Assessing the Oil Pollution Trend in Surface Sediments along the Coastal Area of the Caspian Sea (Mazandaran Province)

S. R. Hosseini Bizaki[1], A. R. Rabbani[1*], A. Riyahi Bakhtiyari[2], M. Cheraghi[3]

[1] Department of Petroleum Engineering, Amirkabir University of Technology, Tehran, Iran

[2] Faculty of Natural Resources and Marine Sciences, Tarbiat Modares University, Noor, Iran

[3] Department of Nature Engineering, Agricultural Sciences and Natural Resources University of Khuzestan, Mollasani, Iran

ABSTRACT: Coastal areas of the Caspian Sea have been affected by pollution in recent years. These areas are exposed to environmental problems due to the presence of hydrocarbon resources in the Caspian Sea basin as well as human factors. To determine the amount of contamination in the coastal strip of this sea, the concentration of normal alkanes in 6 different stations was investigated by taking 30 samples from a depth of 5 meters from the water surface. Investigating the concentration of normal alkanes in the studied stations show that the amount of hydrocarbons contaminated in the studied area, compared with the previous year's studies, shows a significant increase in concentration. The concentration of *n*-alkanes are among the 24.3 µg/g (the minimum concentration) in Nashtarood Station to 690.7 µg/g (the maximum concentration) in Noshahr Station, and most of the stations have moderate concentration of *n*-alkanes. The increase of pollution in recent years as a result of increased oil activities related to the exploration, production, and exploitation of oil resources and human factors. Also, the presence of Hyrcanian forests on the southern shores of the Caspian Sea and increasing seizure of forests in recent years have led to increased contamination in the region due to pollution transmission to the Caspian Sea. To determine the origin of normal alkanes in the region, the indexes of CPI, LMW / HMW, Pristane / Phytane, n-C17 / Pristane and n-C18 / Phytane were used. The results show petrogenetic and biogenic inputs at sampling stations that petrogenetic contamination is prevalent in the region.

1. INTRODUCTION

The Caspian Sea is the largest lake in the world that is important due to having a special ecosystem. Increasing oil activities and the population in the coastal area of the Caspian Sea caused concerns about the pollutants [1]. The main sources of pollutants in the Caspian Sea area the production of petroleum and the land resources [2].

Saturate aliphatic hydrocarbons are contained 60 percent compositions of petroleum. Normal alkanes (*n*-alkanes) are one of the components of aliphatic hydrocarbons [3].

n-alkanes have different sources. These components have both human or natural sources. Petrogenic sources are the contaminants that enter the environment by oil spills or oil seepages, and natural sources are from plants, Phytoplanktons, animals, and algae [4]. Thus, *n*-alkanes can be used to identify the origin of contaminants.

South parts of the Caspian Sea are the coastal areas in the north of Iran that contain Golestan, Mazandaran and Gilan provinces. Recently, Several studies have done in Mazandaran province. Now in this study, we compare our results with the results from the past studies.

2. METHODOLOGY

Six points are selected for sampling in the south part of the Caspian Sea in Mazandaran Province. These sampling points are in Amirabad (T_1), Neka (T_2), Babolsar (T_3), Fereydonkenar (T_4), Noshahr (T_5) and Nashtarood (T_6) that are shown Figure 1. Samples are collected from surface sediments in the depth of 5 meters under sea level by Van Veen Grab and each sample is immediately stored in an aluminum container. Samples are kept in the freezer at -20 °C.

200 grams of each sample are freeze-dried for 72 hours at -60 °C. Samples are powdered and passed throw sieve. Five grams of each sample were mixed with dichloromethane, then placed in soxhlet. After extraction, non-polar compounds separated, and then *n*-alkanes separated and prepared for injection to GC-MS. The injection volume was 2µl at the rate of 1.5 ml/min.

3. RESULTS AND DISCUSSION

The results of the GC-MS analysis show that the total concentrations of *n*-alkanes in surface sediments of coastal areas in Mazandaran province are between 690.7 µg/gr in T_5 station and 24.3 µg/gr in T_6 station (figure 2). The surface sediments that have concentrations between 10 to 100 µg/gr are moderately pollution and the surface sediments that have

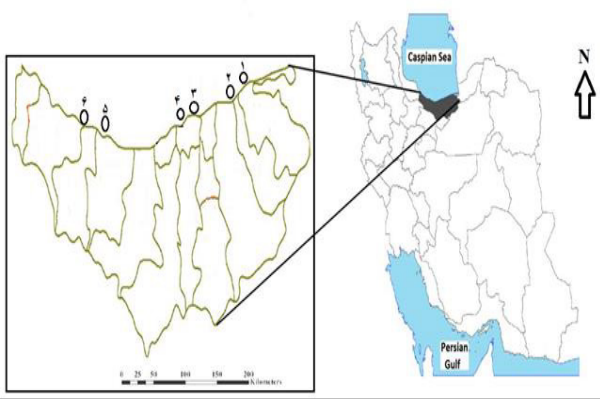*Corresponding author's email: Rabbani@aut.ac.ir

Fig. 1. Sampling points in the coastal area of the Caspian Sea in Mazandaran Province
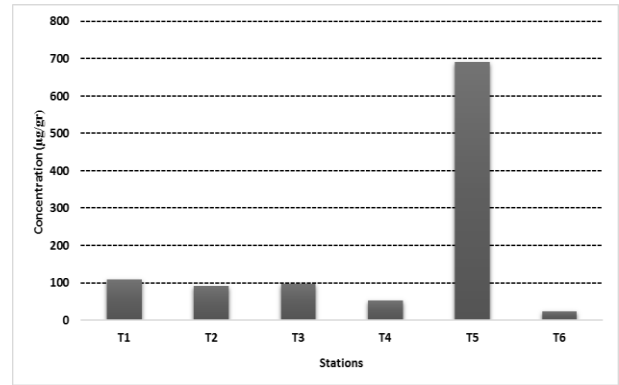

Fig. 2. Concentration of n-alkanes in sampling stations in studied area of the Caspian Sea

Table 1. Diagnostic ratios for the stations in coastal area of the Caspian Sea in Mazandaran Province

Ratio \ Station	T_1	T_2	T_3	T_4	T_5	T_6
CPI	0.54	1.66	0.93	0.22	0.27	0.53
LMW/HMW	82.10	1.31	1.49	0.96	0.57	1.30
n-C_{17}/Pri	0.60	1.00	0.41	0.61	1.03	0.36
n-C_{18}/Phy	0.51	0.31	1.31	2.05	2.96	2.38
Pr/Phy	0.44	0.25	0.27	0.38	0.30	0.46

a concentration lower than 10 μg/gr are non-pollution [5].

The high concentration of *n*-alkanes in T_1 and T_6 stations can be caused by oil product transportation and also factory activities in these areas.

Diagnostic ratios are used to source identification of *n*-alkanes. These ratios are CPI, Pristane/Phytane, LMW/HMW, n-C_{17}/Pristane and n-C_{18}/Phytane (Table 1).

Due to CPI index [6], all the stations have values lower than 1 that show the petrogenic origin of hydrocarbons. For LMW/HMW ratio [7], values show that stations T_1, T_2, T_3, and T_6 have petrogenic contaminants and stations T_4 and T_5 have biogenic Contaminants.n-C_{17}/Pristane, *n*-C_{18}/Phytane and also pristane/Phytane ratios [8] show the petrogenic sources for all stations. Thus, petrogenic sources exist in all of the stations.

As mentioned, some studies were done in the coastal area of the Mazandaran province. Now we want to compare the results of our study with those studies. The first study was done in 2004 by Tolosa [4]. Stations that they studied are in T1, T3 and T5 stations in this study. The concentration of *n*-alkanes in these same areas in Mazandaran Provines is increased in comparison to the last study. This increase in contaminant concentration can be related to shipping activities, ports and human activities. Also, in the last study, hydrocarbons were almost from biogenic sources, but now the contaminants have petrogenic origins.

Another study was done by Abesi & Saeidi in the same areas of T_2, T_4 and T_6 stations [9]. In these areas, the concentration of *n*-alkanes is increased due to the high entrance of rivers in recent years and also, petrogenic contaminants are increased.

And the last study that is done in the same area of T_1 and T_3 stations by Fereyduni in 2013 [10]. The results of that study are near to our study.

4. CONCLUSIONS

Stations that are studied in coastal areas of Mazandaran Province have moderate and high concentrations of *n*-alkanes. Because of increasing oil and human activities in recent years, concentration values are highly increased. Exploration and production of oil and gas, oil products transportation and factory activities can be the petrogenic sources. The existence of Hirikani forests in the north of Iran and south of coastal areas can be the source of biogenic and natural contaminants.

Station T_5 in Noshahr due existence of port has the highest concentration of *n*-alkanes.

Petrogenic contaminants exist in all stations and also some stations have both petrogenic and biogenic origins.

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