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Research Article

Trace Metals in the Arabian Seawater and Freshwater Samples in Oman by Using By ICP-OES

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ABSTRACT

Water is an inorganic, transparent, tasteless, odorless, colorless liquid which is the main component of the earth and living organisms. Trace metals are elements that usually occur at very low levels in the environment. These metals are needed for life. However, at high concentrations of the trace metals can be toxic. The contamination with trace metals in water samples are health hazards and it can create many health problems such as liver, kidney, and intestinal damage, anaemia, and cancer. Therefore, the aim of this work was to assess the levels of Lead (Pb), Arsenic (As), Nickel (Ni), Chromium (Cr), and Cadmium (Cd) in the sea and freshwater samples, which was collected from five major seaport areas in Oman and one fresh water canal by using sensitive Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). To achieve these objectives, sixty-four water samples were collected from six different locations in Oman. A total sixty seawater samples were collected from Matrah port, Al Mouj Marina, Sohar port, Salalah port, and Al Duqm port and four freshwater samples were collected from Falaj Daris. The conductivity of the collected seawater samples were very high therefore, the seawater samples were diluted 200 times and analyzed by ICP-OES. The results obtained from ICP-OES showed that the level of all analyzed water samples, the concentrations of trace metals (As, Ni, Cd, and Cr) in sea and freshwater samples were within the permissible limit except the concentration of Pb, which exceeded the permissible limit in several samples. The toxic Pb contaminated water samples can create a health risk therefore appropriate water treatment should be applied to reduce the concentration of Pb within the safe limit so the accumulation of toxic waste in both humans and animals can be avoided. So far of our knowledge, the ICP-OES method is the first analytical technique for the detection of toxic heavy metals in water samples. In conclusion, the developed method could be used routinely for the detection of heavy metals in water samples.

Keywords: Sea and fresh water; Trace metals; Quantification; ICP-OES; Oman

INTRODUCTION

The world's freshwater supply is dependent on surface or ground water, particularly in Oman [1]. Good quality water is the basic requirement for human health [2]. The polluted water may become dangerous to human health and it causes various diseases namely cancer, cardiovascular diseases, skin and neurological diseases [3]. Some trace metals in low concentration are needed for human health [4]. The concentration of heavy metals in water should be kept in the low ppb range, which is acceptable for human health [5]. Some basic elements named Co, Cr, Fe, Mn, Ni, and Zn are essential for human growth and they have significant beneficial uses. The elements named Cd, Hg and Pb. have non-effective metabolic function. They are called non-essential elements [6]. Natural sources of trace elements in our seas, lakes and groundwater are, for example, rock weathering, soil erosion, and the dissolving of water-soluble salts [7]. Many trace metals and non-essential elements can

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induce morphological abnormalities such as decreased growth, higher mortality, and mutagenesis effects in the human body, hence it is critical to human health if they are present at high quantities [8]. Trace element concentrations are more likely to be a concern in groundwater than in surface water because groundwater travels through rocks, causing sediments. The interaction of broken up follow metals with particles suspended in saltwater might have a significant impact on the concentration and distribution of the following metals in seawater. Water plays an important role to facilitate the metabolic function by intake of biologically active trace elements. The World Health Organization (WHO) establishes broad guidelines for trace elements and heavy metals in drinking water. The organizational point of view is beneficial to human health. Checking ponder of follow metals in marine coastal waters are critical in determining the source, conveyance, and fate of chemical pollutants in seawater in order to develop persuasive programs and procedures for managing the marine framework and protecting coastal conditions. The quality of marine waters in terms of follow-up metal concentrations are within acceptable standards for ensuring human health. In the past few years, water pollution has increased remarkably and reached frightening levels that are threatening for human life on earth. Therefore, the objectives of this research is to determine the degree of pollution in the sea and fresh water samples collected from different port areas in Oman and to assess whether it follow the international standards to ensure the safety of water and to come up with solutions to prevent water pollution. The majority of Batina's residents rely on private wells for their water supply. Specialists do not control or test the quality of such water. As a result, if water is contaminated, consumers' health may be jeopardized. There are few heavy metals contaminating water, like lead, chromium, nickel, and copper. Previous report showed that 80 percent of the tests for lead and chromium exceed the safe threshold. Lead contamination is attributed to well depth, inadequate security, and mechanical activities, whereas chromium contamination is generated by ophiolitic shake weathering. A number of processes used to control the distribution of trace metals in saltwater that transport trace metals, naturally dissolved or from human activities. The target of this study is to check the trace metal levels and accommodate with worldwide measures for drinking water, additionally to decide pattern levels of follow components in provided drinking waters within the environment of Oman. The target of the present work is to quantify the trace metal levels and ensure compliance with international drinking water regulations, as well as an endeavor by this group to identify baseline levels of trace elements in different water samples. Majority of previous reports showed that the concentration of toxic heavy metals in water samples was determined by AAS. However, none of them used the ICP-OES analytical technique for the detection of heavy metals in seawater samples. Accordingly, literature search showed that there is no report available with respect to the concentrations of toxic heavy metals by ICP-OES in seawater and freshwater samples in Oman [9]. Therefore, the aim of this work was to determine the toxic heavy metals in the sea and freshwater samples by using ICP-OES and comparing the data to WHO guideline.

MATERIALS AND METHODS

Collection of samples

In each port, 12 samples were collected at different locations. Each water sample was 1 litre from a particular point. The first two samples were collected from water beneath ship. The first sample was taken from the surface water beneath the ship, the second sample will be taken from 30 cm bellow the same point. One kilometre away from the first point, two samples each 1 liter were collected from surface of water and depth of 30 cm in the same way. The fifth and sixth samples are taken from one kilometre away in the other side from the ship. Similarly, six water samples were collected parallel to each point but towards 1 kilometer of the deep sea (Figure 1). A total 60 of samples were collected from five seaports such as Matrah Port, Almouj Port, Salalah Port, Al Duqm Port, Sohar Port and 4 samples from Falaj Dares. All the water samples were bought to the research lab at the university of Nizwa.

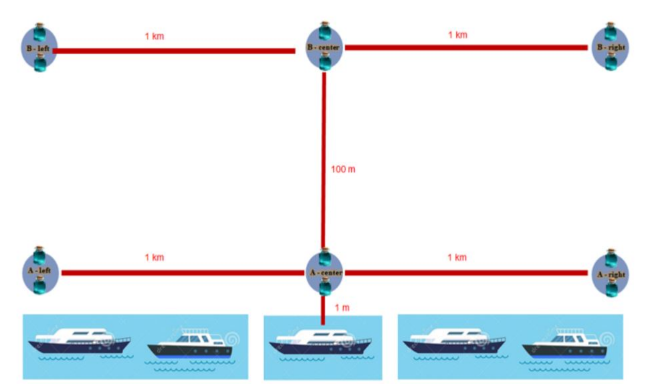

Figure 1: Water samples collection of each ports.

Analytical methodology

Immediately after collection, the samples were acidified with 4 ml of supra-pure HNO_3 (pH<2) and stored at room temperature for analysis. All collected water samples were filtered through Whatrnan No. 41 filter papers. The conductivity of all 64 samples were measured by using conductometer. Based on the conductivity the collected water samples were diluted 200 times with deionised water. The diluted samples were ready for the trace metal analysis by using ICP-OES.

RESULTS

Water is the vital components for the living organisms on Earth. Water is an odorless, colorless and tasteless liquid, but the water is often contaminated by the several contaminants such as human and animal wastes, effluents discharge from industries as well as dissolved gases [10]. Among the contaminants, sewage is one of the major source of contamination and the data showed that about two million children die due to contamination by sewage [11]. Another major cause of water contamination is acid rain, it can unbalance the level of metallic constituents such as Iron (Fe), Magnesium (Mg), Lithium (Li), Zinc (Zn), Copper (Cu), Chromium (Cr), Nickel (Ni), Cobalt (Co), Arsenic (As), Selenium (Se) etc. After following the standard operating procedure (SOP, the water samples were analyzed by ICP-OES.

The concentration of trace metals in the water samples at six different collection points are presented in Table 1.

Table 1: Level of trace metals in the sohar water samples.

Elements (mg/L)	A-left-surface	A-left-deep	A-right-surface	A-right-deep	A-center-surface	A-center-deep	B-right-surface	B-right-deep	B-left-surface	B-left-deep	B-center-surface	B-center-deep
As	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cd	5.833	0.006	0.352	0.554	0.153	0.25	0.163	0.43	0.5	0.223	0.299	0.304
Cr	1.905	0.006	ND0.058	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ni	0.154	0.001	ND0.588	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pb	8.081	0.035	0.177	5.156	ND	3.624	ND	5.027	5.156	2.085	2.658	3.206

ND=Not detected

Sohar water samples (Table 1) were analyzed for the elements like arsenic, cadmium, chromium, nickel and lead. It provided some exciting data regarding cadmium. Cadmium was present in almost all the samples starting from a highest amount of 5.833 mg/L (in A-left-surface) to a lowest amount of 0.0060 mg/L (in A-left-deep). Then the second prominent element was Lead (Pb). It was also present in almost all the samples except in A-center-surface and B-right-surface, where the amount was not within detectable limit. In case of lead, A-left-Surface contains the highest value, which was 8.0810 mg/L and rest of the samples contained it to a comparatively higher amount. After that chromium was found in only two samples (A-left-surface and A-left-deep) and in other samples, it was not present in detectable amounts. The results are similar for nickel. The most relaxing point is arsenic, which was below the detectable limit in all the samples.

Analysis for Al Duqm water samples was also completed with slightly different results. Cadmium was present in all samples but the amounts were lower. The second frequent presence was of lead, which was present in eight samples in high amounts and in four samples; it was not present in detectable limit. The other three elements-Arsenic, chromium and nickel were present in only one sample (A-right-surface) but for other samples, not all of these elements were below the detectable limit (Table 2).

Table 2: Level of trace metals in the AI Douqom water samples.

Elements (mg/L)	A-left-surface	A-left-deep	A-right-surface	A-right-deep	A-center-surface	A-center-deep	B-right-surface	B-right-deep	B-left-surface	B-left-deep	B-center-surface	B-center-deep
As	ND	ND	0.506	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cd	0.381	0	0.513	0	0.001	0.398	0.38	0.567	0.413	0.433	0.599	0.495
Cr	ND	0	0.521	0	0	ND	ND	ND	ND	ND	ND	ND
Ni	ND	ND	0.519	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pb	3.621	ND	0.51	ND	ND	ND	4.107	6.132	3.039	4.199	4.337	4.864

In the Al Mouj water samples, cadmium and lead was found in all the samples except in one sample. The quantities for lead were high in most of the cases, while cadmium was present in low quantities. Arsenic, chromium and nickel were not present in detectable quantities (Table 3).

Table 3: Level of trace metals in the AI Mouj water samples.

Elements (mg/L)	A-left-surface	A-left-deep	A-right-surface	A-right-deep	A-center-surface	A-center-deep	B-right-surface	B-right-deep	B-left-surface	B-left-deep	B-center-surface	B-center-deep

As	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cd	0.551	0.41	0.406	0.44	0.404	0.567	ND	0.42	0.445	0.253	0.468	0.365
Cr	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ni	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pb	4.911	3.472	4.201	4.321	4.695	2.966	4.006	4.552	3.537	1.675	2.949	ND

Water samples from Matrah claims for the rich content of lead at all the sampling points except A-right-surface, where it is not in the detectable limit. Cadmium was present in all the samples except three points (being not detectable). Both of chromium and nickel was below the detectable limit in most of the samples and the amount in the few samples was in minute amounts. Arsenic, in all the sampling points, was not detectable (Table 4).

Table 4: Level of trace metals in the AI Matrah water samples.

Elements (mg/L)	A-left-surface	A-left-deep	A-right-surface	A-right-deep	A-center-surface	A-center-deep	B-right-surface	B-right-deep	B-left-surface	B-left-deep	B-center-surface	B-center-deep
As	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cd	0.221	0.225	0.4	0.22	0.309	0.204	0.281	ND	0.431	0.321	ND	ND
Cr	ND	ND	ND	ND	ND	ND	ND	0.372	0.321	ND	0.23	0.31
Ni	ND	ND	ND	ND	ND	ND	ND	0.233	ND	0.325	0.315	ND
Pb	ND	4.025	5.1	4.333	4.777	4.533	5.2	4.3	4.8	4.1	3.9	4.3

Cadmium was found in the highest number of sampling points in the Salalah samples, but the amounts were in lower level. The second highest number of points contain lead and in a moderate level. The most exciting part of the Salalah water samples is that there was no arsenic, chromium or nickel present in detectable quantities (Table 5).

Table 5: Level of trace metals in the Salalah samples water samples.

Elements (mg/L)	A-left-surface	A-left-deep	A-right-surface	A-right-deep	A-center-surface	A-center-deep	B-right-surface	B-right-deep	B-left-surface	B-left-deep	B-center-surface	B-center-deep
As	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cd	ND	0.467	ND	0.366	0.355	0.355	0.395	0.411	0.354	0.297	0.321	0.485
Cr	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ni	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pb	2.1	2.3	1.689	1.986	2.211	2.132	1.899	1.566	ND	ND	1.769	ND

The Falaj Daris water samples do not contain any of the elements (arsenic, cadmium, chromium, nickel and lead) in detectable amounts (Table 6).

Table 6: Level of trace metals in the Falaj Dares water samples.

Elements (mg/L)	Surface	Deep	Surface	Deep
As	ND	ND	ND	ND

Cd	ND	ND	ND	ND
Cr	ND	ND	ND	ND
Ni	ND	ND	ND	ND
Pb	ND	ND	ND	ND

DISCUSSION

Adverse health effects from heavy metals are extensively documented, with lead being the most often discussed component. Whenever lead enters the body, it has the potential to affect every organ and natural framework. It has an impact on both adults and children immune system [12]. It increases the weight of blood vessels. It has an effect on the regeneration framework in both humans and animals, and it affects the kidney and the safe immune system. Water supply contamination with lead can occur through lead channels, chrome-plated taps, and unethical mechanical exercise transfer [13]. Chromium in drinking water is mostly the product of mechanical waste. There are two stable oxidation states of Chromium: Cr (III) and Cr (VI), with the latter being more harmful than the former. Many nations allow chromium levels in drinking water ranging from 50 ppb to 100 ppb. Long-term chromium exposure has been linked to kidney and liver damage, as well as the development of cancer

It has been well documented that trace metals play vital roles in the sea. Some of the trace metals specially Iron (Fe), Copper (Cu), and Cadmium (Cd) are indispensable marine algae [14]. Iron is well known element for the use of chlorophyll production as well as nitrogen fixation [15]. It can regulate the productivity and marine biogeochemical cycles. Both Cu and Cd can be toxic under some conditions. In the last decade, various methods have been developed to allow trace metal analysis with a simpler procedure and a smaller sample volume. These methods include the titrimetric one as the simplest one, in which these are quantified using titrant and indicator solution. There are also different types of titrimetric methods as well and among which complexometric titration is the most frequently used procedure in titrations. There are also some instrumental methods, which are very much useful for the quantification of metals. Among those, AAS (Atomic Absorption Spectrophotometry is a widely used method. This instrument works in two modes: flame and electrical mode. Generally, flame mode is used for most of the metals and furnace mode is used for few metals [16]. Electrochemical method can also be used for the quantification of different metals. Stripping analysis is the most valued process for the quantification of trace metals. Nowadays ICP-OES has taken a prominent position in the field of trace metal analysis. Therefore, in the current study this method was adopted for analysis of water samples of various points of different places and or localities.

In the present study, it was observed that in all the cases, arsenic was below the detectable limit indicating that all these water sources are free from any type of toxicity due to arsenic. Nickel content shows different pictures [17]. At some points in Sohar, Al Duqm and Matrah, the nickel content is higher than limit value, which may be due to the contamination of water by industrial waste, spillage from water transportation and and other sources. The water samples from other water samples had low nickel content. Regrettably, the cadmium content is more worrying. In almost all the places (except Falaj Dares), it is so high that it may affect any type of living organism [18]. Chromium is absent with an exception of one or two places in Sohar, Al Douqom and Matrah. The lead content is also too high in all the places except Falaj Draes [19]. Its presence of high content that it can be designated as the risky state.

The quantities of different trace elements may change so it is advisable to take immediate action just after getting and comparing the results with some other results from convenient methods. In that case, ICP-MS can be used t for the confirmation of those data [20].

CONCLUSION

The aimed of this work was to detect the contamination in water. To achieve of this objective, we had collected 64 samples from five seaports areas and determined the concentration of toxic heavy metals in the seawater and freshwater samples by using ICP-OES. The results showed that at some points such as Sohar, Al Duqm and Matrah, the nickel content exceeds the WHO standard. The Cadmium (Cd) concentration is so high concentration in all seawater samples. However, the concentration of Falaj Dares is normal. The lead is also present in dangerously high concentration in all marine samples. As a conclusion, the results shows that the nickel, cadmium and lead contents are over the maximum allowable concentration in the seawater samples. On the other, the samples from the Falaj Daris irrigation canal did not contain any of the examined metals in detectable quantities. Thus, it is highly recommended to accomplish this type of old work in some other places of Oman and to confirm the data by different prominent methods.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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