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Comparison Atrazin concentration levels in the water at the inlet to the bottled water factories and water treatment plant No. 2 in Ahvaz City and outlet water of them after the water treatment process

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Abstract

Background: Atrazin is one of the water pollutants and used in sugarcane, pineapple and banana cultivation. The aim of this research was to measure Atrazin concentration levels in the water at the inlet to the Anahita and Byblus bottle water factories and water treatment plant number 2 (WTP2) in Ahvaz City and outlet water of them after the water treatment process. **Materials and Methods**: For this purpose fourteen composite water samples (each comprising five grab samples) were collected from each of six types water during five months (September 2013, and January-April 2014). The pH of 100 ml of each of water was adjusted to 2 by addition of phosphoric acid. After adding 5gr sodium chloride the samples were mixed well and percolated through the conditioned C18 SPE column with 10ml methanol and water respectively, under vacuum. Then the column was washed with 5ml of water, the elution discarded, the sorbent bed dried and finally the bonded Atrazin in all of the samples were eluted with 1ml of methanol. Then methanol was evaporated under nitrogen and the residue was dissolved in 1ml of mobile phase and was analyzed by HPLC using a C18 column with a UV detector at 230nm, mobile phase of methanol-water (60:40) at pH 4.6 and a flow-rate of 1.1ml/min. **Results:** The mean concentrations of Atrazin in investigated water at the inlet and outlet of WTP2, Anahita and Byblus bottled factories were(4.286, 3.444), (.405, .330) and .0607, 0.0092 ppb),respectively. The average concentration of Atrazin in studied water at inlet of WTP2 and outlet water from it were higher than the Maximum Tolerable Limit for Atrazin set for drinking water (0.1 pp) by World Health Organization.**Conclusion:** The results showed that Atrazin removal process by Anahita and Byblus bottled water factories well done, but the reduction of Atrazin concentration was not statistically significant in Ahvaz WTP2.

Keywords: Herbicide, Atrazin, Bottled water, HPLC, water treatment plant.

1. Introduction

Pesticides have played a key work in the world's increasing crop yields. Herbicides are used in agriculture to kill weeds or other plants that grow where they are not wanted. The triazine herbicides are used for pre- and post-emergence weed control. Today, more than 30% of all agricultural herbicides are triazines. Table 1 shows the major triazine herbicides and their uses. S-Triazine derivatives are among the most important selective herbicides. S-Triazine, and their metabolites, are very toxic, highly persistent, have accumulation potential and remain in the environment for many years(1). 2-ethylamino-4-isopropylamino-6-methythio-s-triazine with trade names Ametryn, Gesapax, Almulex, Ametrex and Evik belongs to the s-Triazines herbicide family. The

World Health Organization (WHO) classifies it as toxicity class II, which is moderately hazardous. Atrazin is used for the control of broad leaf and grass weeds in corn, sugarcane, banana, pineapple, and plantains (2). Due to it wide spread use, it has been detected in the surface and ground water resources.

Table 1: Major Triazine herbicides and some of their uses

Triazine herbicide	Uses
Ametryn	Sugarcane, corn, pineapple
Atrazine	Corn, sorghum, sugarcane
Hexazinone	Alfalfa, sugarcane, forestry, noncropland
Metamitron	Sugarbeet, other beet crops
Metribuzin	Sugarcane, potato, soybean
Prometon	Noncropland
Prometryn	Cotton, celery
Simazine	Corn, citrus, grape, apple, almond, walnut, peach
Terbuthylazine	Corn, sorghum, grape

Nowadays the consumption of bottled water has been increasing among people (2-5). People believe that bottled water is safer than tap water (6-8).

Karun River water provides the drinking water source for many cities at khuzestan province The Karun River is the largest river in Iran. It lies in the west of Iran and flows from north to south until it impounds into the Persian Gulf. The other source of drinking water in this province is bottled water produced by Anahita and Byblus factories. This research was done to compare Atrazin concentration levels in the water at the inlet to the Anahita and Byblus bottle water factories and water treatment plant number 2 (WTP2) in Ahvaz City and outlet water of them after the water treatment process.

2. Materials and Methods

2.1. Chemicals

Atrazin was obtained from Sigma–Aldrich (UK). The methanol (Merck) was HPLC grade. NaCl and H_3PO_4 (analytical grade) were purchased from Merck Co. The Extraction cartridges were C_{18}(silica- octadecyl) from Capital Co. 500mg/5ml.

2.2 Sampling:

For this research, fourteen composite water samples (each comprising five grabs samples) were collected from each of water at the inlet to the Anahita , byblus bottled water factories, water treatment plant number 2 (WTP2) in Ahvaz City and the outlet water of them after the water treatment process (six types water) during five months (September 2013, January-April 2014).

2.3.Apparatus

The Shimadzu 10ADvp HPLC system (Japan) was equipped with a Shimadzu RF-10AXL fluorescence detector. Shimadzu LC-10 ADvp pump, isocratic mode, Shimadzu DGU-14A Degasser, Shimadzu SCL-10Avp System Controller, Shimadzu FCL- 10ALvp flow controller, LC solution software. The column (4.6 × 150 mm), which was packed with particles of silica modified with octadecylsilyl groups (5 µm in diameter), was purchased from Capital, Co., England.

The pH of the mobile phase was measured using a *pH meter* (*Corning pH meter*, *Model* 7, *Corning* Ltd, *England*).

2.4.Procedure

Stock standard solution of Atrazin was prepared in methanol at concentration 40 ppm. Atrazin working standard solutions were prepared by serially dilution of stock standard solution in mobile phase at the concentrations ***(***400, 200, 100, 50, 20, 10, and 5 ppb***).***

The mobile phase was comprised %60 methanol and 40%water (v/v) and the pH was adjusted to 4.6 with concentrated H3PO4.

The pH of 100 ml of each of collected water was adjusted to 2 by addition of phosphoric acid. After adding 5gr sodium chloride the samples were mixed well and percolated through the conditioned C18 SPE column with 10ml methanol and water respectively, under vacuum. Then the column was washed with 5ml of water, the elution discarded, the sorbent bed dried and finally the bonded Atrazin in all of the samples were eluted with 1ml of methanol. Then methanol was evaporated under nitrogen and the residue was dissolved in 1ml of mobile phase and 20 µl of each of the extracted solutions was injected into the HPLC. Wavelength was set on 230 nm. Methanol–water (60:40, v/v) at pH 4.6 (phosphoric acid) was used as mobile phase at the flow rate of 1 ml/min. Atrazin peak in the chromatogram was identified by comparing its retention time with that of the analyzed Atrazin standard under the same conditions.

The peak was quantified from the area under the curve of sample chromatogram by using the equation of calibration curve ***(***y = 147.067*X+107.49, R^2= 0.999331***).*** Calibration curve was drawn at concentrations 400, 200, 100, 50, 20, 10, and 5 ppb. The limits of detection (LOD) and quantification (LOQ) before and after preconcentration were ***(1.5, 0.015)*** and (***5, 0.05 ppb***) ppb respectively. Recovery was performed by the standard addition method. For this purpose 1 ml of each standard solution at concentrations ***5, 50 and 400***ppb (6 repeats for each level) were transferred into 100 ml volumetric flaskses and evaporated under nitrogen gas. The residues in the volumetric flaskses were diluted to the mark by adding the required amount of one of the water samples whose content of Atrazin was being analyzed. Then, the procedures above were followed. The results are summarized in Table 2. All recoveries were more than ***93.5%,*** indicating good accuracy. Intra-day and inter-day precision is shown in Table 2. All measurements were repeated 6 times. The %RSDs of intraday and inter–days analyses were in the ranges of ***3 – 1.3*** and ***6.8 – 4.1*** respectively. These data indicated that the method has acceptable precision.

2.5. Statistical Analysis

The data were expressed as mean ± standard error of mean and were analyzed with Statistical Package for the Social Sciences ($SPSS_{20}$) software.

The differences between the concentrations of Atrazin in the investigated water samples were applied using the independent samples Kruskal Wallis test and paired comparisons were performed by the Mann-Whitney- test if significant differences occurred. All tests were carried out at the 5% level of significance. The differences between concentrations of Atrazin in the investigated water samples with the Maximum Tolerable Limit (MTL) for Atrazin (0.1 ppb) set by WHO, were performed using One Sample T- test.

3. Results

The retention time for Atrazin under this condition was 4.55 min(Figure 1). The average recoveries, relative standard deviation (RSD %) for the intraday and inter days of the applied analytical methods for Atrazin in the tested water samples are shown in Table 2. All the recoveries were more than ***93.5%***, indicating the high accuracy of the method. The highest mean concentration of Atrazin in the tested water samples was ***5*** ppb (Table 3). The mean concentrations of Atrazin in investigated water at the inlet and outlet of WTP2, Anahita and Byblus bottled factories were ***(4.28 3.44),*** (***0.40, 0.32***) and (***0.06, 0.009 ppb***), respectively (Table 3). Atrazin mean concentrations in tested water samples of inlet and outlet of WTP2 were significantly higher than the MTL for Atrazin (***0.1*** ppb) set by WHO (Table5). Atrazin mean concentrations in tested water samples of outlet of Anahita, inlet ad outlet of Byblus factories were significantly lower than the MTL(Table5). There were significant differences between the Atrazin concentrations in the tested water samples (Table 4).

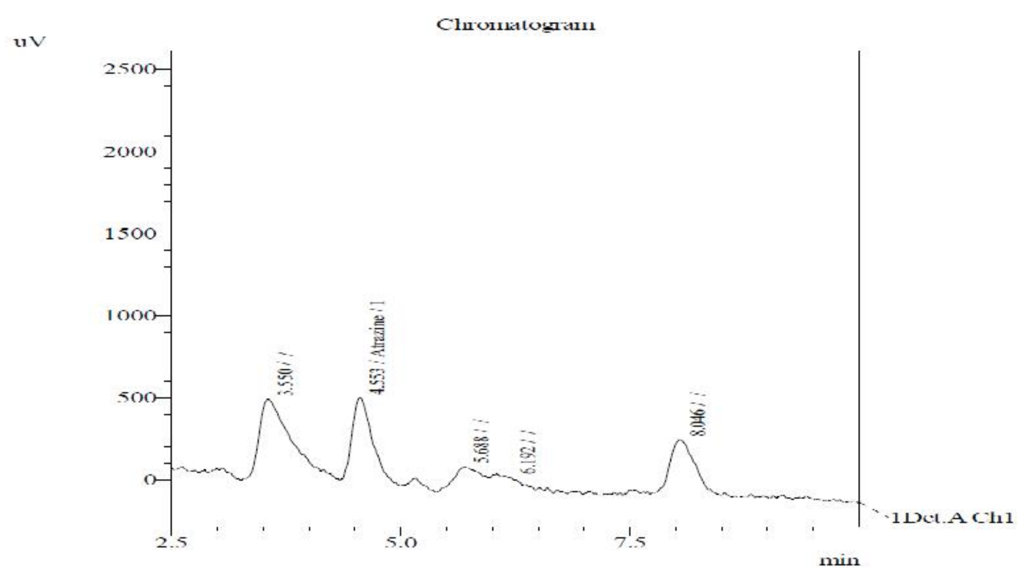

Figure 1 Chromatogram showing Atrazin standard (50ppb). Mobile phase: Methanol–water (60:40, v/v) at pH 4.6, flow rate 1.1 ml/min, wavelength = 230 nm, injection volume = 20 µl

Table 2: Intraday, Inter days RSD % for investigated concentrations of **Atrazin** standard solution at ranges (***5 - 400*** ppb) and recovery from spiking into the one of the water samples at concentrations (***5, 50 and 400ppb***) (n = 6).

Atrazine concentration(ppb)		**5**	**10**	**20**	**50**	**100**	**200**	**400**
RSD%	Intraday	3	2.9	2.3	2	1.8	1.8	1.3
	Inter days	6.8	6.1	5.8	5.1	4.7	4.7	4.1
Spike levels(ppb)		4.68				75		
Mean Recovery%		93.5				95.2		

Table 3: Descriptive statistics of data about Atrazin concentration in investigated water samples.

Atranzine Concentration(ppb)		**Type water**					
		Karun at inlet to WTP 2	**from outlet of WTP2**	**at inlet to Anahita factory**	**from outlet of Anahita factory**	**at inlet to Byblos factory**	**from outlet of Byblos factory**
Mean		4.2857143	3.4442857	.4050000	.3292857	.0607143	.0092857
95% Confidence Interval for Mean	Lower Bound	.8888739	1.8268785	.1877823	.0932643	.0098489	-.0043897
	Upper Bound	7.6825547	5.0616930	.6222177	.5653071	.1115797	.0229611
Median		1.7000000	2.8800000	.4400000	.2500000	.0200000	0E-7
Variance		34.612	7.847	.142	.167	.008	.001
Std. Deviation		5.88316858	2.80127365	.37621087	.40877800	.08809648	.02368521
Minimum		.89000	.09000	.00000	.00000	.00000	.00000
Maximum		18.70000	6.74000	1.02000	1.37000	.28000	.07000
Range		17.81000	6.65000	1.02000	1.37000	.28000	.07000
Skewness		2.121	.036	.198	1.927	1.724	2.328
Kurtosis		3.312	-2.031	-1.539	3.105	2.349	4.050
Std. error of Mean		1.57234294	.74867187	.10054658	.10925052	.02354477	.00633014

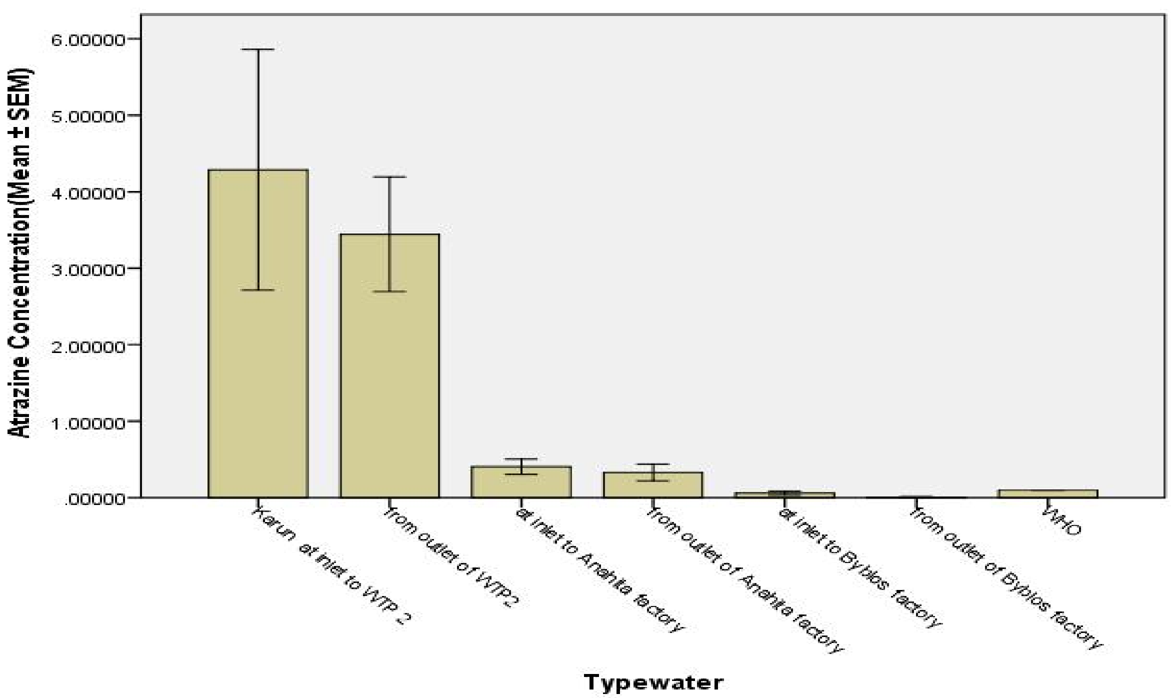

Table 4: Comparison the average of Atrazin concentrations in the tested water with the MTL set by WHO for **Atrazin**

Discussion

Almost all of the planet's water (97%) exists in the oceans. Of the remaining 3%, occur as snow and ice in polar and mountainous regions, which leaves only about 1% of the global water as liquid fresh water. AT the beginning period of civilization, surface water was the only source for usage and was relatively clean. But nowadays the contamination of water, ground water, water of river and springs is one the most important problems in the world (2-4, 9-11).

The consumption of bottled water has been increasing. Why do people consume bottled water? One of the reasons is invalid reports of the water supply contamination (4). Many consumers believe bottled water is better than tap water (5). But, contamination of bottled water has been documented in many scientific literatures (3, 12-14). People pay the cost of bottled water, so they have a right to kwon what chemicals are in the water. Clean water is one of the basic needs of the people. Therefore, many researchers have been investigated toward this path. R. Carabias-Mart´ınez et al. developed solid phase extraction and non-aqueous capillary zone electrophoresis method for measuring triazine herbicides in natural waters(15). M.C. Bruzzoniti et al. optimized a solid phase extraction (SPE) method for the gas chromatography–mass spectrometry (GC–MS) for simultaneous determination of herbicides belonging to the following different families: carbamate (molinate), atrazines (atrazine, propazine, simazine, atrazin, cyanazine, terbutylazine, deethylterbutylazine, deethylatrazine), dinitroaniline (trifluralin, pendimethalin), chloroacetamide (alachlor, metolachlor)(16). John R. Dean et al. have reviewed the extraction and subsequent chromatographic analysis of the triazine herbicides from environmental samples. They focused on the extraction of the herbicides from aqueous samples(17). Berg, Michael et al. monitored pesticides in groundwater (the primary source of potable water on the island) for the dry seasons of March–June, 1991 and January–May, 1992 and the wet season, July–December, 1992.They detected residues of either Atrazine or Atrazin in all 277 groundwater samples collected from 23 wells in three major groundwater catchments underlying heavily cultivated sugar cane fields. The concentration of AT and the metabolite deethylatrazine (DEAT) were in the range 0.11–2.61μg/l(18).

The aim of this research was to measure and compare Atrazin concentration levels in the water at the inlet to the Anahita , Byblus bottle water factories and water treatment plant number 2 (WTP2) in Ahvaz City and outlet water of them after the water treatment process.

The highest concentrations of Atrazin(2.46 ppb) belonged to Karun river water at inlet to WTP2 (figure 2 & Table 3).

According to the results, the mean concentrations of Atrazin in investigated water at the inlet and outlet of WTP2, Anahita and Byblus bottled factories were (4.28, 3.44), (0.4, 0.33) and (0.06, 0.009 ppb), respectively. The average concentration of Atrazin in studied water at inlet of WTP2 and outlet water from it were higher than the Maximum Tolerable Limit for Atrazin set for drinking water (0.1 pp) by WHO(Table 3, 5). The results showed that the mean Atrazin concentration in the Outlet water from Anahita, inlet and outlet water of Byblus were significantly less than the MTL of 0.1 ppb (Table.3,5).The results showed that Atrazin removal process by Anahita and Byblus bottled water factories well done, but the reduction of Atrazin concentration was not statistically significant in Ahvaz WTP2(Table.3,5). The estimated daily intake of Atrazin from water depends on both the Atrazin concentration in water and the daily water consumption. In addition, the body weight of the human can influence the tolerance of contaminants. The estimated daily Atrazin mean intake from each of the tested outlet water by a person is calculated as follows:

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