Some Organophosphorous Pesticides and Polycyclic Aromatic Hydrocarbons along the Eastern Caspian Sea Coast, Mazandaran State, Iran

C. Mohammadi Zadeh [1]*, A. Javanmard [2]

[1] Department of Geology, Islamic Azad University, Sari branch, Sari, Iran
[2] Department of Biology, Islamic Azad University, Sari branch, Sari, Iran

Received 13.11.2011
Revised 19.02.2012
Accepted 29.02.2012

*Corresponding author:
Changiz Mohammadizadeh
E-mail: mohammadi@iausari.ac.ir

ABSTRACT

Surface sediment samples collected from twenty-five sites (Amirabad(10),Sari(5), Babolsar(5) and Noushahr(5) of Caspian Sea coast of Mazandaran province were determined for 8 polycyclic aromatic hydrocarbons (PAHs) by GC-MS method. In this study the concentrations and some main sources of PAHs in southern Caspian Sea coast sediments were determined. We analyzed 8 PAHs such as Benz[a]anthracene, Benz[a]pyrene, Fluoranthene, pyrene, Chrysene, Benz[e]pyrene, Benz[k] Fluoranthene and Benzo [ghi] perylene in this research. There was high spatial variability in the PAH concentrations that ranged from 12 to 453ng/g. Result of this study showed that Concentrations of all PAHs except Pyr, B (a) A and B (a) P in Amirabad are below the concentration to elicit toxic effects in benthic organisms (Effects Range-Low). To elucidate sources, two molecular indices (Pyr/Fluo, BaA/ (BaA+Chr) ratios were used to determine the pyrogenic and petrogenic sources. Amirabad-Behshahr region receives input primarily from oil activity; therefore, it can be inferred that the main source of PAH could be petrogenic (Pyr/Fluo =1.07). The PAH source in Sari is pyrogenic for Neka power plant that uses fossil fuels (BaA/BaA+Chr) =0.38).
Water samples were collected from 20 wells (twenty locations in different parts of mazandaran Province) during a period of 1 year. The average Concentrations of diazinon,chlorpyrfos, ethion and edifenphos in the ground waters were 0.018, 0.017, 0.014and 0.013 µg/l, respectively . This study describes the seasonal distribution of Organophosphorus pesticides in ground waters of the eastern side of Mazandaran province (Sari-Goharbaran) in north of Iran.

KEYWORDS

pollution, sediment, gas chromatography

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of global environmental concern because they cause many health problems including cancer and inflammation of tissue in humans. The hazardous pollutants PAHs are poorly studied.

There are two types of anthropogenic sources of PAHs: petrogenic and pyrogenic. Petrogenic sources include crude oil and petroleum products such as kerosene, gasoline, diesel fuel, lubricating oil, and asphalt. Pyrogenic sources form by the incomplete combustion of organic matter (e.g., coal, petroleum, and wood) in industrial operations and power plants that use fossil fuels, smelting, garbage incinerators, and vehicle engines powered by gasoline or diesel fuel, and forest fires. (Blummer, 1976)

The distributions of PAHs in sediments have been studied since the mid-1970s. PAHs are distributed globally, from inland lakes and urban rivers to the open ocean, over a wide range of concentrations. (Al Katheeri, 2004) Very few reports indicated the predominance of petrogenic PAHs, which were mostly associated with accidental oil spills or were localized (Abdullah and Boonyatumanond, 2007). Pyrogenic sources predominated in the East China Sea, whereas both sources were comparable in the coastal sediment of the Pearl River, China. (Clrak and Bixian, 2001)

Moderate to high petrogenic contamination was found in the South Caspian Sea, in particular in the offshore oil fields near Baku, Azerbaijan. Contaminant patterns indicated that the PAHs were mainly from fossil sources, with higher contributions of pyrolytic only near industrialized and urban areas. A high contribution of perylene, a geochemically derived PAH, to the total PAHs was found in the west and south at sites influenced by the Kura, Safid Rud, Terek, Sulak and Samur Rivers. (Tolosa *et al.*, 2004)

However, very limited information on the environmental distribution of PAHs in Caspian Sea is available, although industrialization and urbanization have proceeded rapidly during the last few decades, and the associated increase in PAHs is of concern in this region.

The Iranian coast of the Caspian Sea stretches for nearly 700 km from Azerbaijan in the west to Turkmenistan in the east (Figure 1).

A large percentage of the more than 10 million people who reside in the Iranian coastal provinces bordering the Caspian Sea are therefore exposed to high concentrations of toxic contaminants. For instance, coastal residents regularly eat sturgeon and other fish from the Sea. The pollutants accumulating in the fish, especially the sturgeon is transferred to the human food chain. Questions have been raised as to whether the higher rates of cancer recorded in the study area could be associated with fish consumption. (Agusa *et al.*, 2004).

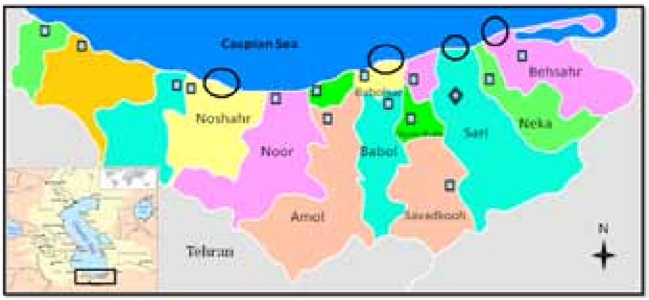

Figure (1) Location of Sampling Sites along the eastern Coast of the CaspianSea

Other than having detrimental impacts on human health, several studies have also reported that pollution and contamination are contributing factors to the precipitous decline in sturgeon catch from the Caspian Sea. According to the Caspian Environmental Program web site (http://www.caspianenvironment.org/newsite/Caspian-EnvironmentalIssues.htm), sturgeon landings have decreased from 30,000 tonnes in 1985 to only 5,672 tonnes in 1995. Here it should be emphasized that 85 to 90% of the world's sturgeon fish is obtained from the Caspian Sea which yields approximately 95% of the world's black caviar. The decline in sturgeon catch is not only threatening the survival of the caviar industry, but also affecting the domestic economy in Iran. (Parizanganeh *et al.*, 2006)

Pesticide contamination of ground water, which has emerged as an important environment problem in past few decades, caused serious concern with respect to the long-term and low-dose effects of pesticides on public health as well as non- target species of aquatic lives.

Mazandaran province is considered as one of the main rice cultivation regions in Iran (Figure 1).Typically, rice is cultivated under submerged flooded conditions and as a result pesticide concentration in water bodies is considerably high because the irrigation increases the likelihood of the transport of pesticides via runoff to water.This province consumes approximately %19 of the annually applied pesticides in Iran.The primary insecticides (Diasinon,Chloropyrfos,Ethion,Edifenfos)were detected corresponding to the Applications during previous agricultural use.This study describes the seasonal distribution of Organophosphorus pesticides in ground waters of the eastern side of Mazandaran province (Sari-Goharbaran) in north of Iran.

MATERIALS AND METHODS

Polycyclic Aromatic Hydrocarbon (PAH) concentrations were measured in Total Suspended Particulate Matter (TSPM) from August 2008 to August 2009 at eastern Caspian Sea (Iran). The sampling stations are Behshar (ten station of Amir Abad port for oil products transportation) Sari (five stations of Khazar Abad, Goharbaran and Neka) Babolsar (five stations for tourism and industry) Noshahr port (five stations for Industry and shipping) were analyzed for individual Polycyclic Aromatic Hydrocarbons (PAHs) Fig.1.

Surface sediments (0□5cm) were collected using a Van Veen grab sampler. After collection, pebbles and twigs were removed and then samples were freeze dried and ground with a mortar and pestle. Samples were stored in HDPE (high density polyethylene) bottles at 20°C until extraction and were extracted using dichloromethane with ultrasonication. PAHs were quantified using a Hewlett Packard 5890 series II gas chromatograph equipped with a 5972 series mass spectrometer detector. A fused silica capillary column (30m_0.25mm i.d.) coated with DB-17 [(50% phenyl)-methyl polysiloxane J&W Scientific, Folsom, CA, USA] at 0.25 mm film thickness was used. The column oven temperature was programmed from 80°C (1 min hold) to 100°C at a rate of25°C/min, and then ramped at a rate of 5°C/min to 100°C with a final holding timeof 6 min. The injector and detector temperatures were maintained at 250 and 300°C, respectively. The PAH standard (AccuStandard, New Haven, CT, USA) consisted of8 priority pollutant PAHs identified by the U.S. Environmental Protection Agency (U.S. EPA Method 8310). The mass spectrometer was operated under selected ion monitoring (SIM) mode using the molecular ions selective for individual PAHs. Concentrations based on individually resolved peaks were summed to obtain the PAH concentrations. The detection limits of individual PAHs in sediment samples were 10 ng/g, dry wt.

For pesticides, well samples were taken at twenty locations in different parts of mazandaran Province in August,November,February and May. At each location, several one liter samples were collected in glass bottles with Teflon-lined caps.The samples were stored on ice on location and then transferred to the Laboratory and were kept at 2° C prior to analysis.

Pesticides analytical standards were (bought from) supplied by Riedel-de Han Stock standard solution consisting of 1mg/l of a Mixture of four Organophosphorous Pesticide standards was prepared in methanol and used for preparation of spike solutions.

In this investigation, Organophosphorous Pesticides were measured using a GC and detected Using a,nitrogen-phosphorous detector(NPD).The GC(model 1000,DANI Co,Italy) was Equipped with a fused silica capillary column (optima 5 location) length of 6m, 0.25mm Inner diameter and0.25µm film thickness.Carrier gas was helium (99.999% purity) with The flow rate of3.6ml/min.Operating condition for the GC is summarized in Table 1.

Table 1. Gas Chromatography (GC) condition

Condition	Value
Injection volume	1µl
Flow rate	3.6ml/min
Injector temperature	250° C
Detector temperature	320° C
Oven temperature	100°-300° C
Total time	40 min

RESULTS AND DISCUSSION

The study data are shown in table 2.

Table 2. PAH concentrations in Caspian Sea sediments (All concentrations ng /gdry wt)

Parameter	Sari (n=10)	Amirabad-Behshahr(n=20)	Noushahr(n=10)	Babolsar (n=10)	Effects Range Low(Guo *et al*.,2006)	Apparent Effects Threshold (Guo *et al*.,2006)
B(ghi)P	192±25	226 ± 23	151±66	120±26	----	----
Pyr	64±9.1	453 ± 15	41±13	32±15	350	1000
B(a)A	67 ± 9.0	270± 22	15± 6.8	12±5.2	230	550
Chry	105 ±10	352 ± 30	81 ± 15	82±21	400	900
B(e)P	141 ± 24	155 ± 21	115 ± 20	91±42	----	----
B(k)F	83 ± 17	110 ± 19	73 ± 28	65±31	----	----
B(a)P	57 ± 16	410±32	62 ± 34	35±9.0	400	700
Flu	72±19	420 ± 24	53±9.0	45±6.1	600	1000
Sum of 8PAHs	781	2392	591	482		

(N=number of samples)

Many other compositional parameters have been used for the differentiation of petrogenic and pyrogenic sources, including the ratios of pyrene to fluoranthene(Pyr/Flou), benz[a]anthracene to benz[a]anthracene + chrysene (BaA/ BaA + Chry)(Al-Lihaibi *et al*.,1996). We examined the validity of these ratios for source differentiation with our source materials (Table.2) although they are useable for source-distinction; they are not definitive, since there are many exceptions. For example, although most of the crude oil samples have Pyr/Fluo > 1, showing a petrogenic source. BaA/ (BaA + Chry) ≈ 0.35, implying a pyrogenic source and having Anth/ (Anth + Phe) < 0.1, shows a petrogenic source of PAHs. All brick manufacturing soot samples and most cooking soot samples with strong pyrogenic characteristics show IP/(IP + BghiP) < 0.5 (i.e., petrogenic). Hence, these ratios can give a rough idea of the source, but they are not authoritative enough to be exact. Highest concentrations were present in sediments collected from Amirabad-Behshahr (mean, 275ng/g, n=20) and were a consequence of oil products transportation in this port. Low levels of PAHs were also found in sediments adjacent to boat landing and mooring areas around Babolsar (60ng/g, n=10) the other site showed moderate values (sari and Noushahr) Table.2.

∑8 PAHs is used as total PAHs in this paper to facilitate the comparison of our data with those reported by many researchers who normally measured parental PAHs. Ratios of Pyr/fluo and BaA/ (BaA+Chr) in Caspian Sea sediments are reported inTable 3. The petrogenic sources have higher value of ratios than the pyrogenic sources. Crude oil has highest values of Pyr/Fluo. All the amirabad sediments showed a strong petrogenic signature with pyr/fluo=1.07 for oil port and Crude oil transportation.

Sari sediments showed a pyrogenic signature with BaA/ (BaA+Chr) =0.38 for Neka power Plant that uses fossil fuels. Long and Morgan assembled and evaluated biological effects data from a wide variety of methods and produced informal guidelines that can be used to screen sedimentary data. The PAH concentrations observed or predicted by the different methods to produce biological effects were ranked, and the lower 10th percentile(identified as Effects Range-Low),median, and overall Apparent Effects Thresholds were identified. The Effects Range-Low and Apparent Effects Thresholds for individual PAH are presented in Table 2 along with concentrations for Caspian Sea sediments. (Guo *et a*l., 2006)

For our Caspian Sea data, concentrations of all PAHs except Pyr, B (a) A and B (a) P in Amirabad are below the concentration to elicit toxic effects in benthic organisms (Effects Range-Low) Table2. Distributions indicate that These PAHs likely have an origin in petroleum hydrocarbons in crude oil that transport in this oil port.

Table 3. The ratios of some component's PAHs in Caspian See

Location	Pyr/Fluo	BaA/(BaA+Chr)
sari	0.88	0.38
Amirabad-Behshahr	1.07	0.43
Babolsar	0.71	0.12
Noushahr	0.77	0.16

The Organophosphorous Pesticides analyzed in this investigation were Diasinon, Chlorpyrfos , Ethion and Edifenphos with mean concentration in the ground water Of the studied area were0.018, 0.017, 0.014and 0.013 µg/l, respectively. In the studied area, Diazinon is used Mostly for rice fields and deciduous trees and the main agricultural use of Pesticides is for these purposes. Chlorpyrfos and, Ethion are nearly in different parts of mazandaran province for controlling pests of deciduous and citrus trees. Diazinon concentration in springs was higher than that of wells, but Ethion was found in higher concentrations in wells.

Table 4. Mean values of pesticides during four seasons in wells of goharbaran area.

	Diazinon	Chlorpyrfos	Ethion	Edifenphos
Spring	0.032	n.d	n.d	n.d
Summer	0.008	n.d	0.002	n.d
Autumn	0.028	0.015	0.025	0.016
Winter	0.017	0.003	0.018	0.07
Standard deviations	0.017	0.006	0.014	0.25

nd: Not detected

The Ministry of Environment of British Colombia has determined guidelines for pesticide concentrations in the water. Comparing our results with these standard values showed that the concentration of Diazinon and Ethion in Authumn extensively exceeded the recommended values Table 4. The results of seasonal mean values of Organophosphorous Pesticides are shown in table 4. As can be seen from these results,water concentrations of Diazinon is highest in spring months for wells. Highest concentrations of Chlorpyrfos, Ethion and Edifenphos were found mostly in autumn .This is probably due to their high application at that time.

CONCLUSION

In Mazandaran province there are many potential pollutant sources including contaminants derived from agriculture discharge, high shipping activities, and industrial sewage and so on. No single predominant cause of toxicity is found, more than one bioavailable toxi-cants are detected to play active roles in causing toxicity of marine waters in the Caspian Sea. Major conclusions are as follows:

1. Results indicate that the pyrogenic source, characterized by the abundance of parent PAHs,is predominant in the heavily contaminated station(Sari)near the Neka power plant,and the petrogenic pahs are more abundant in the stations(Amirabad-Behshahr)adjacent to petrochemical plant and shipping harbor.

2. In this region (Mazandaran province) the loam-clay soils adsorb these pesticides before the Enter the water wells, so pesticides were leached weakly.

ACKNOWLEDGEMENTS

Authors are grateful to Islamic Azad University Sari branch for supporting this research.

REFERENCES

Abdullah, A.R., Woon, W.C., Bakar, R.A. (1996). Distribution of oil and grease and petroleum hydrocarbons in the Straits of Johor. *Peninsular Malaysia Bulletin of Contamination and Toxicology*, 55: 155–162.

Agusa, T., Cainito, T.S., Tanabe Pourkazemi, M., Aubrey, D.G. (2004) Concentrations of trace elements in muscle of sturgeons in the Caspian Sea. *Marine Pollution Bulletin*, 49: 789-800.

Al Katheeri, B.S. (2004) *Geochemical studies to assess marine oil pollution Zakum field, Abu Dhaabai, UAE*. M.Sc. Thesis, UAE University pp. 1.

Al-Lihaibi, S.S., and Al-Omran, L. (1996) Petroleum hydrocarbons in offshore sediments from the Gulf. *Marine Pollution Bulletin* 32: 65–69.

Bixian, M., Jiamo, F., Gan, Z.L., Zheng Yushun, M., Guoying, S., Xingmin, W. (2001) Polycyclic aromatic hydrocarbons in sediments from the Pearl River and estuary, China: spatial and temporal distribution and sources. *Applied Geochemistry*, 16: 1429–1445.

Blummer, M. (1976) Polycyclic aromatic compounds in nature. *Scientific American Journal*, 234: 34–45.

Boonyatumanond, R., Murakami Wattayakorn, M., Togo, G.A., Takada, H. (2007) Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. *The Science of the Total Environment* 384:420–432.

Clark Jr., R.C. and MacLeod, W.D. (1977) Inputs transport mechanisms and observed concentrations of petroleum in the marine environment. In: D.C. Malins, Editor, Effects of Petroleum on Artic and Subartic Marine Environments and Organisms, Academic Press Inc., New York, pp: 91–223.

Guo, Z., Lin, T., Zhang, G., Yang, Z., Fang, M. (2006) High-resolution depositional records of polycyclic aromatic hydrocarbons in the central continental shelf mud of the East China Sea. *Environmental Science and Technology,* 40: 5304–5311.

Gustafson, O., Haghseta, F.C., Chan, J., Macfarlane Gschwend, P.M. (1977) Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability, *Environmental Science and Technology*, 31: 203–209.

Parizanganeh, A.H., Lakhan, V.C., Ahmad, S.R. (2006) Pollution of the Caspian Sea Marine Environment along the Iranian Coast. *Environmental Informatics Archives*, 4:35-37.

Sudo, M., Kunimatsu, T., and Okubo, T. (2002) Concentration and loading of pesticides Residues in lake Biwa basin (Japan). *J.Water Res*., 36(1):315-329.

Tolosa, I., DeMora, S. (2004) Aliphatic and aromatic hydrocarbons in coastal Caspian Sea sediments. *Marine Pollution Bulletin*, 48:44-60.