VOL. 3, NO. 7, July 2013 ISSN 2225-7217
ARPN Journal of Science and Technology

http://www.ejournalofscience.org

Some Organophosphorous Pesticide (OPPS) and Heavy Metals along the Southern Caspian Sea Coast, Mazandaran State, Iran

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ABSTRACT

Concentrations of six heavy metals (Pb, Cd, As , Zn ,Co, and Cr)in surface sediment from Mazandaran province along the southern Caspian Sea Coast, Iran were determined to evaluate their levels and spatial distribution.
The ranges of the measured concentrations in the sediments are as follows: 20.08-71.37ng/g for Pb, 1.67-3.81 ng/g for As, 32.01-51.12 ng/g for Cd, 16.91-32.32 ng/g for Zn, 7.63-11.92 ng/gforCr,24.39-52.41ng/gdry weights for Co. The concentrations of all metals in sediment samples are lower than the proposed TECs indicated that there are no harmful effects from these metals. The content of Pb, Cd, As, Zn, Co, Cr in sediment samples were Analyzed by ANOVA followed by students T-TEST ($p<0.05$). The Organophosphorous Pesticides analyzed in this investigation were Diasinon, Chlorpyr fos, Ethion and Edifenphos with mean concentration in the ground water Of the studied area were 0.018, 0.017, 0.014and 0.013 µg/l, respectively. Diazinon concentration in springs was higher than that of wells, but Ethion was found in higher concentrations in wells.

Keywords: *heavy metals; pesticides; Caspian Sea, Mazandaran*

1. INTRODUCTION

Agriculture, urban settlement and industrial activities around the world have contributed to the widespread contamination of global marine ecosystems with organochlorine compounds, petroleum products and heavy metals.

Heavy metals are natural constituents of rocks and soils and enter the environment as a Consequence of weathering and erosion (Forstner 1989). Many metals are biologically essential, but all have the potential to be toxic to biota above certain threshold concentrations. Following industrialization, unnatural quantities of metals such as arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni) and zinc (Zn) have been released, and continue to be released into the aquatic environment through storm water and wastewater discharges. As, Cd, Cu, Hg and Zn are the five metals with most potential impact that enter the environment in elevated concentrations as a consequence of agricultural activity. Zn and Cu are used in small amounts as fertilizers in some soils deficient in these elements, and As, Cd and Hg are constituents of some fungicides (Hunter, 1992). Cu is also used as an algaecide, and Cd and Zn occur as contaminants of phosphatic fertilize. Metals discharged into near shore areas of marine environments are likely to be scavenged by particles and removed to the sediments.

The sediments, therefore, become large repositories received increased global attention by investigators (Fatima et al [1]. Ryan & Windom [2]. Ergin [3]. McMurtry et al [4]. Balls et al [5]. Uriarte et al [6]. Çelo et al [7]. Zhang et al [8]. Zabetoglou et al [9]. Caccia et al [10]. Chen et al [11]. Santos et al [12]) nevertheless, there is very limited research on concentrations of heavy metals in the near shore environment of the Caspian Sea.

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]

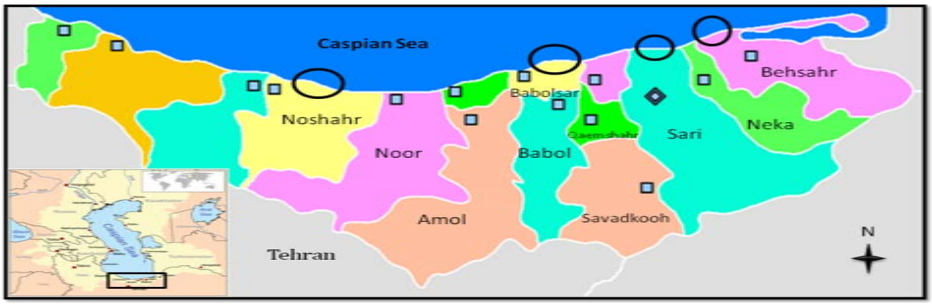

Fig 1: Location of Sampling Sites along the eastern Coast of the Caspian Sea

Ecosystems, especially in the near shore 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 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.[14] 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.

2. MATERIALS AND METHODS

Twenty sampling stations were established along four regions, Behshar (five stations of Amir Abad port and myankale 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) Fig.1. The sampling stations were chosen based on ecological settings and human activities in the area.

The concentrations of Pb, Cd, As, Cr, Zn, Co, were determined using Atomic Absorption. The content of Pb, Cd, As, Cr, Zn, Co, in sediment samples were Analyzed by ANOVA followed by students T-TEST ($p<0.05$).

Samples were taken from twenty sites along southern part of the Caspian Sea coast. The surface sediment samples were collected from 5 cm layer bottom sediments using a Van Veen type grap sampler. After collection, sediment samples were dried in a vacuum oven (Meldin, OV-12) at 70 C for 3-4 days until constant weight, lightly ground in an agate mortar for homogenization and prepared for analysis. Approximately 0.2 of dried sample was extracted overnight with 2 ml concentrated nitric acid (HNO3) and evaporated until near dryness and no nitrous vapors were released. After cooling, 5 ml of an acid mixture made of concentrated acids HF: HCLO4:HNO3 6:2:3 ratios were added. The digestion continued until no colored vapors were released. The working standard solutions was freshly prepared by diluting an appropriate aliquot of the stock solutions (IAEA-UNEP, 1990).

Flame atomic absorption spectrophotometer (Varian 10 Plus) was used for determination of the eight heavy metals under investigation (Pb,Cd,As,Cr,Zn, Co).
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.

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 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

3. RESULTS AND DISCUSSION

The study data are shown in table 2 and 3.

Table 2: 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

Table 3: Heavy metals concentrations in Caspian Sea sediments (All concentrations ng /gdry w)

H.metals	Sari	Behshahr	Noushahr	Babolsar	EPA guidelines(not polluted)
Pb	36.66±0.25	57.46 ± 0.23	71.37±66	20.08±0.45	≤ 40
Fe	27.33±0.50	33.45 ± 0.33	40.28±1.83	15.32±0.23	≤ 45
Co	11.92 ±1.23	11.16± 1.23	7.69± 0.68	7.63±0.52	----
Ni	11.16 ± 1.50	10.56 ± 1.67	39.19 ± 0.94	6.97±0.22	≤ 20
Cu	19.13 ± 1.50	22.64 ± 1.67	21.33 ± 1.39	17.08±1.33	≤ 25
As	3.22± 0.83	1.80±0.33	1.67 ± 0.22	3.81±0.66	≤ 15
Cd	32.01±0.55	51.12 ± 2.32	48.34±3.45	33.56±0.34	----
Zn	19.12 ± 1.17	22.51±0.23	32.32±1.18	16.91±1.67	≤ 35
Cr	31.78±1.78	36.41±0.91	40.41±1.89	24.74±0.48	-----

The Organophosphorous Pesticides analyzed in this investigation were Diasinon, Chlorpyrfos, Ethion and Edifenphos with mean concentration in the ground water of the studied area were 0.018, 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.

For heavy metals, the chemical contamination in the sediments was evaluated by comparison with sediment quality guideline proposed by USEPA (United States Environmental Protection Agency. These criteria are shown in table 3 .Fe,Cu,As, and Zn in all stations under investigation were belong to unpolluted sediments. Pb in Behshahr and Noushahr and Ni in Noushahr are considered as moderately polluted.

The study data for each element are defined in following charts:

The data for ZINC are shown in chart 1
The data for CADMIUM are shown in chart 2.
The data for CHROMIUM are shown in chart 3.
The data for ARSENIC are shown in chart 4.
The data for COBALT are shown in chart 5.
The data for LEAD are shown in chart 6.

Following statistical reviews about each metal and the reason of their frequency distributions in various regions as well as comparing the cases with some similar findings of foreign studies, the data include as follows:

a. Table 3 indicates that the highest concentration of zinc is in Noshahr (32.32±1.28). Considering zinc concentration average in the studied city, it is not found in the other city's $p<0.05$ (Chart 1, Test T).

According to the chart1 the difference between zinc concentration average in $p<0.05$ is not significant. There is no significant difference between zinc concentrations in various stations of each city. Zinc is found in most agricultural soils in average proportions. In this study there is no much difference between zinc concentration in studied stations and present industries may not affect zinc concentration. The data have been compared with Bertolotto's study reviewing the importance of sediments to mark good health in Italy (2003).

b. According to the chart 2 for Cadmium, the highest concentration are related to Behshahr (51.12 ± 2.32) and Noshahr port (48.34 ± 3.45) respectively. There is no significant difference between Cadmium concentration average in Behshahr and Noshahr $p>0.0$ in proportion to other cities (Chart 2, Test T).

According to the chart 2 there is a difference between Cadmium concentration average in Behshahr and Babolsar sig= 0.00. There is no significant difference between Cadmium concentrations in various stations of the other cities. Cadmium element results more from fertilizers, agricultural poisons, and factories gases. The data indicate clearly Amirabad's sediments pollution.
The data could be compared with the results obtained by Alessandro and et al 2006 on marine gulf sediments, Taranto in south of Italy.

c. Considering the chart 3, the single difference between Chromium difference concentration average in $p<0.05$ is significant (sig=0.00). There is no significant difference in Chromium

concentration of each city's stations. Chromium may be often seen in most agricultural soils. Agricultural fertilizers and fumes resulting from factories are the most source of it. This study agrees to the one by Omer Dalman and et al 2006 on the sediments of south west Aegean Sea, Turkey.

d. According to chart 4 for Arsenic, the highest concentration is related to Sari (3.22±0.83). There is a significant difference on arsenic concentration average in Sari and Babolsar ($p<0.05$) (Chart 4, Test T).

Considering the chart there is a single significant difference between arsenic difference concentration average ($p<0.05$) (sig=0.010) but there is no significant difference between arsenic concentration in each city's various stations.

Arsenic element is most found in the areas having mines. One of the main products in gas power plants is arsenic. Therefore it seems true that arsenic is increasing in Sari (Because of Neka power plant). The data agree to the study by Alessandro and et al 2006 on marine gulf sediments, Taranto in south of Italy.

e. Table 3 indicates that the highest concentration of cobalt is in Sari (11.92 ± 1.23) and Behshahr (11.16 ± 1.23) respectively. According to the chart 5 there is no significant difference between cobalt difference concentration average in $p<0.05$ (Chart 5, Test T).

Also, no significant difference between cobalt concentrations in various stations of each city is observed most agricultural poisons and pesticides may increase cobalt concentration in sediments and this is underlined by Bertolott (2003) in an article reviewing the importance of sediments to mark good health in Italy.

f. Table 3 indicates that the highest concentration of lead is in Noshahr (71.37±0.45) and Behshahr (57.44) respectively. There is a significant difference between lead concentration average in Babolsar and Noshahr in ($p<0.05$) (Chart 6, Test T).

The single difference between lead concentration average in $p<0.05$ is significant (sig=0.025), but there is no significant difference between lead concentration average in each city's various stations. Lead is most found in oil substances, fuel terminals, and the ports with too much ship traffic. This is observed clearly in the study. The data agree to the study by Hamed Emara (2006) upon 7 different western stations of Suez Canal. The measure of lead in eastern stations is higher than the standard quantity because of oil tankers transit which is a contaminated factor for marine ecology.

ACKNOWLEDGEMENTS

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

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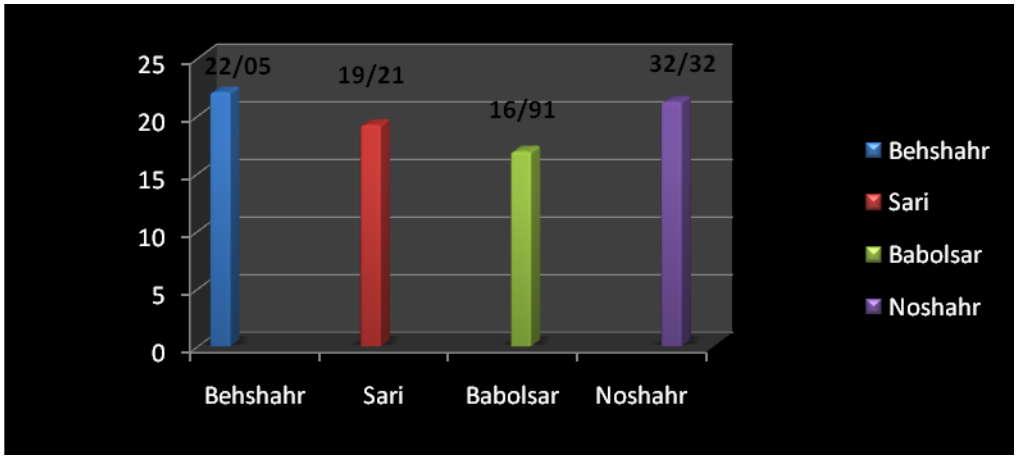
CHARTS

Chart 1: Diagram of ZINC concentration average in the studied cities

ZINC concentration average



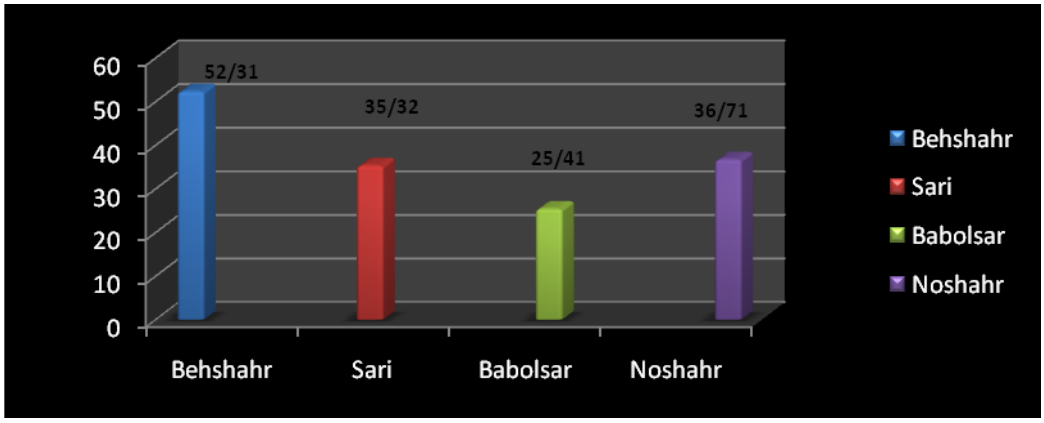
Std. Deviation	Mean	Max	Min	station
0.53602	22.0567	22.43	21.32	Behshahr
0.78193	19.1217	20.41	18.02	Sari
0.22392	16.1217	17.22	16.72	Babolsar
2.033150	32.3228	36.32	30.18	Noshahr

Descriptive statistics

Sig	Correlation	pairs
0.604	-0.131	1&2
0.168	0.339	1&3
0.624	0.124	1&4
0.000	-0.882	2&3
0.887	0.035	4&2
0.621	0.125	3&4

Paired samples correlation

Chart 2: Diagram of CADMIUM concentration average in the studied cities



Descriptive statistics

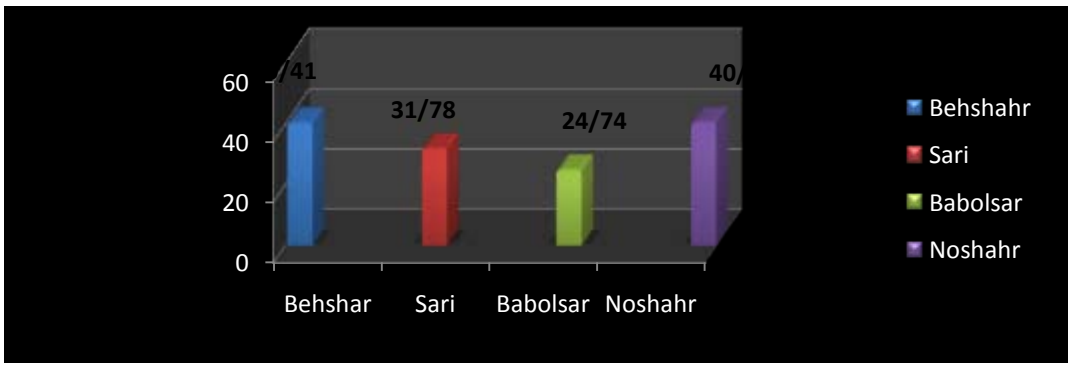
Std. Deviation	Mean	Max	Min	Station
0.87806	51.1233	52.31	50.34	Behshahr
1.78949	31.7383	35.32	30.40	Sari
0.48310	24.7467	25.41	24.39	Babolsar
2.45749	40.7711	43.49	36.71	Noshahr

Sig	Correlation	Pairs
0.091	0.410	1&2
0.000	0.990	1&3
0.585	0.138	1&4
0.053	0.463	2&3
0.699	0.098	4&2
0.537	0.156	3&4

Paired samples correlation

Chart 3: Diagram of CHROMIUM concentration average in the studied cities

CHROMIUM concentration average



Descriptive statistics

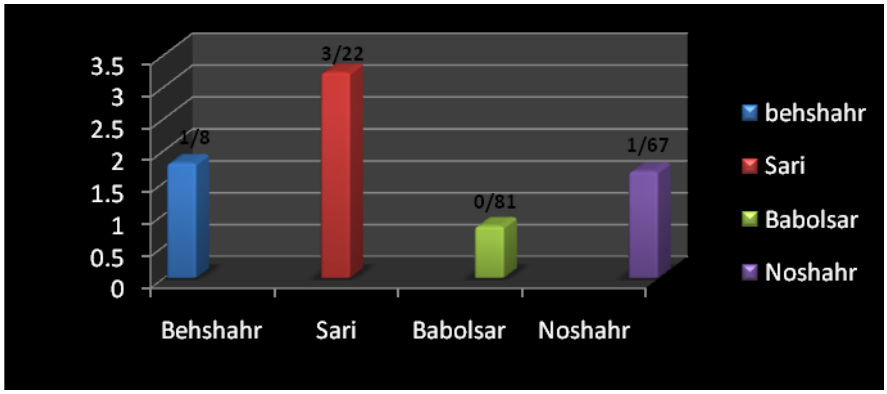
Std. Deviation	Mean	Max	Min	Station
0.90412	40.41	41.52	36.37	Behshahr
1.78949	31.73	35.32	30.40	Sari
0.48310	24.74	25.41	24.39	Babolsar
2.22866	40.51	42.49	36.71	Noshahr

Sig	Correlation	Pairs
0.012	0.578	1&2
0.000	0.867	1&3
0.382	0.219	1&4
0.053	0.463	2&3
0.848	0.049	4&2
0.566	0.145	3&4

Paired samples correlation

Chart 4: Diagram of ARSENIC concentration average in the studied cities

ARSENIC concentration average



Descriptive statistics

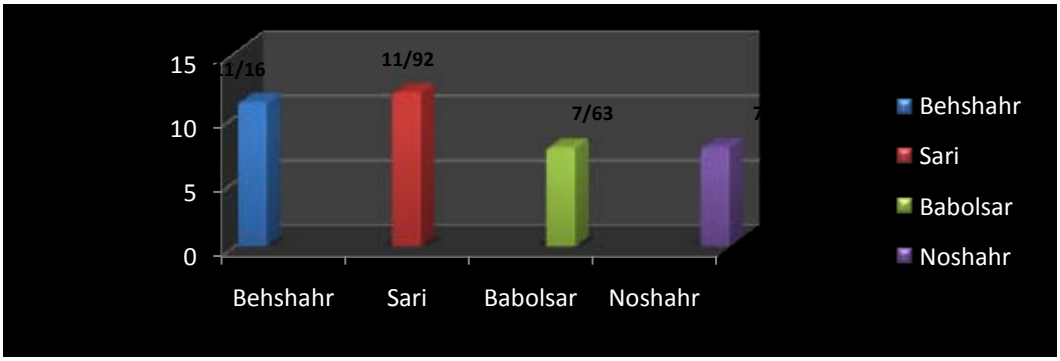
Std. deviation	Mean	Max	Min	Station
0.37708	1.8033	2.32	1.51	Behshahr
0.51193	3.2283	4.10	2.85	Sari
0.25210	0.8167	1.12	0.52	Babolsar
0.46484	1.7622	2.32	1.33	Noshahr

Sig	Correlation	Pairs
0.317	-0.250	1&2
0.100	0.835	1&3
0.789	0.068	1&4
0.010	0.591	2&3
0.749	0.066	4&2
0.949	-0.023	3&4

Paired samples correlation

Chart 5: Diagram of COBALT concentration average in the studied city

COBALT concentration average



Descriptive statistics

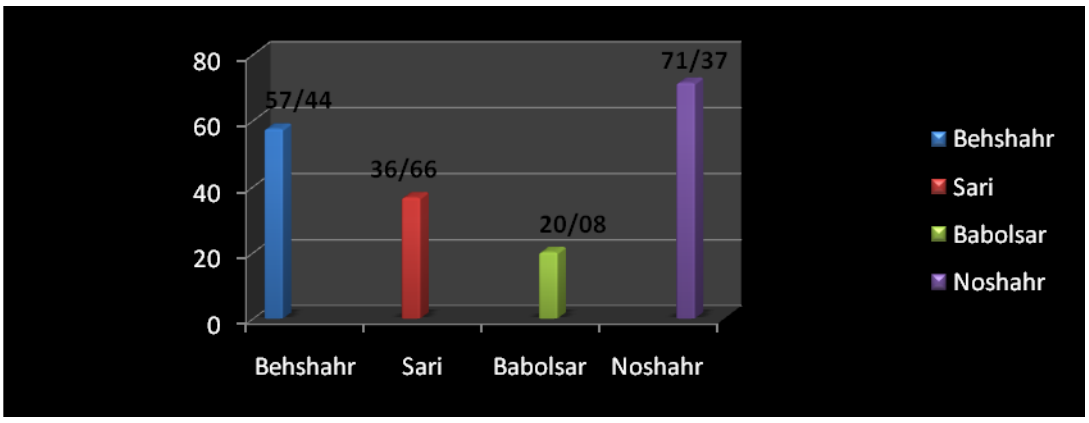
Std. deviation	Mean	Max	Min	Station
0.26951	11.1600	11.44	10.81	Behshahr
0.93324	11.9250	13.22	10.64	Sari
0.88932	7.6367	8.82	6.78	Babolsar
0.78065	7.7911	11.33	1.23	Noshahr

Paired samples correlation

Sig	Correlation	Pairs
0.221	-0.304	1&2
0.114	0.568	1&3
0.424	-0.201	1&4
0.723	-0.090	2&3
0.687	-0.102	4&2
0.439	-0.195	3&4

Chart 6: Diagram of LEAD concentration average in the studied cities

LEAD concentration average



Descriptive statistics

Std. deviation	Mean	Max	Min	Station
2.22320	57.4467	60.41	55.32	Behshahr
3.77348	36.6650	42.32	31.36	Sari
0.27730	20.0867	20.36	19.72	Babolsar
1.50051	71.3789	73.21	69.32	Noshahr

Paired samples correlation

Sig	Correlation	Pairs
0.110	0.389	1&2
0.57	0.474	1&3
0.614	0.127	1&4
0.218	-0.305	2&3
0.816	0.059	4&2
0.025	0.116	3&4