Original Article

Determination of cyanide and nitrate concentrations in drinking, irrigation, and wastewaters

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Background: The chemical contamination of water is a major concern for the environmental and health authorities globally. Some anions present in the water are required for human health, but some of them are harmful. Free cyanide and nitrate are amongst the toxic agents in the aquatic environment. Cyanide is highly toxic for human beings. Industrial plants could be attributed to a major source of these toxic agents. Therefore, cyanide and nitrate concentrations in the drinking and irrigation water wells in the high industrial plants were evaluated. **Materials and Methods:** The samples (57) were taken from drinking and irrigation water wells as well as from a wastewater refinery in north of Mashhad in three stages – March 2009, June 2010, and July 2010. Determination of cyanide and nitrate were performed by a spectrophotometer using commercially available kits according to the manufacturer's protocols. **Results:** Cyanide and nitrate concentrations in the drinking water samples of the three stages were 0.0050 ± 0.0007, 0.0070 ± 0.0018, 0.0008 ± 0.0014 mg/L and 6.50 ± 2.80, 7.20 ± 1.80, 7.50 ± 1.90 mg/L, respectively. Cyanide mean concentration during March, June, and July was significant ($P = 0.001$), whereas nitrate mean concentration was not ($P = 0.5$). Cyanide and nitrate concentrations in the irrigation water samples of the three stages were 0.0140 ± 0.0130, 0.0077 ± 0.0025, 0.0087 ± 0.0047 mg/L and 12.37 ± 8.12, 8.04 ± 3.99, 8.40 ± 2.60 mg/L, respectively. Cyanide ($P = 0.754$) and nitrate ($P = 0.705$) concentrations were not significant during three occasions. Cyanide and nitrate concentrations in the wastewaters of the three stages were 0.1020 ± 0.033, 0.1180 ± 0.033, 0.1200 ± 0.035 mg/L and 1633.80 ± 40.74, 279.00 ± 152.17, 298.40 ± 304.74 mg/L, respectively. Cyanide ($P = 0.731$) and nitrate ($P = 0.187$) concentration in wastewaters were not significant during different months. **Conclusion:** Although nitrate and cyanide concentrations in the drinking and irrigation water were within the standard range (0.07 mg/L for cyanide and 50 mg/L for nitrate) and was not a health problem at the time of our study, regular estimation of the toxic chemicals due to the development of industrial plants in this area is recommended.

Key words: Cyanide, drinking water, human health, irrigation water, nitrate, wastewater

INTRODUCTION

Water is essential for human survival and important to many sectors of the economy. Therefore, contamination of water resources should be a matter of concern to the human health.[1] Some anions present in the water are needed for the body, but sme of them are harmful.[2]

Cyanides, which are powerful poisons, can both occur naturally – by certain bacteria and algae– or be man-made. Many of the cyanides in soil and water come from industrial processes like electroplating, metallurgy, production of organic chemicals and plastics, photographic developing, and mining. The primary source of cyanide in the air is from car exhaust. Smoking is another important source of cyanide.[3,4] Common toxic cyanide compounds include hydrogen cyanide gas (HCN), potassium cyanide, and sodium cyanide.[5] At pH less than 8, cyanide exists in water as HCN, which is more harmful to aquatic life than the free cyanide ion.[6] HCN is also a chemical warfare weapon.[7] The cyanide toxic effect is due to its reaction with the trivalent iron in the cytochrome oxidase (cyt aa3) to inhibit electron transport and thus preventing the cells from consuming oxygen, leading to rapid impairment of the vital functions.[8] Several cyanide poisonings in fire cases, which led to death, have been reported. Hyperbaric oxygen (HBO), hydroxocobalamin, dicobalt-EDTA, 4-Dimethylaminophenol (DMAP) are cyanide antidotes, which are effective in experimental and human cyanide poisoning.[9]

Nitrogen in the forms of nitrate, nitrite, or ammonium is a nutrient needed for the plants growth. Nitrate is the common form of nitrogen found in natural waters. The greatest use of nitrates is as fertilizers. Once taken into the body, nitrates are converted to nitrites.[10] High intake of nitrates in drinking water can be potentially toxic to young infants under 3 months of age (blue baby syndrome) or livestock.[11] Under certain circumstances, nitrate can be reduced to nitrite in the gastrointestinal tract, which reacts directly with hemoglobin to produce methemoglobin, consequently impairing

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oxygenation.[12,13] Nitrate through sewage and fertilizers are the vast majority of water contamination. Chemical fertilizers are commonly used by farmers in rural areas. Groundwater contamination by nitrates is a main problem associated to the use of fertilizers in intensive agriculture.[14]

Since acute effects of high doses of cyanides and nitrates are clearly established and chronic exposure could possibly lead to deleterious effects, there is a need to evaluate cases of contamination by cyanide and nitrate in order to propose adequate preventive measures and public health interventions.

Numerous analytical techniques have been proposed for direct and indirect determination of cyanide and nitrate. Spectrophotometry,[7,15] flow injection spectrometry,[8,16] and fluorescence methods[17] have been used for cyanide determination. Moreover, spectrophotometry,[18] coloric methods,[14] and ion chromatography[19] have been used for nitrate measurement.

Some parts of drinking tap water of Mashhad city are coming from water wells of an area near Mashhad called Dashte Mashhad (DM). Most of the irrigation waters for agriculture in this area are also from the irrigation water wells of DM. There is also a wastewater refinery (Parkand-Abad) close to DM. The effluent of the refinery enters the Kashaf River. The water of Kashaf River has been used for irrigation of vegetables in this area. Common diseases which may be related to cyanide and nitrate are histotoxic hypoxia[20] and methemoglobinemia,[3] respectively. High concentrations of cyanide and nitrate in water were assumed to be a major source for chronic toxic human exposure. Toxic chemical residues in the vegetables of north-east part of Iran (Mashhad) have been a major concern for recent years. The local media warn the agricultural, environmental, and health authorities on this matter. There was no estimation of toxic chemicals in the irrigation water. We thus aimed to carry out the present study to evaluate cyanide and nitrate concentrations in the drinking and irrigation water wells and also in the entrance and effluent of the refinery by spectrophotometric methods.

MATERIALS AND METHODS

Study design

DM covers an approximate area of 3351 km^2 and is located in the north-east of Iran. DM is one of the most industrialized urban areas in Mashhad. It is confined to Kashaf River and Hezar Masjed, Kopedagh Mountains in the north and continuous mountains to central desert in the south [Figure 1]. The study area chosen represents an important hot spot of chemical industries in Mashhad.

Possible contaminant source areas and the probability wells being affected were the criteria in selecting 19 different wells, which consisted of 10 drinking wells, 4 irrigation wells, and 5 wastewater samples. Wastewaters are consisted of industrial town waste, two input to the refinery (W2 and W3), output of the refinery (W4), and refinery encountering the Kashaf River. Sampling was performed at the selected points in three stages, and a total of 57 samples were measured for cyanide and nitrate. Water samples were collected using 1 L polyethylene bottles, labeled and stored in the refrigerator until testing. In the current study, determination of cyanide and nitrate were performed using spectrophotometry method.

Instrumentation

Determination of cyanide and nitrate concentrations was performed via colorimetric method using DR-2800 Hach Spectrophotometer and commercially available colorimetric kits according to the manufacturer's protocols.

Statistical analysis

Data analysis was performed using SPSS version 11.5 (SPSS Inc. Chicago, Illinois, USA). Then, concentration of each type of wells (drinking, irrigation and wastewater) were compared by ANOVA test among the different months, and in case of significant results, POST-HOC Bonferoni test was used to compare each two individual months. Values reported are means ± standard deviation (SD), and P values less than 0.05 were considered significant.

RESULTS

Measured concentration of cyanide and nitrate in the drinking, irrigation, and wastewater samples of DM are summarized in Tables 1 and 2, respectively. Cyanide and nitrate levels were compared to maximum contaminant limit (MCL) provided by the WHO criteria,[21] 0.07 mg/L for cyanide and 50 mg/L for nitrate.

Distribution of cyanide and nitrate concentrations in Mashhad Dasht water samples is monotonous in drinking and irrigation water samples [Figures 2 and 3].

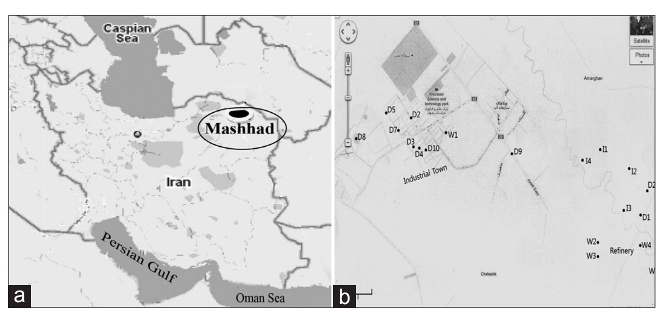

Figure 1: (a) Dashte Mashhad, Mashhad City, (b) Overall view of sampling stations

Cyanide and nitrate concentrations in drinking water samples during three occasions – March 2009, June 2010, and July 2010 - have been compared [Table 3]. Cyanide mean concentration in different months was significant ($P = 0.001$), whereas nitrate mean concentration in different months was not ($P = 0.5$).

Furthermore, cyanide concentrations have been compared in each two individual months [Table 4]. Cyanide mean difference in March 2009 and June 2010 was 0.002, which is significant ($P = 0.02$). Moreover, cyanide mean difference in March 2009 and July 2010 was 0.002, which is significant ($P = 0.008$).

Cyanide and nitrate levels in irrigation water samples and wastewaters during three occasions were compared [Table 5]. Cyanide ($P = 0.754$) and nitrate ($P = 0.705$) concentration in irrigation water samples were not significant during different months. In the same way, cyanide ($P = 0.731$) and nitrate ($P = 0.187$) concentration in wastewaters were not significant during different months.

DISCUSSION

Since a major source of chronic toxic chemical exposure is from drinking water and from fruits and vegetables which irrigated with contaminated water, it is essential to determine toxic chemicals in the water. Cyanide and nitrate are among the toxic chemicals that may contaminate the drinking or agricultural water. Based on our clinical observation in Mashhad, high concentrations of cyanide and nitrate were assumed to be a source for the health problems. Cyanide is a fatal compound, and its acute poisoning is usually readily diagnosed. However, chronic cyanide poisoning which comes from contaminated drinking water or from contaminated fruits and vegetables may well not be detected.[22] Acute nitrate intoxication in comparison to cyanide poisoning is much less severe, but chronic nitrate

Table 1: Cyanide concentration (mg/L) in water samples of Dashte Mashhad

Entry	Well	March 2009	June 2010	July 2010
1	D1	0.006	0.006	0.006
2	D2	0.005	0.010	0.009
3	D3	0.005	0.005	0.005
4	D4	0.006	0.006	0.006
5	D5	0.005	0.006	0.006
6	D6	0.004	0.007	0.006
7	D7	0.005	0.006	0.007
8	D8	0.004	0.006	0.006
9	D9	0.005	0.008	0.008
10	D10	0.005	0.010	0.009
11	I1	0.029	0.010	0.014
12	I2	0.005	0.008	0.005
13	I3	0.008	0.005	0.007
14	I4	0	0.020	0.018
15	W1	0.160	0.060	0.180
16	W2	0.100	0.130	0.120
17	W3	0.090	0.120	0.100
18	W4	0.080	0.140	0.100
19	W5	0.080	0.140	0.100

D=Stands for drinking water; I=Stands for irrigation water; W=Stands for wastewaters; Mean cyanide concentration in drinking water of Dashte Mashhad=0.006±0.001. Mean cyanide concentration in irrigation water of Dashte Mashhad=0.010±0.008. Mean cyanide concentration in wastewaters of Dashte Mashhad=0.113±0.032

Table 2: Nitrate concentration (mg/L) in water samples of Dashte Mashhad

Entry	Well	March 2009	June 2010	July 2010
1	D1	6.10	5.30	
2	D2	5.30	7.70	7.80
3	D3	9.50	7.50	5.60
4	D4	11.60	10.50	11.05
5	D5	5.00	6.40	6.70
6	D6	99.00	10.00	10.60
7	D7	5.00	5.80	5.60
8	D8	5.00	7.00	7.10
9	D9	4.70	6.00	7.30
10	D10	3.00	5.80	6.50
11	I1	16.70	12.60	11.40
12	I2	3.00	5.20	6.90
13	I3	17.40	6.30	7.00
14	I4	0	15.10	10.20
15	W1	317.00	550.00	842.00
16	W2	165.00	233.00	201.00
17	W3	144.00	212.00	145.00
18	W4	94.00	193.00	158.00
19	W5	99.00	207.00	146.00

D=Stands for drinking water; I=Stands for irrigation water; W=Stands for wastewaters; Mean nitrate concentration in drinking water of Dashte Mashhad=7.06±2.1. Mean nitrate concentration in irrigation water of Dashte Mashhad=9.31±5.5. Mean nitrate concentration in wastewaters of Dashte Mashhad=247.06±114.6

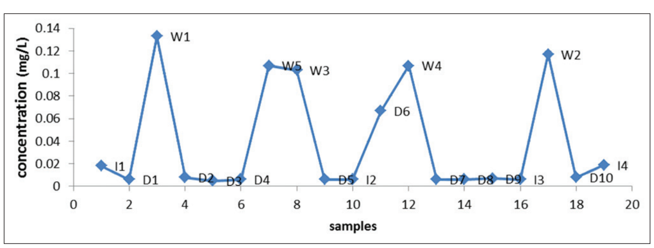

Figure 2: Distribution of cyanide concentration in the water samples of Dashte Mashhad, D=stands for drinking water, I=stands for irrigation water, and W=stands for wastewaters

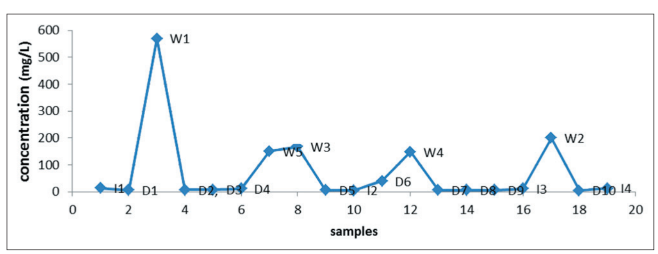

Figure 3: Distribution of nitrate concentration in the water samples of Dashte Mashhad, D=stands for drinking water, I=stands for irrigation water, and W=stands for wastewaters

Table 3: Comparing mean concentration of cyanide and nitrate in drinking water samples

Constituent	March 2009	June 2010	July 2010	Results
Cyanide (mg/L)	0.0050±0.0007	0.0070±0.0018	0.0068±0.0014	*P*=0.001
Nitrate (mg/L)	6.50±2.80	7.20±1.80	7.50±1.90	*P*=0.5

Table 4: Comparison of cyanide in drinking water samples in each two individual months

Months	Mean difference	*P* value
March 2009–June 2010	−0.002	0.02
March 2009–July 2010	−0.002	0.008
June 2010–July 2010	0	1

Table 5: Comparing mean concentration of cyanide and nitrate in irrigation and wastewaters

Constituent	March 2009	June 2010	July 2010	Results
Irrigation				
Cyanide (mg/L)	0.0140±0.0130	0.0077±0.0025	0.0087±0.0047	*P*=0.754
Nitrate (mg/L)	12.37±8.12	8.04±3.99	8.40±2.60	*P*=0.705
Wastewater				
Cyanide (mg/L)	0.1020±0.033	0.1180±0.033	0.1200±0.035	*P*=0.731
Nitrate (mg/L)	1633.80±90.74	279.00±152.17	298.40±304.74	*P*=0.187

exposure which comes from contaminated drinking water is more common.[23]

Cyanide enters air, water, and soil from both natural processes and industrial activities. Most cyanide in surface water will form hydrogen cyanide and evaporate. However, the amount of hydrogen cyanide formed is generally not enough to be harmful to humans. Some cyanide in water will be transformed into less harmful chemicals by microorganisms.[3]

Excessive nitrate exposure can result in acute acquired methemoglobinemia, a serious health condition. Sodium nitrate has not been directly implicated as a carcinogen. A metabolic pathway is available for nitrites to react with molecules in organisms to form N-nitroso compounds, some of which may cause cancer. Therefore, because of nitrate conversion to nitrite, a constant oral intake of nitrate-containing foods or water could lead to formation of carcinogenic N-Nitroso compounds.[3]

Several groundwater sites were examined in northern China where nitrate levels exceeded the limits allowed for drinking water.[24] Nitrate concentration in the drinking water samples from Kohdasht region of Lorestan, Iran were at the range of WHO guidelines with a maximum of 41.36 mg/L.[25] A recent study in Tabriz, Iran found the maximum of 0.0069 mg/L cyanide concentration in industrial effluents.[26]

In our study, mean cyanide and nitrate levels in drinking water samples during three stages were 0.006 ± 0.001 and 7.06 ± 2.1, respectively. According to the WHO guidelines for water quality, cyanide and nitrate concentration in drinking water samples were below the permissible limit [Tables 1 and 2]. Cyanide and nitrate regulations in irrigation water were not found in the US EPA Guidelines for Water Reuse, FAO Water quality for Agriculture, Alaska Water Criteria, and Guidelines for Canadian Drinking Water Quality. Therefore, only the WHO Guidelines in drinking water were used to compare irrigation water samples. Measures of cyanide and nitrate in irrigation water samples did not exceed the MCL [Tables 1 and 2]. We observed a low level of cyanide and nitrate in March 2009 in comparison to the other months. This could be as the result of more rain in March. However, even in June and July 2010, it was within the normal limit.

Monitoring of cyanide and nitrate in drinking, irrigation, and wastewaters is highly demanded for environmental control. Based on cyanide and nitrate concentrations in the drinking and irrigation water wells, it seems that industrial town had no major contamination effect. W2 and W3 are input effluents to the refinery, and W4 is output effluent of the refinery. Having compared these data, it is considered that clearance in the refinery has not been successful.

Although cyanide and nitrate concentrations in the drinking and irrigation water wells under the existing circumstances were within the standard limits, the development of industrial factories and their wastes may contaminate the underground waters in the long term. This can make a health problem via contaminated waters, fruits, or vegetables in the future. In addition, high levels of cyanide and nitrate in the wastewaters and its penetration to the soil may contaminate the water wells in the coming years. Therefore, regular estimation of cyanide and nitrate and other toxic elements in drinking and irrigation water wells of DM is recommended. The agricultural, environmental, and health authorities should act accordingly with co-ordination.

Limitations

Due to technical difficulties and lack of co-ordination between the relevant organizations, it was not possible to carry out samplings in regular months. In the current study, the concentration of cyanide and nitrate in whole of drinking, irrigation, and wastewater were determined as a mean level. Consequently, there was no need to special statistical analysis. However, data were analyzed during different months by ANOVA.

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