DISTRIBUTION OF TRACE METALS IN THE COASTAL WATERS OF CASPIAN SEA, BAKU, AZERBAIJAN

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ABSTRACT: *In 2015, dissolved As, Cu and Pb levels were measured for the winter and summer seasons in the coastal waters of Caspian Sea in Azerbaijan. Ten stations were sampled around the vicinity areas of the Hovsan channel and Hovsan WWTP discharge outfall, while control samples were obtained 3 km away from the effluent. Levels of heavy metals were assessed using ICP-MS. Due to the rapid dilution, the concentrations of trace metals increased from coastal to seaward stations. High values of As and Pb were recorded in the Hovsan channel area and control zone in summer, while in winter it was constant high for both area. The hot spot area for Cu was observed in the Hovsan channel site in winter. Heavy metals and solids were generally considerably deleterious at discharge area. The high levels and behavior of the metals were assessed, and it is therefore, correlated to salinity, nitrites and ammonium. Moreover, As and Cu appear to co-vary more with Ammonium and Nitrite ions in the control area for the winter samples compared to the summer samples.*

KEYWORDS: Arsenic, Copper, Lead, Trace Metals, Caspian Sea, Coastal Pollution

INTRODUCTION

Baku is the largest and capital city of the Republic of Azerbaijan, located on the Caspian Sea cost and major commercial hub in the Caucasus Region. Actual number of residents of the city exceeds 3,5 million, which is in large extend caused by the rapid urbanization, migration of refugees and internally displaced people.. A situation has put a huge strain on the sewage network, whereas around 78% of the city being linked to sewerage pipeline. However, the use of septic tanks is still an alternative tool in the wastewater carriage.

According to the latest data available, there are 276 discharge points appointed alongside Baku (AzerSu). City coast line extends for about 60 km eastward into the Caspian Sea and 17 km of current area belongs to Hovsan district, which is located on the South coast of Absheron peninsula, in the vicinity of our study. It receives large quantities of untreated and semi treated wastewater by the discharges of Hovsan (HC) and Hovsan Aeration Station's (HA) channel (WWTP) (Salamnov et al., 1995). The appointed area is the most contaminated territory along the peninsula (Mammadov et al., 2010). Subsequently, among the 6 existing waste water treatment plants the HA, with 640 000 m3/d nominal treatment capacity, is the most important treatment station that receives 51% of Baku city wastewater (Ministry of Ecology, CCEMA). Consequently, estimated average daily flow at Hovsan channel is above the 100 000m3. According to the data of Laboratory of Caspian Complex Ecological Monitoring Administration under the Ministry of Ecology and Natural Resources of Azerbaijan Republic. and AzerSu Joint-Stock Company which is in charge ofthe sewerage across the country, the amount of received wastewater largely exceed its nominal volume and the volume of solid materials, trace metals, phosphorus and nitrogen, as well as the concentration of microbial

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communities are considerably high even at treated sewage discharge region. Environmental pollution has been drawing worldwide attention and is becoming progressively a critical area of global concern (El-Sayed ., 2002a). For this reason, there is a great urgency to adequately and continuously observe our living environment and preserve it from additional degeneration. Since the coastal region and oceans are at times being utilized as the disposal area for environmental wastes, seawater analysis has specifically become significant. In order to conduct environmental studies, reliable analytical data for trace elements in seawater are required (Nham 2010).

Trace metals are main hazards to marine coastal ecosystems (Bruland, 1980). The application of heavy metals (Saad and Fahmy., 1984) for the sake of assessing and anticipating the further arising hazardous effects of sewage discharges at coastal areas of Baku, the Caspian Sea may assist the further forecast. Moreover, its development may extend trust that quality of environment depends upon several changes in communities and real alterations in biota (El-sSayed., 2002b). In the past, there is a very limited number of studies that has been carried out in order to investigate potential impacts caused by human activities in Azerbaijan, Caspian Sea such as industrialization, water desalination (Salmanov et al., 1995) oil refining and tourism activities (Efendiyeva., 2000) There is also drawbacks and a shortage of accurate data on distribution of trace metals along the coastline of Caspian Sea.

Quantification of metal levels in ecological samples can be performed with various methods. Atomic absorption spectroscopy (AAS) is still a good alternative to inductively couples plasma-mass spectroscopy (ICP-MS). However, ICP-MS has become the leading technique due to its high sensitivity and facility of concurrent analysis of various metals at trace levels in the numerous sample matrices (Y. Ha, O.G. Tsay and D.G. Churchill., 2011). Therefore, the objective of this study is to assess the level of trace metals by ICP-MS, and to investigate their consistent variability in response to sewage effluents.

The rest of the article is structured as follows. In Section 2 we describe the materials and methods of our sampling and analysis. Section 3 discusses the results of variations between the trace metals and nutrients, while Section 4 concludes the study.

MATERIALS AND METHODS

Study area: Sampling stations were sited in Caspian Sea, at Western region of Hovsan area, Baku, Azerbaijan. The main sewage effluent area was formed by means of Hovsan and Hovsan Aeration channel outfalls, with exits to surface and considerably disseminated along the shore. The temperature ranges of between 9^0-26^0C throughout the year. Aquatic basin is characterized by low salinity around 13g/l, however in the vicinity of Volga it reduces down to 5-10g/l. Temperature of endorheic water basin, with acute oscillations, varies between 0^0C and 10^0 C from North to South in winter period and from 23^oC to 28^0C during the summer period, that comprehends a diversity of features such as lakes and seas. In comporision with ocean waters, the Caspian Sea maintains less chloride (Cl^-) than the sulphate (SO_4^{2-}) and bicarbonates (HCO_3). The pH ranges between 7.9- 8.55 at shallow areas.

Sampling strategy: Sampling stations were set based on radial design. Water samples were collected from the five assigned stations around the Hovsan channel outfall and from five stations around the Hovsan Aeration mouth and form control area. Main aquatic parameters of sea were measured. Sampling was carried on the second part in two time period in 2015.

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Sampling procedure: Water samples were collected within the vicinity of three spatial different sewage outfall areas at increasing distances from source of contamination. Control zones appointed 3 km far from the polluted areas. Samples were taken alongside the boat using Niskin bottles at 3 m depth of each station and transferred into prewashed polyethylene canisters and bottles, via plastic pipes, which refined with Milli-Q and its screen was changed at each station. Simultaneously, conductivity and temperature were defined at the same distance down using the CDT. Canisters rinsed with a solution of chlorine and water then rinsed with Milli-Q. The samples transferred to acid washed bottles for metal samples. All withdrawn samples capped and stored inside iced-chest for carriage. At once upon arrival in the laboratory approximately 130 ml of sample water filtered via vacuum pump (Sartorius,Typ 16511, 250 ml) and placed into small tubes for metal analysis, were acidified with chloric acid an stored at refrigerator.

Metal Analysis: All measurements of metal contents were carried out using a Model 7700x ICP-MS (Agilent, USA). Analysis procedure described by E. Aricaand others (2018) was followed. Samples were pretreated by introducing of 10 mL of 8% (v/v) nitric acid. To prepare calibration standards at the concentrations of 1.0, 5.0, 10.0, 25.0, 50.0 and 100.0 µg/L, multi element stock solutions containing 10 µg/mL of each element to be analyzed was diluted in 4% (v:v) HNO_3. All glassware was kept in 10.0% (v:v) nitric acid for at least one night before the analysis so as to prevent potential contaminations.

RESULTS AND DISCCUSSION

The average concentration of As was 1,28 µg/L in winter (Table2), while in summer samples determined around 3.37µg/L, which were three times higher than those measured in winter. Significant contribution of As observed at the stations appointed far from the sewage discharge point at HC2, HC3, HC4 and HA4 during the summer period. Elevated level of As were observed at C1 station of control area, pointed close to shore in winter. Nevertheless, slightly constant concentration were recorded at the rest of the stations in winter. Surprisingly, the lowest concentration was recorded at the discharge points in the both time of period. This could be the sign of rapid dilution that happens in the discharge area and could be considered a harmful effect of the effluents.

Table 1. Comparison of the seawater analysis (µg/L) with theWHO, EU and US EPA standards

	Metals		
	As	Cu	Pb
WHO (µg/L)	10	2000	10
EU (µg/L)	10	2000	10
US EPA (µg/L)	10	1300	15
Present Study, Mean in Winter (µg/L)	1.28	1.24	1
Present Study, Mean in Summer (µg/L)	3.37	84.4	991.8

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The average concentration of Cu was 1,24 µg/L in winter, while in summer samples it was determined around 84.4 µg/L way higher than those measured in winter. The highest amount of Cu represented by the HC1, HC3 and C1 stations during the winter. Unlike the As distribution, the high levels of Cu were recorded at the sewage discharge points in the winter period. However, in summer samples concentration of Cu remained slightly stable. The highest concentration of Cu was observed at the control area in summer, with a mean around 84.4 µg/L. Control area was appointed 3 km far from the sewage channels, in the population expanded area.

Lead concentration was a stable during the winter, however it was ranged around 992 µg/L in summer. The highest levels of *Pb* were recorded at far distances from the vicinity. Highest distribution were observed at control area stations in summer period. The records for As and Lead were similar in winter period. In order to clarify the processes that effects distribution of trace metals in the study area, several environmental parameters were examined. Thereby, the salinity gradient almost was stable.

Table 2. Concentrations of metals in coastal waters of Caspian Sea, Baku

Location/Stations	Winter			Summer		
	As	Cu	Pb	As	Cu	Pb
HC1	1.3	1.6	1	2.37	78.8	944.99
HC2	1.4	1	1	4.6	76.5	979.29
HC3	1.3	1.6	1	4.84	76.6	956.37
HC4	1.1	1	1	3.55	83.1	958.26
HC5	1.1	1	1	3.69	77.43	950.28
HA1	1.1	1.2	1	4.53	84.21	967.89
HA2	1.3	1	1	4.2	79.98	958.29
HA3	1.2	1.1	1	3.18	80.09	980.14
HA4	1.1	1.2	1	3.86	83.63	1006.71
HA5	1.1	1.4	1	2.71	90.91	1035.08
C1	2	1.6	1	2.41	88.92	1005.09
C2	1.3	1.1	1	2.4	95.58	1046.8
C3	1.1	1.2	1	3.08	89.24	1032.86
Mean	**1.28**	**1.24**	**1**	**3.37**	**84.4**	**991.8**

According to the horizontal distribution scheme of trace metals in two period of time, the variations seems to be different. In general, close variations observed in a few areas, the stations appointed at the shore side animated high association with trace metals. In winter samples, Cu appears to co-vary with ammonium (Muller et al., 2001) at the HC site stations and control shore station. It seems that they have good association in winter period. Both elements recorded stable correlation in summer samples at HC and HA sites. At control site *As* correlated to the salinity, ammonia and nitrites, while in summer samples it showed the same range to

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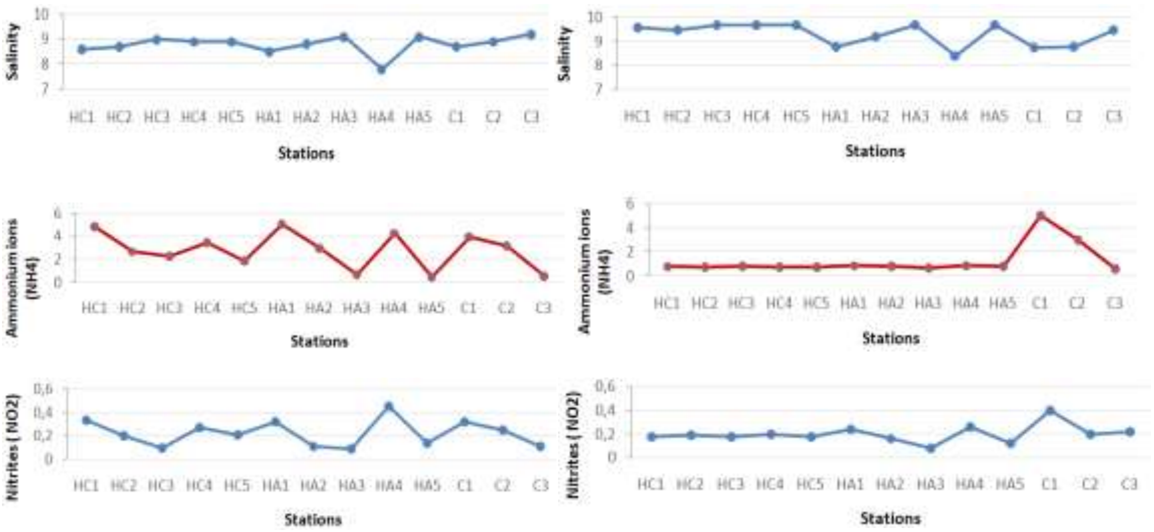
salinity. Ammonia concentrations obviously shows peak value at the discharge points at all stations during the winter period, accordingly 4.9 mg/l at discharge point of HC site and 5.1 mg/l at outlet location of HA site. These values much higher than the prior years' numbers in Caspian Sea on the current area measured by the Laboratory of Caspian Complex Ecological Monitoring Administration.

Nitrite highest concentrations was recorded at the HC site discharges point with 0.33mg/l and the highest value of 0.45mg/l was measured at 500 m away from the shoreline. The distribution of Nitrites in summer were significantly lower at HC and at shore stations of HA around 0.3mg/l. The highest concentration for Nitrites appears to have similar distribution values of 0.50mg/l at HA_4 station.



Metal levels in winter **Metal levels in summer**

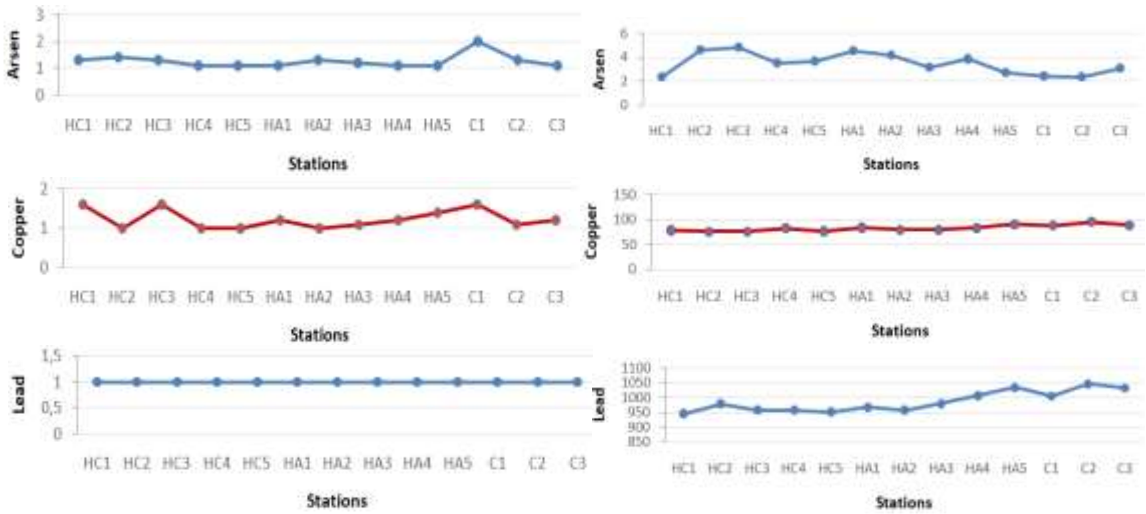


Figure 1. Horizontal distribution of metals and nutrients in the Hovsan area in 2015 summer and winter

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Accordingly, the high and low levels of NH_4 ions accompanied with Cu during the summer at HC and control site in summer samples. The high levels of *Pb* accompanied by high levels of nitrites at HA and control sites.

Figure 1 shows the spatial variability of metals and nutrients along the coastal waters of Baku during winter and summer. In general, there are two areas that show close variations of metals and nutrients; an area between HA4-C1 and area between HC2-HA1. Also, *As* and *Cu* appear to co-vary more with Ammonium and Nitrite ions in the control area for the winter samples compared to the summer samples. It also shows a good association between *As* and other mentioned parameters during the two sampling periods. On the contrary, Lead remains stable across sampling areas, hence does not confirm any association with other parameters. *Cu* is well recognized and a key element for biological functions. However, its level higher than norms can lead to negative consequences. Although *As* are being used as respiratory metabolites, this metal is treated as harmful for biological functions. At the same time, Lead affects the nervous system and causes blood disorders. Moreover, overall analysis reveal that the sampling areas with high levels of those elements are closely associated with high levels of microbial communities(Caruso et al., 2016). This is again an indication of an increase of the mentioned elements in the Sea water due to the sewages.

CONCLUSION

The results of study revealed that the elevated levels of trace metals at near shore stations can be considered human impact on coastal areas. In this case, some metals can be the potential tracers of sewage effluents. The concentration of pollutants in the Caspian Sea water reflects the temporary balance of pollution. Thus, may range periodically, either remains stable. Eventually, The Caspian Sea waters categorized as a special protected water object within the Azerbaijan territory. Hence, the more proper monitoring studies shall be regulated for potentially better indication of the point sources of contamination.

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