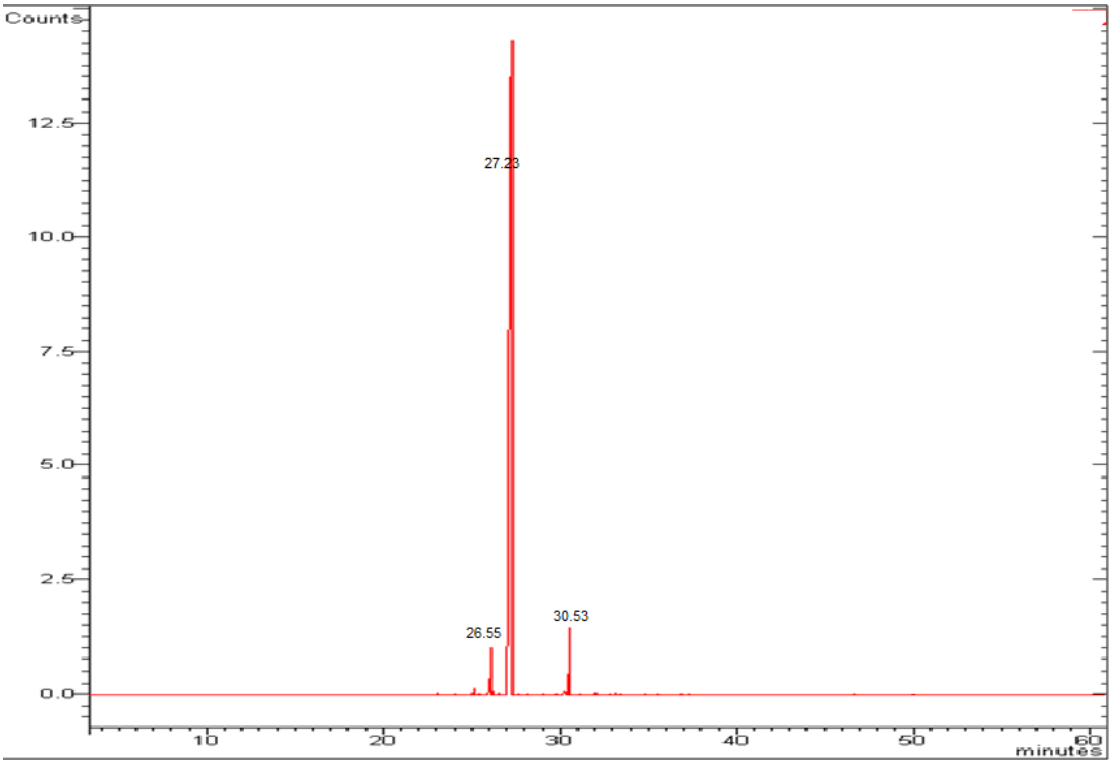

Figure 3.10: Gas chromatogram of the organic material extracted from the aqueous phase after the irradiation (natural sunlight) of 1,8-DMN mixed with Sudanese heavy crude oil in distilled water at 35°C (container 8 in Table 2.1).

3.3.1 Photochemical transformations of water-soluble fraction (WSF) of crude oil

Changes in the chemical nature of the water-soluble fraction (WSF) from Norwegian crude oil caused by irradiation using low-pressure mercury lamp were investigated qualitatively by gas chromatography-mass spectrometry (GC-MS) and gas chromatography. Aromatic hydrocarbons with low molecular weights in the WSF , resulting from crude oil slick solubilization on distilled water, were confirmed by chromatogram (major peaks with a retantion time between 30-40 min in Figure 3.11). Comparison between Figure 3.11 and Figure 1.6 shows that not all of the constituents of the oil are present in the WSF because of evaporation of the light hydrocarbons (peaks with a small retention times), and the low solubility of heavier ones (peaks with a high retention time).

A total of (15-20) peaks were detected in the chromatograms (see Figure 3.11 and 3.12) of WSF of the Norwegian oil, but after irradiation by low-pressure mercury lamp these compounds were not detected (see Figure 3.13). These results emphasize photodegradation as an effective weathering process for the transformation of dissolved crude oil fraction (WSF), particularly in high solar radiation environments as in the Red Sea. Also, phototransformation of the WSF is more efficient than the phototransformation of 1,8-DMN (see Figure 3.4). This might be due to the sensitization process which takes place in WSF since photosensitizers are present.

Salt effects on the phototransformation of WSF from Norwegian oil can be seen by comparing Figure 3.13 with Figure 3.14. In the latter chromatogram two peaks at (13.13 and 15.73) min are present while only a small peak with a retention time of 4.01 exists in Figure 3.14. This indicates that the phototransformation of WSF from the Norwegian oil is favoured in distilled water. This may be due to a heavy metal effect caused by dissolved salt(s) in the artificial water.

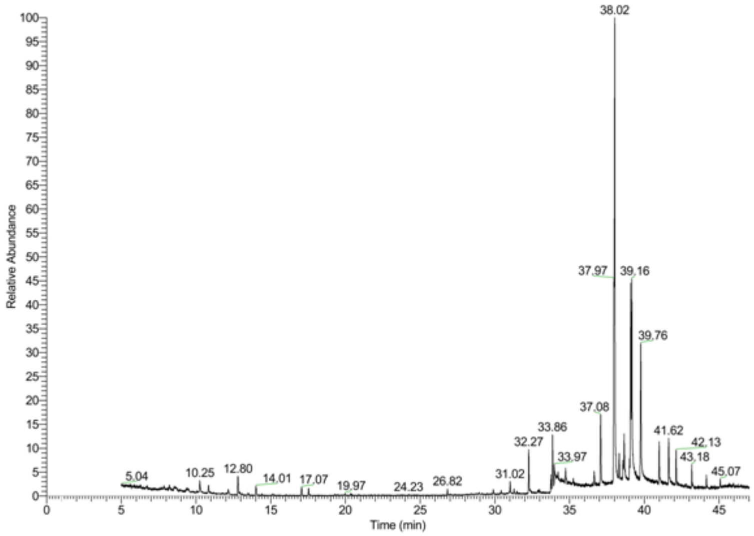

Figure 3.11: Gas chromatogram of the water-soluble fraction (WSF) of Norwegian crude oil (25 ml oil per 500 ml of distilled water(1:20)) without irradiation

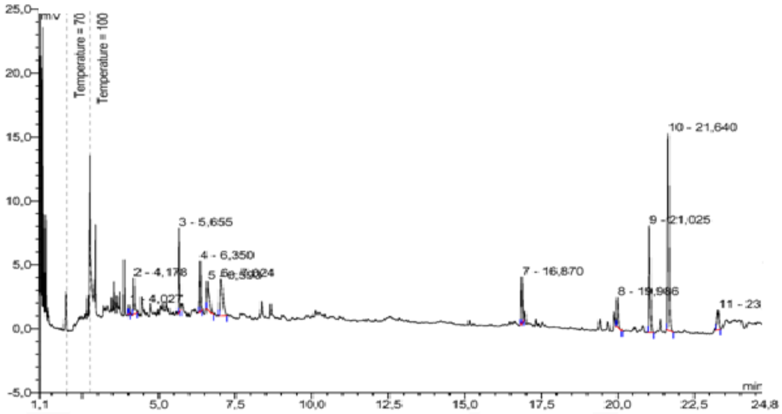

Figure 3.12: Gas chromatogram of the water-soluble fraction (WSF) of Norwegian crude oil (25 ml oil per 500 ml of distilled water(1:20)), after 2 days at room temperature in a dark room.

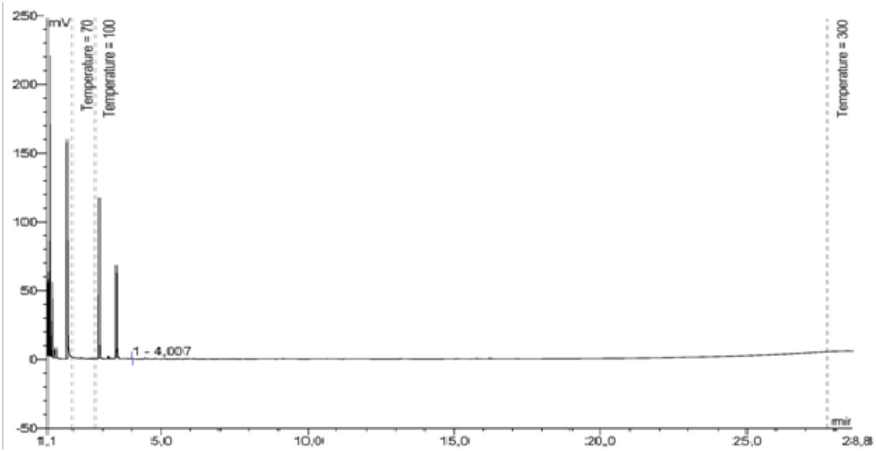

FIGURE 3.13: Gas chromatogram of the water-soluble fraction (WSF) of Norwegian crude oil (25 ml oil per 500 ml of distilled water(1:20)) in distilled water after two days of irradiation by low-pressure mercury lamp

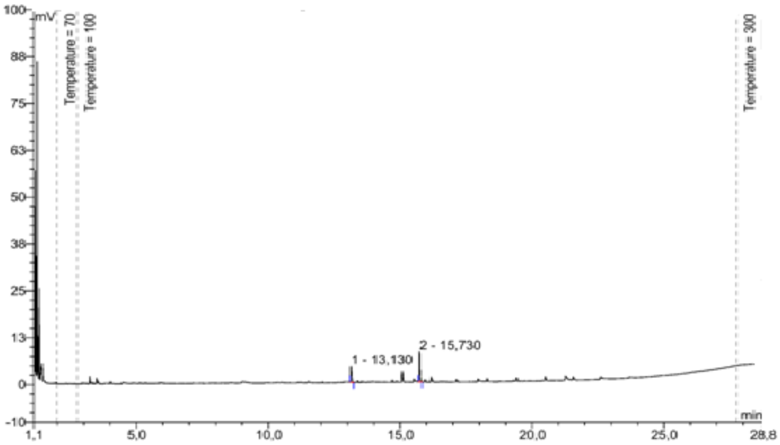

FIGURE 3.14: Gas chromatogram of the water-soluble fraction (WSF) of Norwegian crude oil (25 ml oil per 500 ml of artificial seawater (1:20)) in artificial seawater after two days of irradiation by low-pressure mercury lamp.

Chapter 4

Conclusion

Red Sea water samples were collected from the Sudanese coast at depth of 10 meter during July 2011 and analyzed for major ions and trace metals. Sodium (Na^+), potassium (K^+), strontium (Sr^{2+}), magnesium (Mg^{2+}), calcium (Ca^{2+}), boron (B), iron (Fe), zinc (Zn), manganese (Mn), nickel (Ni), copper (Cu), cadmium (Cd), cobalt (Co), lead (Pb), arsenic (As), barium (Ba), chromium (Cr), europium (Eu), lanthanum (La), silicon (Si), and titanium (Ti) were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES). Sulfate (SO_4^{2-}), chloride (Cl^-), and bromide (Br^-) were analyzed using ion chromatography (IC). The analysis of these elements was done in order to determine their insitu concentration, their distribution patterns, and level of contamination in the Sudanese coastal water by heavy metals. The data of the analysis was used in the preparation of Red Sea artificial water which was used to study how salinity affects the photooxidation of 1,8-dimethylnaphthalene and the water-soluble fraction (WSF) from Norwegian crude oil in the Red Sea water.

The average concentrations in ppm (mg/L) of the major ions Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, and SO_4^{2-} are 11870.25, 1449.2, 468.967, 388.955, 23240.515, and 3138.26025 respectively. The results show a small range of spatial variation for Na^+, Mg^{2+}, Ca^{2+}, Cl^-, K^+, and SO_4^{2-}. The results revealed that the concentration of Na^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} in the Sudanese coastal water is high compared to all other water basins and average seawater. The reason of this is the high evaporation and low precipitation in Red Sea.

The concentrations of the metal ions Na^+, Mg^{2+}, Ca^{2+}, and K^+ at the coastal stations are some what lower than at the other stations. This might be because these stations are close to the coast where suspended particles can adsorb these metals and reduce their concentration.

The concentration of Br^- in the Sudanese coastal water is 61.795 ppm whereas its concentration in average seawater is 68 ppm. The ratios between the major ions to chlorinity in Sudanese coastal water were also compared to the average seawater.

Cu, Ti, As, Co, Cr, La, and Eu did not give any instrumental response, which means either that their concentrations in the Sudanese coastal water are below the detection limit of the instrument or the elements do not occur in these waters. Thus, in order to detect their concentrations, preconcentration should be done or another more sensitive method should be used.

The average concentrations of trace metals in ppm, B, Ba, Fe, Li, Mn, Si, Sr, Zn are 4.1935, 0.005515, 0.02524, 0.25073, 0.000085, 0.0656, 7.59765, and 0.006795 respectively. Except for Fe, Si, and ZN, there are no significant spatial variations.

Measurements done near the detection limit are not quantitative measurements. Thus, the precision of the analysis of Si, Zn, and Fe is low (high RSD) and that is because their concentration close to the detection limit of the instrument.

The results show a small concentration of Sr (7.59 mg/L) compared to the concentration of Sr in average seawater (8 mg/L) and this decrease in Sr concentration may be due to the presence of Acantharians.

The results show that the concentration of B is low compared to the concentration of B in average seawater and the reason for this is that boron is partly present in seawater as the neutral compound $B(OH)_3$ which can be distilled from surface water in the tropics during evaporation process.

The unfiltered seawater samples (1 m depth) were collected from five stations in Sudanese coastal water in order to asses the level of dissolved oil residues. The concentration of petroleum hydrocarbons were determined by the intensity of their fluorescence (310 nm excitation, 360 nm emission wavelengths) and quantification was at 360 nm using an ultraviolet fluorescence(UVF) Spectrofluorophotometer. The extractable organic matter (EOM) concentrations in surface seawater samples from the Sudanese coastal water ranged from 1.3 to 10 mg/L, with an average concentration of 4.46 mg/L. The highest concentration of EOM was observed at station 1, where there is continuous discharge from ships. The dissolved/dispersed petroleum hydrocarbons concentration equivalent to Sudanese heavy crude oil ranged between 15.84 and 95.92 μg/L with an average of 40.95 μg/L. the level of the Red Sea Sudanese coastal water by DDPHs does not affect the planktonic ecosystem because the threshold value for effects from oil lies in the range 50-100 μg/L.

Photooxidation experiments of 1,8-dimethylnaphthalene (1,8-DMN) under artificial sunlight and natural sunlight in distilled water, Red Sea natural water, and

Red Sea artificial water, revealed that the oxidation of 1,8-DMN does not occur in the absence of light at 8° C but it does if the temperature of the media is 35°C because the high temperature can induce the formation of some reactive species such as peroxides and these species oxidize the 1,8-DMN. The results also show that the efficiency of the photooxidation of 1,8-DMN in the absence of crude oil is low. Salinity appears to have no clear effect on the photooxidation of 1,8-DMN, but it might affect the kinetic of the reaction. The results show that the nature of the oil affects the photooxidation of 1,8-DMN.

The qualitative study of the changes in the chemical nature of the water-soluble fraction (WSF) from Norwegian crude oil caused by artificial sunlight showed that the WSF consists of low molecular weight aromatic hydrocarbons. These compound were disappeared after two days of irradiation. These compound were disappeared after two days of irradiation. The presence of aromatic hydrocarbons in the WSF before irradiation, resulting from crude oil slick solubilization on seawater, was confirmed by their chromatograms. However, in the irradiated WSF these compounds were not detected. The results reinforce photodegradation as an effective weathering process for the transformation of dissolved crude oil fraction, particularly in high solar radiation environments such as the Red Sea.

Appendix A

Seawater analysis

A.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Boss and Fredeen (1999) argued that, the emitted wavelengths form a polychromatic light. Then in order to identify the different atoms with individual wavelengths in the sample, the polychromatic light must be separated into monochromatic light by a spectrometer. The detection of each wavelength is done using a photosensitive detector such as a photo-multiplier tube (PMT) and the intensity is measured. To obtain the concentration of the analyte, software makes the calibration curve; plots emission intensity versus concentration of standard solutions of the analyte, then the intensity is checked against this curve and the concentration corresponding to that intensity is the concentration of the analyte. Figure A.1 shows the major components of a typical ICP-OES instrument.

Table A.2 shows the operating conditions of ICP-OES used in this study.

A.1.1 Quality control

Quality control is defined as those operations undertaken in the laboratory to make sure that the data are generated within known probability limits of accuracy and precision (James, 1990).

Quality control samples are usally run along with the real samples to help in estimating the types of errors related to the analytical procedure. Table A.4 shows the calibration of ICP-OES by international standard.

As discussed by SPL (2005), the data quality is usually judged in terms of accuracy and precision. In a single-element method, experimental conditions can be

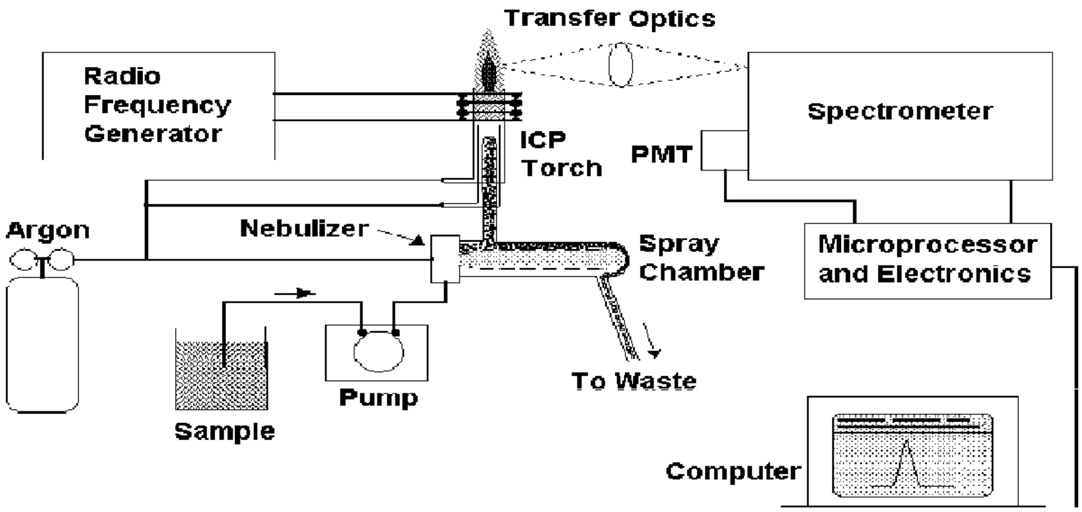

FIGURE A.1: Major components of a typical ICP-OES instrument (taken from Boss and Fredeen (1999))

TABLE A.1: Detection limits (ppb) of the determined elements

Element	Detection limit(ppb)
Ca	20
K	300
Mg	2
Na	1000
Si	25
As	75
B	20
Ba	0.5
Co	5
Cr	50
Cu	5
Eu	2.5
Fe	10
La	5
Li	5
Mn	1.5
Pb	30
Sr	0.5
Ti	10
Zn	10

ppb: part per billion.

optimized to the best conditions for that specific analyte in a specific matrix. But this is not the case in in a multi-element method, since one best condition for one element could be a worst condition for another element. So, there are differences between the quality of the data obtained by a single-element method and that

Table A.2: Operating conditions of ICP-OES.

Parameter	The value
Radio frequency	27 MHz
RF power	1550 W
Nebulizer flow	0.8 L/Min
Auxiliary gas	1.0 L/Min
Cool gas	13 L/Min
Integration time	13 Seconds

Table A.3: Emission lines (wavelengths in nm) used in ICP-OES

Element	Emission line	Element	Emission line
Ba	4554	Co	2286
Al	3082	S	1807
Ca	3179	B	2089
Ca	3933	Li	6707
Fe	2599	La	4086
K	7664	Ni	2216
Mg	2802	V	2924
Mn	2576	Zn	2062
Na	5895	As	1890
P	1774	Pb	2203
Si	2516	Eu	3819
Sr	4077	Cu	3247
Ti	3349	Cr	2677

Table A.4: Calibration of ICP-OES by international standard solutions $SPS-SW2$ and artificial mixtures ($Artif.mix$) containing elements with certified values of concentrations (ppm)

Element	Ca	K	Mg	Na	As	B	Ba
$SPS-SW2$	10	1	2	10	0.05	0.25	0.25
ICP-OES	10.14	0.7781	2.050	9.610	ND	0.2505	0.2543
RSD %	0.1494	0.1839	0.1391	0.4478	9.013	1.166	0.2062
$Artif.mix$	15	15	42	420	0.06	3	0.06
ICP-OES	14.33	14.14	38.76	395.9	ND	2.829	0.0567
RSD %	0.0878	0.0897	0.6810	0.5585	8.944	0.6261	0.5267

obtained by a multi-element method (SPL, 2005).

A.1.2 Internal reference standard (IRS)

In instrumental analysis, the signal from an unknown sample is compared with the one from a standard signal (SPL, 2005). These two signals are unlike each other since the matrix (sample viscosity, presence of other inorganic or organic material,

Cu	Eu	Fe	La	Li	Mn	Pb	Si	Sr
0.1	0.0025	0.1	0.0025		0.05	0.025	5	0.25
0.1015	0.0025	0.0985	ND	ND	0.0501	ND	4.947	0.2483
0.6922	3.202	1.204	36.87	62.65	0.1662	33.65	0.3520	0.4611
0.06	0.06	0.6	0.06	3	3	0.06	15	3
0.0556	0.0543	0.5717	0.0529	2.664	2.846	0.0673	14.13	2.692
0.8620	0.5035	0.8818	3.246	0.1273	0.2542	5.200	0.2791	0.1819

RSD: Percentage relative standard deviation.

ND: Not detected, below the detection limit.

etc.) is not the same (SPL, 2005). But if both samples are spiked with equal amounts of scandium (Sc) as the internal IRS, the signal ratios of the analyte/Sc of both samples are less affected by matrix effects (SPL, 2005).

A.2 Ion Chromatography (IC)

Nutrient anions in sea water are usually determined by adding reagents to form a colored complexes that are detected spectrophotometrically (Strickland and Parsons, 1968). Ion chromatography (IC) presents new procedures for assessing information about environmental samples, namely waters samples of different composition, ranging from high-purity water to highly saline ones (Gros et al., 2008). Ion chromatography (IC) has been recognized as a valuable technique for the determination of inorganic anions in a variety of natural waters (Tanaka et al., 2000).

Figure A.2 show the basic components of an ion chromatograph. The pump is used to deliver the mobile phase through the chromatograph. The sample is injected into the system via a valve injector at atmospheric pressure (Weiss, 1995). Typical injection volumes are between 10 -100 μl. The conductivity detector is used with a suppressor unit or without suppressor. The suppressor is used to reduce the high background conductivity of the electrolytes in the eluent and to convert the sample ions into a more conductive form (Weiss, 1995). To obtain the quantitative results, digital integrators are used to evaluate the peak area, which are proportional to the concentration of the anion of interest (Weiss, 1995).

Table A.5 show the characteristic of an IC instrument used for inorganic analysis with Metroun 1C column (250 mm L X 4.0 mm ID).

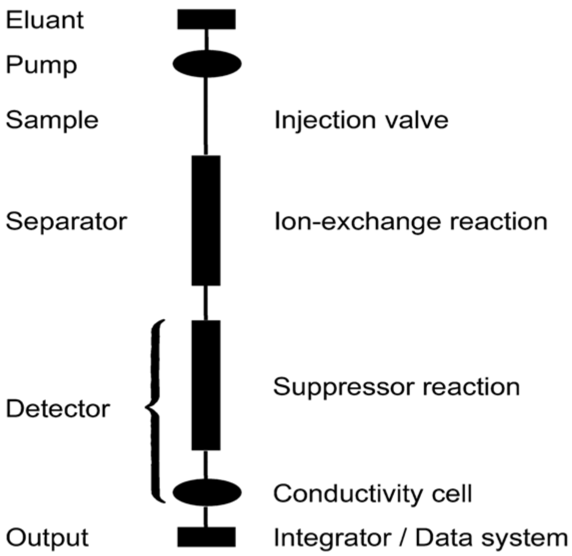

Figure A.2: Typical components of IC chromatograph, taken from Weiss (1995)

Table A.5: IC parameters.

Parameter	
separation center	733 IC
Detector	732 IC
Pump unit	752
Interface	830 IC
Sample processor	838
Software	IC NET SR5

Appendix B

Crude oil analysis

B.1 Fluorescence spectroscopy

As discussed by Christian (2004), fluorescence depends on the structure of the nature of the molecule. Aromatic compounds fluoresce, particularly if they contain electron-donar groups such as -OH, -NH_2, and -OCH_3. Many substances causes fluorescence quenching by competing for the electronic excitation energy and decrease the quantum yield (the efficiency of conversion of absorbed light to fluorescent light).

Christian (2004) argued that, fluorescence intensity, F, is proportional to the source intensity P_0;

$$F = \Phi P_0 (1 - 10)^{-abc} \tag{B.1}$$

where Φ is the quantum yield (proportionality constant), a is the absorbance, b is the cell width, and c is the concentration.

If the concentration of the solution is low, fluorescence intensity, F, is directly proportional to the concentration as shown in Equation B.2;

$$F = 2.303 \varnothing P_0 abc \tag{B.2}$$

The emitted radiation (fluorescence) is measured perpendicular to the incident light. Figure B.1 shows a simple fluorometer design. An ultraviolet source such as a low pressure mercury lamp is required, in which a spark is passed through mercury vapor at low pressure causing an emission of spectral lines. The filter 1 in Figure B.1 filters out the wavelengths close to the emission wavelength, and allows the passage of excitation wavelength. Filter 2 filters out the scattered excitation wavelengths and passes the wavelength of emission only (Christian, 2004).

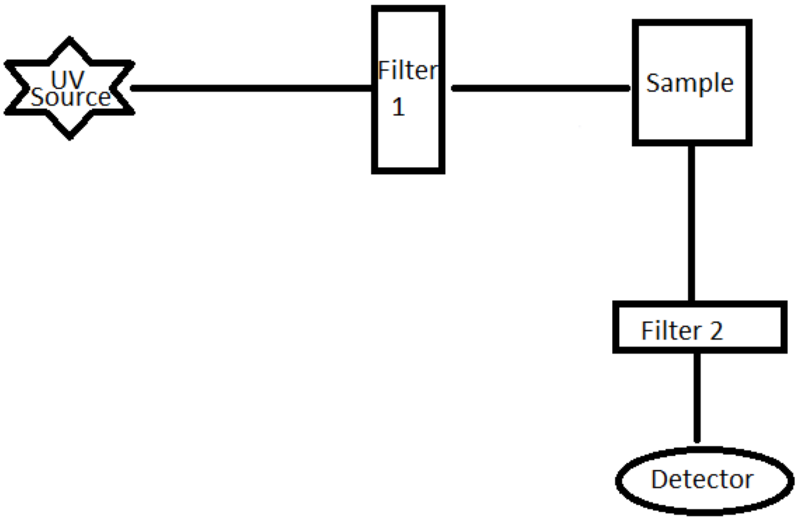

Figure B.1: A simple Fluorometer, taken from Christian (2004)

The aromaticity of the molecule determines its fluorescence intensity (Ryder et al., 2004). Polycyclic aromatic hydrocarbons (PAHs) found in the crude oil and can be simple in structure like naphthalene or very complex ones like asphaltene (see Figure B.2). They have highly fluorescent aromatic characteristics and thus can be easily detected using fluorescence techniques (Ryder et al., 2004).

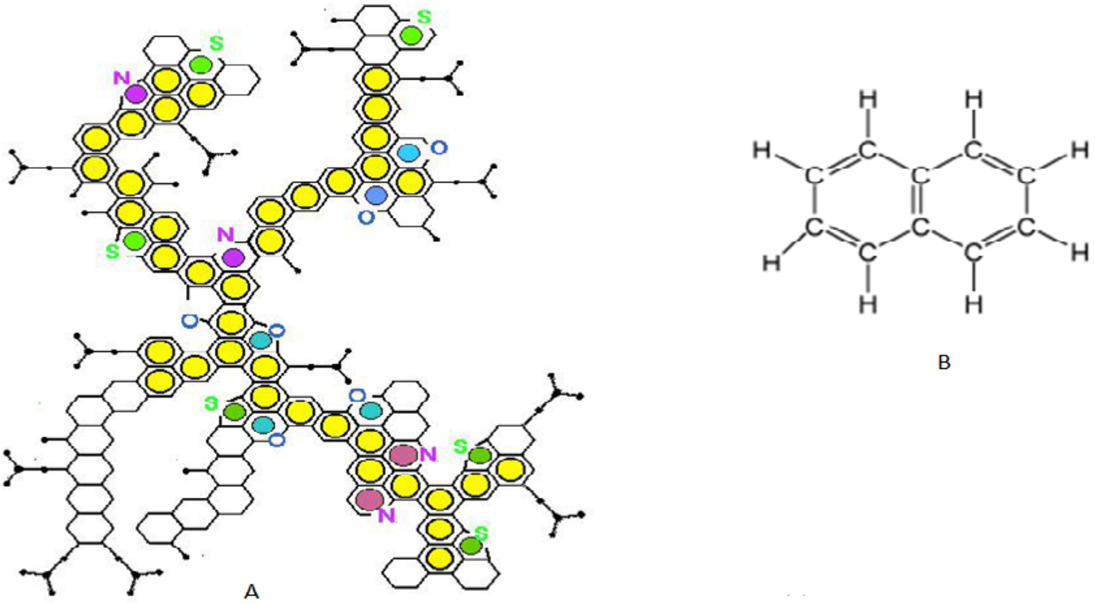

Figure B.2: Asphaltene (A) and Naphthalene(B), taken from (Ryder et al., 2004)

B.2 GC-MS method

As discussed by McMaster and McMaster (1998), there are many GC/MS configurations, but all have the same common types of components. These common components involve an injector to carry the sample to the chromatograph, a gas chromatograph, an interface module in which the separated compounds are transferred to the mass spectrometer's ionization source without remixing, the mass spectrometer system, data processing and interfacing to the GC, and an injector (see Figure B.3). The gas chromatograph consists of gas source, temperature controlled oven, and a column coated with a stationary phase in which the separation takes place. The mass spectrometer system is made-up of the ionization source, focusing lens, mass analyzer, ion detector, multistage pumping, and finally a data/control system to provide mass selection, lens and detector control (McMaster and McMaster, 1998).

Tables.B.1 and B.2 show the properties of the GC-MS used in this study.

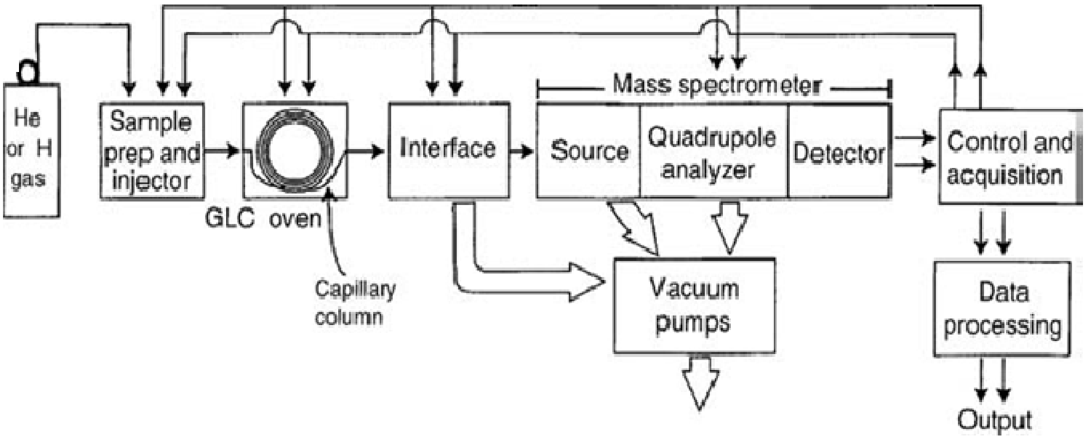

FIGURE B.3: A typical GC-MS system diagram, taken from McMaster and McMaster (1998)

Table B.1: Thermo DSQ II-Trace GC Ultra with a nonpolar, flexible silica capillary column.

Injector	
Auto injector	AI/AS 3000
Injection volume	1 μl
Injections temperature	250°C
Injection pressure	140
Injection mode	split
GC	
Instrument	Trace GC Ultra
Column	Ultra 2 from Agilent
Column diameter	0.20 mm
Outside column diameter	0.11 mm
Inside column length	25 m
Carrier gas	Helium
MS	
Instrument	Thermo DSQ II
Start	4.00 min/6.00 min
Ion source	EI by C
Mode	Full scan
Mass range	50.00-650.00
Ion type	Positive
Program	Thermo Xcalibur 2.0.7

Table B.2: Temperature program used in GC.

Temperature program	Rate (°C/min)	Temp(°C)	Plateau (min)
Start		40	0.00
Ramp 1	6.0	200	0.00
Ramp 2	10.0	300	1.00

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