Some Organophosphorous Pesticide (OPPs) and Polycyclic Aromatic Hydrocarbons (PAHs) along the Eastern Caspian Sea Coast, Mazandaran State, Iran

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ABSTRACT

PAHs form one of the most important classes of persistent pollutants .Sediment samples were taken from the eastern Caspian Sea coast of Mazandaran state analyzed by (GC-MS) for PAHs . Sediment samples were collected from eastern part of southern Caspian Sea in Mazandaran Province. Stations were Amirabad(10), Sari(5), Babolsar(5) and Noushahr (5) to determinate distribution and to source of PAHS. 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. 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).

There was high spatial variability in the PAH concentrations that ranged from 12 to 453ng/g. 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 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 research found that the residues of pesticides are major threat to aquatic life of the regional ecosystems.

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. PAH with increasing environmental pollution and anthropological disturbances to ecosystems. The hazardous pollutants PAHs are poorly studied. PAHs consist of two or more benzene rings, which make these molecules highly persistent in the environment. Examples include naphthalene, Benz[a]anthracene, and Benz[a]pyrene, which contain 2–5 aromatic rings.

Many PAHs in the environment are by-products in petroleum-based manufacturing. They are present in coal tar, asphalt, tires, and other oil-containing products and are released into the environment during incomplete combustion, and through oil spills, for instance [Committee on In Situ Bioremediation, 1993] in animals, PAHs have a broad impact on health. They interact with DNA resulting in mutations and cancer, Benz[a]pyrene being one of the most toxic and carcinogenic compounds known. [1]. 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. PAHs are also derived from some natural sources such as oil seeps, ancient sediment erosion, and early digenesis. However, in many areas affected by human activities, natural sources are overwhelmed by anthropogenic sources of all PAHs except perylene. [2]

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. [3] Very few reports indicated the predominance of petrogenic PAHs, which were mostly associated with accidental oil spills or were localized [4- 5]. Pyrogenic sources predominated in the East China Sea, whereas both sources were comparable in the coastal sediment of the Pearl River, China. [6-7]

Petrogenic PAHs may be more available for biological uptake than pyrogenic PAHs, since it tends to bind more strongly to sedimentary particles. Hence, to evaluate the risks of PAHs to aquatic biota, source-distinction is essential. [8-9]

There have been proposed many molecular markers to identify contribution from sources of PAHs. Some unique compounds, specific to certain fuels have been reported. For example, retene 1, 7-dimethylphenanthrene has been proposed as tracers of wood combustion. However, any universal compounds generated through all the fuels for combustion (e.g., biomass, coal, and petroleum) have not been reported. One approach is to focus on the difference in thermodynamic stability among PAH species to distinguish pyrogenic and petrogenic PAHs. Thermodynamically stable species of PAHs are enriched in combustion products because thermodynamically unstable species disappear during combustion. There are some other homolog series including fluoranthene–pyrene group and chrysene–benz[a]anthracene group and individual homologs sometimes have different sources. [10]

It is estimated that approximately 6.1 million metric tons of petroleum products are released to global oceans annually, the majority of which is derived from anthropogenic sources and which pass through the coastal zone before being carried out to sea. [11]

Worldwide, major inputs of petroleum into the marine environment occur via industrial discharge and urban runoff (37%), vessel operations (33%), tanker accidents (12%), atmospheric deposition (9%), natural resources (8%) and exploration production (2%). [12]

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). This coastline is now becoming increasingly polluted with massive loads of contaminants discharged into the Caspian Sea from various anthropogenic sources. Motavalli (1999) reported that the World Bank estimated that a million cubic meters of untreated industrial wastewater is discharged directly into the Caspian, with the bulk coming from oil and mining operations. The Volga River is one of the major contributors of a wide variety of industrial and agricultural contaminants collected from its extensive river basin. The Report by Neville mentioned scientific estimates of annual average discharges of 60,000 metric tonnes of petroleum byproducts, 24,000 tonnes of sulfites, and 400,000 tonnes of chlorine. [13]

Given the fact that the Caspian is a non-tidal sea and is landlocked, the bulk of the discharged contaminants remain trapped within its basin. Sea currents transport and circulate the entrapped pollutants along the Iranian coast of the Caspian Sea. 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.[14] 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. [13]
Ecosystems, especially in the nearshore marine environment of the Iranian coast, are now under severe stresses from the cumulative impacts of a mixture of highly toxic contaminants. Pesticide contamination of ground water, which has emerged as an important invironment 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 Organo-phosphorus 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.

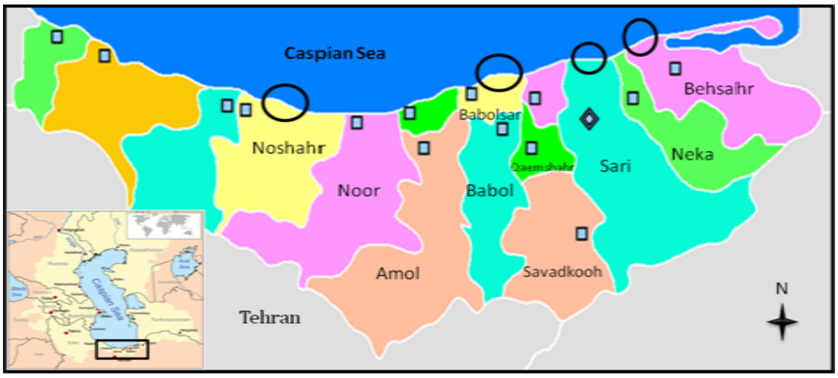

Figure 1. Location of Sampling Sites along the eastern Coast of the CaspianSea

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 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.

Table 1: Gas Chromatograph (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

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.

RESULTS AND DISCUSSION

The study data are shown in table 2.

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

Parameter	Sari (n=10)	Amirabad-Behshahr (n=20)	Noushahr (n=10)	Babolsar (n=10)	Effects Range Low**[16]**	Apparent Effects Threshold **[16]**
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		

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)[4-15]. 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 1 along with concentrations for Caspian Sea sediments. [16]
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.

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

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

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.

	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

nd:no detect

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

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.

ACKNOWLEDGEMENTS

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

REFERENCES

1. Wang, W., 2002. Alteration of vascular response to norepinephrine, calcitonin gene-related peptide, and acetylcholine in orchidectomized rats.Peking University pp:985-990.
2. Blummer, M., 1976. Polycyclic aromatic compounds in nature, *Scientific American Journal*, 234: 34–45.
3. Al Katheeri, B. S., 2004. Geochemical studies to assess marine oil pollution Zakum field, Abu Dhaabai, UAE, M.Sc. Thesis, UAE Universitypp . 1–1.
4. Abdullah, A. R., W.C. Woon and R.A. Bakar,. 1996. Distribution of oil and grease and petroleum hydrocarbons in the Straits of Johor, Peninsular Malaysia. *Bulletin of Contamination and Toxicology* 55: 155–162.
5. Boonyatumanond,R., M. Murakami, G. Wattayakorn, A. Togo and H. Takada, 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.
6. Clark Jr, R.C.andW.D. MacLeod, 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.
7. Bixian,M., F. Jiamo, Z. Gan, L. Zheng, M. Yushun, S. Guoying and W. Xingmin, 2001. Polycyclic aromatic hydrocarbons in sediments from the Pearl River and estuary, China: spatial and temporal distribution and sources, *Applied Geochemistry* 16, pp:1429–1445.
8. Farrington,J.W., E.D. Goldberg, R.W. Risebrough, J.H. Martin and V.T. Bowen, 1983. US “Mussel Watch”: an overview of the trace-metal, DDE, PCB, hydrocarbons, and rtificial radionuclide data, *Environmental Science and Technology* 17: 490–496.

9. Gustafson,O., F. Haghseta, C. Chan, J. Macfarlane and P.M. Gschwend, 1977. Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability, *Environmental Science and Technology* 31: 203–209.
10. Long, E.R. and L.G.Morgan, 1990.The potential for biological effects of sediment-sorbet contaminants tested in the National Status and Trends Program.NOAA Technical Memorandum NOS OMA 52;NOAA Ocean Assessments Division,Seattle,Washington. Pp:172+appendices.
11. Capone,D.G. and J.M.Bauer, 1992.Environmental Microbiology,Microbial processes in coastal pollution, R.Michell,Willey-Liss.USA, ,PP:191-237.
12. Colombo,J.C., A. Barreda, C. Bilos, N. Cappeleetti, M.C. Migoya and C.Skorupka. 2005. Oil spill in the Rio de la Plata estuary, Argentina: 2-hydrocarbon disappearance rates in sediments and soils. *Environment Pollution*, 134:267–276.
13. Parizanganeh,A.h., V. C. Lakhan and S .R. Ahmad, 2006. "Pollution of the Caspian Sea Marine Environment along the Iranian Coast "*Environmental Informatics Archives*. 4: 35-37.
14. Agusa,T., T. Cainito, S. Tanabe, M. Pourkazemi and D.G. Aubrey, 2004. Concentrations of trace elements in muscle of sturgeons in the Caspian Sea. *Marine Pollution Bulletin.* 49: 789-800.
15. Al-Lihaibi, S.S. and L. Al-Omran, 1996. Petroleum hydrocarbons in offshore sediments from the Gulf. *Marine Pollution Bulletin* 32: 65–69.
16. Guo, Z., T. Lin, G. Zhang, Z. Yang and M. Fang, 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.
17. Sudo, M., T. Kunimatsu and T. Okubo,2002.Concentration and loading of pesticides Residues in lake Biwa basin(japan).J.Water Res.,36(1):315-329.