تعيين تركيز المعادن الثقيلة في مياه الشرب من مصادر مختلفة في محافظة البصرة

د.إحسان عبد الكريم عبد الحسين [1] أنغام عمير صاحي [2] د.رفعت محمد دخيل [3]

الخلاصة:

تم جمع عينات مياه من سيارات حوضية وخزانات وبرادات المياه الصالحة للشرب من مناطق مختلفة في محافظة البصرة للفترة من 2008/10/1 ولغاية 2009/4/1 لتخضع للدراسة المختبرية وذلك لغرض تحديد تركيز العناصر الثقيلة (الرصاص، الكادميوم، الكوبالت، الزنك، النحاس، الزئبق و النيكل) في هذه المياه ومعرفة مدى تأثير كل من السيارات الحوضية والخزانات والبرادات على المياه الموجودة فيها. استخدمت تقنية الامتصاص الذري للحصول على النتائج وتمت مقارنة النتائج مع التركيز الأمثل المحدد من قبل منظمة الصحة العالمية. تم استنتاج أن المياه الصالحة للشرب المأخوذة من الأماكن أعلاه ملوثة بالعناصر الرصاص ، النحاس و النيكل والتي تعد من العناصر المؤثرة على صحة الإنسان. كما تم معالجة النتائج إحصائيا"باستخدام التحليل الإحصائي التجميعي وكانت التفسير ألمختبري والإحصائي متطابقان لذا فيوصى بضرورة التنظيف الدوري لكل حاويات مياه الشرب وتعريضها للتهوية خلال فترة لا تتجاوز ثلاث أيام واستبدال المياه يومياً.

كلمات رئيسية: نوعية المياه، المعادن الثقيلة، التحليل العنقودي

[1] مدرس، قسم هندسة تقنيات البيئة والتلوث، الكلية التقنية/البصرة، البريد الالكتروني:.(Corresponding Author) drengihssan@yahoo.com

[2] مدرس مساعد، قسم هندسة تقنيات البيئة والتلوث، الكلية التقنية/البصرة، البريد الالكتروني:angham.omeer@yahoo.com

[3] مدرس، قسم هندسة تقنيات البتر وكيمياويات، الكلية التقنية/البصرة، البريد الالكتروني:rifat234dakhil@yahoo.com

Introduction:

The contamination of water by metal compounds is a worldwide environmental problem. Concentration of metals is widely related to biochemical values, which are used in diseases diagnosis due to environmental toxicity.

In 2000 it was estimated that in excess of 1 billion persons still lacked access to improved drinking water sources (WHO and UNICEF, 2000). Most of these are the rural and urban poor living in developing countries that remain disadvantaged in terms of access to basic services and whose health and well-being is put at risk from poor and contaminated environments.

Drinking-water supply and quality both have important impacts upon health and socioeconomic development and therefore remain important components of the poverty cycle. (Philippe and Thompson, 2006). Approaches to the management of drinking water and of drinking-water quality vary widely between countries in response to factors such as environmental and climatic conditions, technical capacity, and level of economic development and cultural and societal norms and practices (David, 2006).

In countries where access to improved water sources or supply is low, the role of legislation, regulation and standards is likely to be best oriented towards encouraging extension of access to higher levels of service, ensuring effective use of existing infrastructure and ensuring that the minimum safeguards are in place to prevent outbreaks of waterborne disease. Improving access to improved drinking- water supply that present limited risks to health and fulfils basic rights to a ‘safe’ and ‘adequate’ water supply implies making best use of limited resources towards these priorities (Raymond, 1999).

Legislation, regulation and standards may promote this directly and may themselves be more or less cost-effective in terms of the resources demanded for their implementation and the impact of their application. In terms of drinking-water quality, most regulations and standards are dominated by health concerns. The World Health Organization publishes Guidelines for Drinking-water Quality to assist countries at all levels of economic development in establishing national approaches to drinking water that is effective in the protection of public health (WHO, 2003a).

Human health can be affected by the quality of the food and drink that we take. Water intended for human consumption must be free from organisms and from concentrations of chemical substances that may be hazardous to health. Recent studies show that the levels of trace elements present in drinking water could seriously affect human health World Health Organization (WHO) places great emphasis on the quality of drinking water and has recommended upper limits for a number of trace elements for drinking water (WHO, 1997).

Heavy Metals in Water:

Heavy Metals in the water treatment field refer to heavy, dense, metallic elements that occur only at trace levels in water, but they are very toxic and tend to accumulate in the body over long periods of time. Most heavy metals are too rarely found in water to justify government regulation at all, but a few have been given Maximum Contaminant Limits (MCLS) and MCL Goals by the Environmental Protection Agency (Faust, 1981) and (Goyer, 1995).

These include:

Lead (Pb) is the most significant of all the heavy metals because it is both very toxic and very common. It gets into water from the corrosion of plumbing materials. Lead can be found in the solder used to join copper pipes, and in fittings and faucets made from brass.

Cadmium (Cd) occurs mostly in association with zinc and gets into water from corrosion of zinc-coated ("galvanized") pipes and fittings.

Cobalt (Co) Cobalt is a naturally-occurring element that has properties similar to those of iron and nickel. Small amounts of cobalt are naturally found in most rocks, soil, water, plants, and animals, typically in small amounts. Elemental cobalt is a hard, silvery grey metal. However, cobalt is usually found in the environment combined with other elements such as oxygen, sulfur, and arsenic.

Zinc (Zn) deficiency in animals including humans causes stunted growth and male sexual immaturity. An excess accumulation of Zn in the human body causes harmful effects such as acceleration of anemic conditions.

Copper (Cu) at very high levels is toxic and can cause vomiting, diarrhea, loss of strength or, for serious exposure, cirrhosis of the liver.

Mercury (Hg) is notorious as an environmental toxin, but it is not a big problem in water supplies. That's because it is found only at very low levels in water.

Nickel (Ni) Nickel is a very abundant natural element. Pure nickel is a hard, silvery-white metal. Nickel can be combined with other metals, such as iron, copper, chromium, and zinc, to form alloys. These alloys are used to make coins, jewelry, and items such as valves and heat exchangers. Most nickel is used to make stainless steel. Nickel can combine with other elements such as chlorine, sulfur, and oxygen to form nickel compounds. Many nickel compounds dissolve fairly easy in water and have a green color. Nickel compounds are used for nickel plating, to color ceramics, to make some batteries, and as substances known as catalysts that increase the rate of chemical reactions.

The objective of the work is to determine the heavy metals concentration in the different types of containers of water by using the atomic absorption spectrophotometer technique and propose recommendations to avoid the increase of these metals in the drinking water.

Materials and Methods:

Forty four samples of water were collected from different water containers at different regions of Al-Basrah city. Water samples were filtered with 0.45 µm endothelial hole membrane filter. The impurities were excluded by passing the water samples through an ion exchange column containing chelex-100-resin. Two forms of resins were used at this study. The sodium form was used for the determination of the positive elements, whereas, the hydrogen form was used for the determination of the negative elements (APHA, 2007).

The concentrations of some trace elements in water samples were determined according to atomic absorption spectrophotometer methods of Riley and Taylor, 1968.

Before using the ion-exchange column, the column was washed three times with; deionized distilled water (DDW), 2N HNO_3 (to get rid of heavy elements), and DDW respectively. While, the resin was regenerated by 3N NH_4OH solution followed by washing with DDW to remove the remaining ammonia.

In order to concentrate the expected trace elements; aliquots of (500 l) of filtered water samples were passed through the column by a rate of (5 ml/ l). The trace elements were concentrated by washing the resin many times with 2N HNO_3 solution and the washing acid was collected. The collected acid was evaporated at 80 C^o to nearly dry. The formed precipitate was dissolved by (1 ml) conc. H_2SO_4. The volume was completed to 25 ml with DDW and stored in plastic bottles until their use. Blank of DDW was carried out simultaneously. The column was regenerated by 3N NH_4OH solution after each use.

Table 1 The Identification of Water Drinking According to WHO in (mg / L) (WHO, 1995) and (WHO, 1997).

NO.	Material	Concentration mg / L
1	Lead	0.05
2	Cadmium	0.005
3	Cobalt	0.1
4	Zinc	0.5
5	Copper	0.1
6	Mercury	0.001
7	Nickel	0.002

Results and Discussions:

The samples are examined in the lab and by using the procedure mentioned above; the values of Pb, Cd, Co, Zn, Cu, Hg and Ni are determined. Tables 2, 3 and 4 illustrate the values of these heavy metals that obtained in the lab in the tanker, house tank and cooler respectively. Also the value of pH and electrical conductivity of each sample are measured and tabulated in these tables. Further, the minimum and maximum values of each metal in each container are determined. Then, the concentration of each metal for different samples of collected water is examined whether it more or less than the permissible limit. The dark color is given for the concentration of the heavy metals more than the permissible limit as shown in the Tables 2, 3 and 4. It is clear from these tables that the concentration of Pb, Cu and Ni are out of permissible limit of WHO mentioned in Table 1 for all types of containers. Also it is observed that the value of Zn is violate the permissible limit only in some tankers and the other values are closer to permissible limit in tankers and other types of container.

The concentration of lead, copper and Nickel exceed the permissible limit that detected from WHO, this increment in the concentration occurred due to the plating of containers and pipes using the heavy metals above. Further, fittings such as taps, which are chromium-plated, release much higher concentrations, and then these concentrations decrease significantly with time.

Table 2 The Concentration (mg / L) of Heavy Metals in Tanker

No.	Source	PH	E.C	Pb	Cd	Co	Zn	Cu	Hg	Ni
1	Al-Zubair	6.5	265	0.5	0.004	0.004	0.4	0.2	0.0001	0.004
2	Khoor Al-Zubair	6.5	269	0.6	0.003	0.004	0.4	0.2	0.0001	0.004
3	Al-Kibbla	6.5	255	0.5	0.003	0.004	0.4	0.2	0.0001	0.004
4	Al-Faw	6.7	272	0.7	0.003	0.005	0.4	0.2	0.0001	0.005
5	Al-Garmaa	6.6	272	0.6	0.002	0.005	0.4	0.2	0.0001	0.005
6	Al-Ashar	6.5	266	0.6	0.002	0.005	0.5	0.2	0.0001	0.005
7	Old-Basrah	6.5	262	0.6	0.002	0.005	0.6	0.2	0.0001	0.005
8	Al-Harthaa	6.5	266	0.6	0.001	0.005	0.6	0.2	0.0001	0.005
9	Al-Dear	6.2	255	0.3	0.003	0.005	0.6	0.2	0.0001	0.005
10	Aby Al-Khasieb	6.1	255	0.3	0.003	0.005	0.6	0.3	0.0001	0.005
11	Tech. college/ Basrah	6.1	254	0.3	0.003	0.005	0.6	0.3	0.0001	0.005
12	Tech. Instit./Basrah	6.1	254	0.4	0.002	0.005	0.5	0.3	0.0001	0.005
13	Basrah University	6.8	280	0.9	0.002	0.005	0.5	0.3	0.0001	0.005
14	Petrochemical Sta.	6.5	256	0.5	0.001	0.006	0.5	0.3	0.0001	0.006
Min.		6.1	254	0.3	0.001	0.004	0.4	0.2	0.0001	0.004
Max.		6.8	280	0.9	0.004	0.006	0.6	0.3	0.0001	0.006

Table 3 The Concentration (mg / L) of Heavy Metals in House Tank

No.	Source	PH	E.C	Pb	Cd	Co	Zn	Cu	Hg	Ni
15	Tech. college/ Basrah	6.5	255	0.5	0.001	0.006	0.5	0.3	0.0001	0.006
16	Al-Zubair	6.5	256	0.5	0.001	0.006	0.5	0.3	0.0002	0.006
17	Al-Basrah	6.5	255	0.6	0.002	0.006	0.5	0.3	0.0001	0.006
18	Al-Kibblaa	6.1	245	0.2	0.003	0.006	0.5	0.3	0.0001	0.006
19	Aby Al-Khasieb	6.1	245	0.2	0.002	0.006	0.5	0.3	0.0001	0.006
20	Al-Faw	6.1	255	0.2	0.002	0.006	0.4	0.3	0.0002	0.006
21	Al-Ashar	6.2	233	0.2	0.002	0.006	0.4	0.3	0.0002	0.006
22	Al-Harthaa	6.1	243	0.2	0.002	0.006	0.4	0.3	0.0002	0.006
23	Al-Dear	6.1	233	0.3	0.001	0.006	0.4	0.3	0.0002	0.006
24	Basrah University	6.1	253	0.33	0.001	0.006	0.4	0.3	0.0002	0.006
Min.		6.1	233	0.2	0.001	0.006	0.4	0.3	0.0001	0.006
Max.		6.5	256	0.6	0.003	0.006	0.5	0.3	0.0002	0.006

Table 4 The Concentration (mg / L) of Heavy Metals in Cooler

No.	Source	PH	E.C	Pb	Cd	Co	Zn	Cu	Hg	Ni
25	Al-Zubair	6.1	243	0.1	0.001	0.006	0.4	0.3	0.0001	0.006
26	Aby Al-Khasieb	6.3	243	0.2	0.001	0.006	0.4	0.2	0.0001	0.006
27	Al-Kibblaa	6.4	255	0.2	0.002	0.006	0.4	0.2	0.0001	0.006
28	Tech. college /Basrah	6.5	256	0.11	0.002	0.008	0.5	0.2	0.0001	0.008
29	Al-Faw	6.5	256	0.22	0.002	0.008	0.5	0.2	0.0001	0.008
30	Basrah University	6.5	256	0.22	0.001	0.008	0.5	0.2	0.0001	0.008
31	Basrah University	6.5	255	0.24	0.001	0.008	0.5	0.2	0.0003	0.008
32	Sea Sciences Center	6.5	255	0.21	0.002	0.008	0.5	0.2	0.0003	0.008
33	Basrah University	6.5	255	0.21	0.002	0.008	0.5	0.2	0.0003	0.008
34	Basrah University	6.4	250	0.22	0.002	0.008	0.5	0.2	0.0001	0.008
35	Basrah University	6.3	250	0.3	0.001	0.008	0.5	0.2	0.0001	0.008
36	Basrah University	6.4	255	0.3	0.001	0.008	0.4	0.2	0.0001	0.008
37	Tech. college /Basrah	6.5	256	0.3	0.001	0.008	0.4	0.2	0.0001	0.008
38	Tech. college /Basrah	6.5	255	0.3	0.001	0.008	0.4	0.2	0.0001	0.008
39	Tech. college /Basrah	6.5	256	0.25	0.001	0.008	0.4	0.2	0.0001	0.008
40	Tech. college /Basrah	6.5	256	0.32	0.001	0.008	0.4	0.2	0.0002	0.008
41	Tech. college /Basrah	6.4	256	0.11	0.001	0.008	0.4	0.2	0.0002	0.008
42	Tech. college /Basrah	6.5	258	0.33	0.001	0.008	0.4	0.2	0.0001	0.008
43	Tech. college /Basrah	6.5	259	0.22	0.001	0.008	0.5	0.2	0.0001	0.008
44	Tech. college /Basrah	6.4	259	0.25	0.001	0.008	0.5	0.2	0.0001	0.008
Min.		6.1	243	0.1	0.001	0.006	0.4	0.2	0.0001	0.006
Max.		6.5	259	0.33	0.002	0.008	0.5	0.3	0.0003	0.008

Statistical Analysis:

The results of the heavy metals concentration are dealt with statistically by using cluster analysis. This analysis is depended on counting several variables of different samples, as well as, finding out the ratio of similarity among variables after comparison with each other, and arrangements in the form of clusters or dendograms depending on the extent of their presence in the different samples. This is called (R-mode) where pairs of variables are compared with each other for all samples. Also, when comparing these samples with each other depending on variables presence and the arrangement of their correlations in the form of clusters (Q-mode) and explaining these correlations, the relationship between all samples and classification could be defined. Pyramid (WARD) method is used in the two types of cluster analysis as it is considered the most modern and best method in such sort of studies (Al-Adili and Maatooq, 2008) .

Cluster analysis can consider as many variables as are available. It is a method of grouping samples into clusters based on similarities and differences between individuals (Davis,1973). Before dealing with cluster analysis the data are first normalized using:

$$K_{ij} = \frac{X_{ij}}{V_i} \qquad (1)$$

Where K_{ij} is the normalized ith variable for the j'th sample, X_{ij} is the data value (concentration of heavy metal), V_i is the permissible limit value of the ith variable (permissible heavy metal concentration). This procedure applies equal weights to each variable. The variables considered in the study are Pb, Cd, Co, Zn, Cu, Hg and Ni. The measure of similarity used is the Euclidean distance between samples in N-dimensional space where N is the number of different variables considered. The computation is carried out with the help of Statistica package.

Cluster Analysis (R-mode):

The (R-mode) depended completely on bilateral correlation coefficients among different variables (heavy metals) which disclosed the similarity in behavior of the variables. Likewise the bilateral correlation coefficients would not show clearly if that group of variables have similar behavior. The cluster analysis (R-mode) for heavy metals concentration result in the appearance of three major groups A, B and C as shown in Fig.1.

The results clearly show that cluster A comprised of only Pb variable as it is distinctly more concentration and violates the permissible limit than the rest. Cluster B is the variables (Cu and Ni) which are next heavily violate the permissible limits. The last cluster C, comprised of the heavy metals that have not violated the permissible limits except the variable Zn which in some samples violates the limit, therefore, it is appear in an individual link with cluster C.

Cluster Analysis (Q-mode):

The purpose of conducting this mode of analysis is to finding out the similarity between samples one or all cases depending on measuring the Euclidean distance. The rate of resemblance among samples increased when the distance became closer and vice versa (AL-Gieali,1989). This is done by comparing samples with each other depending upon their variables. It is provided in applying this mode that the number of these samples is greater than the calculated variables for each sample or at least be equal in number (Aqrawi and Al-Basree 1988). The number of samples in this analysis is amounted to 44 ones of 7 variables (7 elements). Due to numerous numbers of samples, Q-mode analysis results are classified cases into three main clusters A, B and C as shown in Fig.2.

Cluster A dominated by the tankers samples with only four samples of house tank. Cluster B included samples from all types of containers. Cluster C is dominated by coolers samples with only three samples of house tank. Thus, this mode assisted us to find out several groups representing the heavy metals samples from different places (sources).

Conclusions:

In the present work, the heavy metals concentration in the different types of containers of water is determined by using the atomic absorption spectrophotometer technique. The heavy metals considered in this study are Lead, Cadmium, Cobalt, Zinc, Copper, Mercury and Nickel. The results indicated that the concentration of lead, copper and Nickel violated the permissible limit detected by WHO, where as Cadmium, Cobalt and Mercury are less than the permissible limits. Also, it is observed that the concentration of Zinc is over the permissible limits in some cases in tanker and less than the limit at the rest.

The results of the heavy metals concentration are analyzed statistically by using cluster analysis. Cluster analysis, R – mode showed 3 major clusters, the first cluster (A), consists of the Lead only with distinctly more concentration and violates the permissible limit, while the second cluster (B) included Copper and Nickel which are next heavily violate the permissible limits. The third cluster consists of the heavy metals that have not violated the permissible limits. Cluster analysis, Q- mode; also, conduct three major clusters of cases (group of samples), each cluster representing samples from certain containers of analyzed variables.

From the above results and in order to reduce the concentration of the different types of heavy metals in the drinking water, it is highly recommended to follow the following steps:

1- Ensure a clean source for the cooler drinking water.

2- Recycling cleaning of the cooler drinking water.

3- Exposure to aeration at least every three days.

4- Blow down every day.

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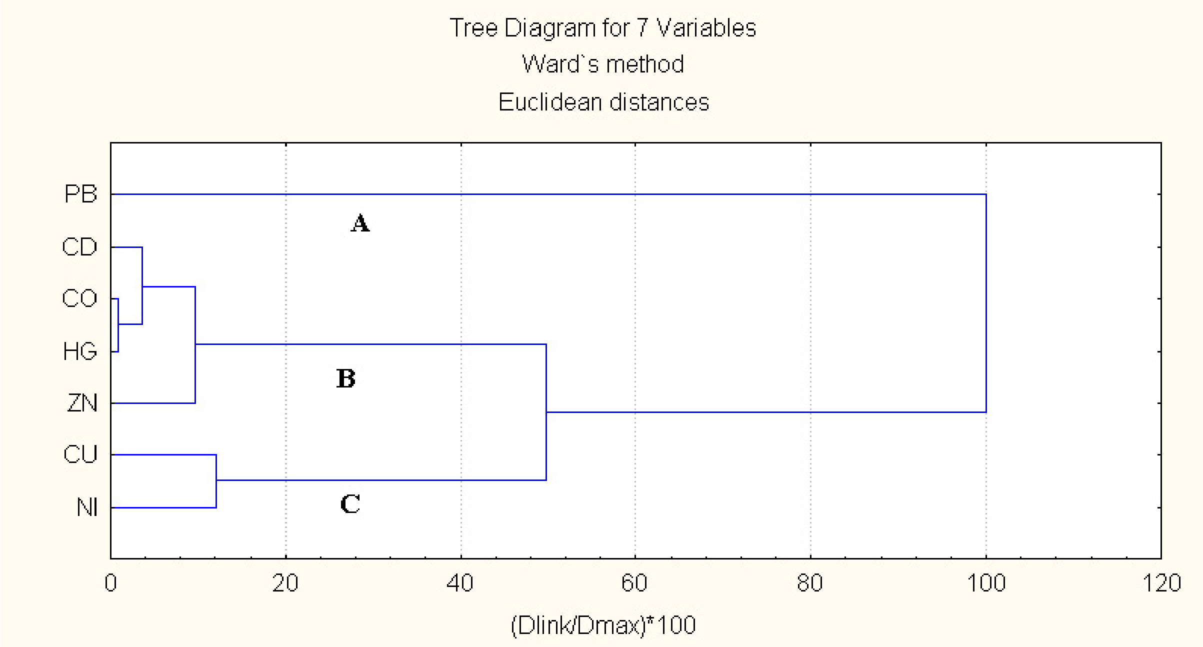

Fig. 1 The Cluster Analysis R-mode for Heavy Metals Concentration in Drinking Water.

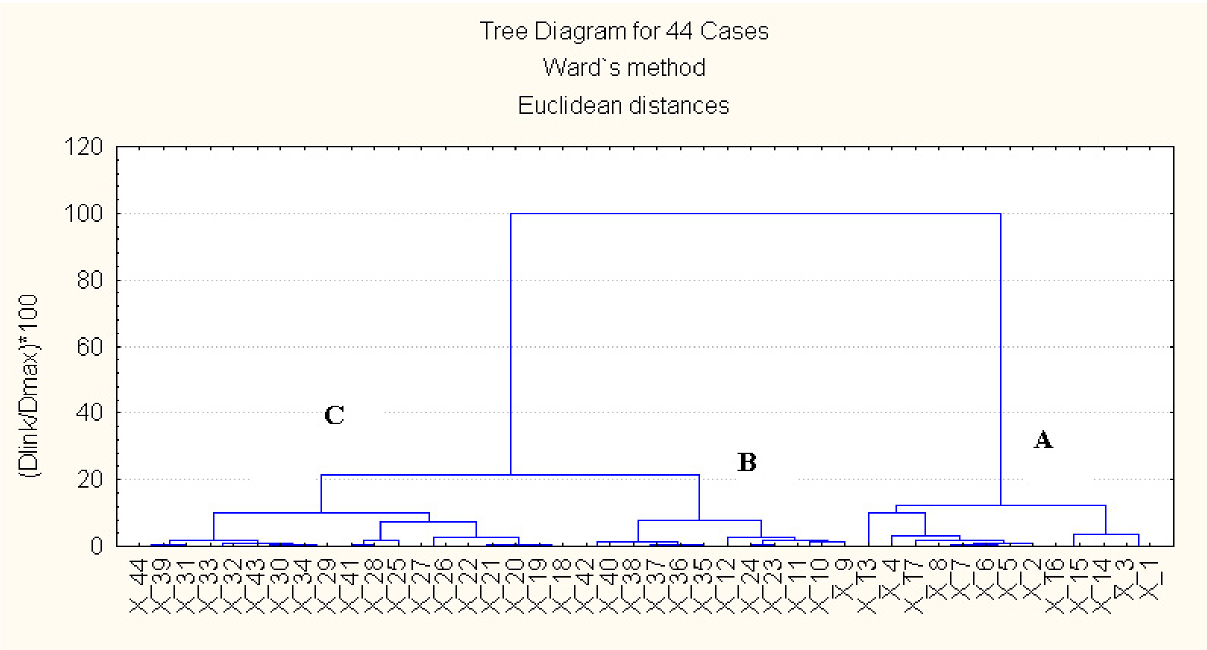

Fig. 2 The Cluster Analysis Q-mode for Heavy Metals Concentration in Drinking Water.