

## Evaluation of Pesticide Residues 2,4-D, Atrazine and Alachlor Concentration in Drinking Water Well of Mahidasht District-Kermanshah, Iran, 2010-2011

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**Abstract:** Nowadays, Pesticides include 2,4-D, Atrazine and Alachlor toxins among chemical compounds extremely used in different issues especially against the weed plant. However, their penetrating into the environment as well as water sources lead to severe health impact and environmental problems. According to the use of pesticides in agricultural land in Kermanshah as well as considerable extraction of ground water by the locals, it enters into water wells. Therefore, the use of pesticides in the province could be a serious threat for drinking water resources. The present study aimed to determine the concentration of pesticide residues (2,4-D, Atrazine and Alachlor) in ground water sources of the Mahidasht district in Kermanshah. In this study, a total of 120 water samples were collected from 5 deep water wells in Mahidasht areas of Kermanshah between 2010-2011. The samples were measured in terms of pesticide residues using dispersive liquid-liquid micro extraction and HPLC instrument. The obtained results showed that the highest concentration of 2,4-D and Alachlor toxin were 58.2 and 26.7 ( $\mu\text{g/L}$ ) ppb, respectively. Therefore, it was more than the standard level suggested by the World Health Organization (WHO) and Industrial Researches Standard of Iran. Statistical analysis using One-way ANOVA indicated that there were significant differences between average concentration of samples based on different seasons and area ( $P < 0.05$ ). According to achieved results and the direct relationship between pesticide consumption and their penetration into drinking water sources, it can be concluded that controlling and monitoring policy needs to be performed by authorized organizations.

**Key words:** Toxin • 2,4-D • Atrazine • Alachlor • Groundwater sources • HPLC • Kermanshah

### INTRODUCTION

Nowadays, pesticides are extensively used to control agricultural, medical and domestic pests regardless how they are used and finally enter into the soil and the environment. Meanwhile, the pesticides are absorbed by plants and enter the food chain, and it can be distributed to far distances by wind or rainfall, consequently enter into surface and groundwater [1]. However, the main purpose

is protecting water, soil and food resources, regarding new found diseases in human, as well as preventing the over use of groundwater resources is required [2].

The organochlorine was the most pesticides which has been utilized till 1970, after that time a wide range of pesticides with a slight resistance to degradation were employed in agriculture, consequently decreased the surface and groundwater pollution [3]. In addition the inherent resistance of pesticides, water-soil system of

region, topography, constant cultivation, and also climate and environmental condition effects on pesticide behavior in water and soil of the area [4-6].

Among other natural resources, freshwater is a significant resource. In most urban regions, groundwater, as an acceptable resource, is available without any treatment for human consumption. But these water resources could be polluted via domestic, industrial and agricultural wastes such as chemical fertilizer and pesticide. So that, a number of studies found a significant relationship between concentration of pesticides and nitrate solubility in water resources with the quantity that have been used in farms [7, 8].

Monitoring studies as the most widely methods have been used in the groundwater pollution assessment and human exposure to this environmental chemical species. In order that, the pesticides measurement during groundwater monitoring in the U.S.A. and Europe showed that the groundwater were polluted with Atrazine, Cyanazine, Simazine, Alachlor, Metolachlor and Chlorophenoxyacetic acids (e.g. 2,4-D) [9-11]. Obtained results of 17 monitored toxins in the U.S.A. freshwater resources indicated that the toxicity was higher than the permissible level of the Environmental Protection Agency [12].

Tran A.T.K. *et al* (2005) in Australia found the simiazin, atrazine and diuron herbicides in all analyzed samples. Additionally, simiazin and diuron had the highest concentration level in all samples. Though, no concentration was exceeded than the authorized level in freshwater [13].

Kuster *et al* (2007) study in Spain recorded that the MCPA toxin and 2,4-D concentration were maximum in all monitoring samples. as well, all samples contained 2,4-D less than 100 ng/l and also the MCPA amount was 1.286 µg/l. The amount of MCPA was higher than the limited standard level of the EU and the amount of 2,4-D was in the threshold limit value [14].

Furthermore, Belmonte Vega *et al.* (2004) study in Spain investigated only 10 out of 32 monitored pesticides (about 30%) in the samples. Totally, 20% of analyzing water samples revealed positive values of pesticides which only 6% of it was above the limited standard level of the EU [15].

Khazaee *et al.* (2007) study on quality and safety of groundwater in Mazandaran (Iran) in term of using organophosphorous pesticides (diazinon) in Mahmoud Abad town area, the obtained results indicated that the measured concentration of diazinon in most analyzing water samples were higher than the standard level of WHO (0.1mg/l) [16].

Khodadadi *et al.* (2007) research on freshwater resources in Hamedan showed that the maximum concentration of carbaryl and chlorpyrifos pesticide in spring season and Jun were 1.8ppb and 58.3ppb, respectively. Consequently the results indicated that there was a significant difference between pesticide residues of samples in various seasons ( $p < 0.05$ ) [17].

However, The distance between water sources and toxin sprayed area and also precipitation rate are the factors that impact on polluted water with pesticides. Thereby, strong rainfall causes enter pesticides into groundwater [18].

According to above mentioned reasons the natural water resources could be polluted by various types of pesticides and derived metabolites from their decomposition. Chlorophenoxyacetic acids are highly toxic, as some Chlorinated metabolites are severely toxic for human and aquatic organisms. Meanwhile, 2,4-D is highly toxic and cause damage to the nervous system, liver, kidneys and adrenal glands which are resistant to microbial degradation [19].

However, 25 mg/kg of body weight of the 2,4-D toxin can be teratogenic (Deformed generator). And the average amount of toxicity of 2,4-D for birds is 300 to 2000mg per each kg of body weight. The maximum limited level of MCLG and MCL for 2,4-D about 70 ppb (70 parts per billion) is recommended by The EPA for prevention these potential problems [20].

Alachlor is one of the other pesticide which is used for controlling weeds and also to control grasses and broad leaf plants and sorghum, soybean oil among cereals and other growing products, annually. However, over using of Alachlor cause entered it into groundwater and polluted it. Thereby, drinking this polluted water for long time lead kidneys, eyes and spleen damage or even anemia and cancer in consumers. Although, Some reports are confirmed the nasal tumors in rats due to constant contact with alachlor toxin. The major chronic toxicity of alachlor has a toxic effect on the blood circulation system.

Turbinate tumors in the nose and gastric and thyroid have been reported in laboratory animals because of the severe toxicity of this pesticide. Alachlor half-life in soil, waters 30 and 200-500 days, respectively, and in the air is 2.544 hours. The reason of being short half life in soil is due to bio degradation and photolysis. However, they cannot easily be degraded in water and also it is not a problem in the air due to its nonvolatile properties. Acute toxicity of Alachlor for aquatic animals is 1.7mg/l for fish

up to 65 mg/l for aquatic plants. Also, its Acute toxicity for bees and other arthropods is 90 -100 µg per each bee [ 21]. The rate of MCLG and MCL for alachlor, 0 and 2 ppb has been recommended by The EPA to prevent the mentioned problems [22-24].

Triazines known as the most important pesticides and widely used for weed control. And also found as a pollutant in all types of soils, water resources and environment. There is much concern about this pesticide because it is soluble in water and can enter ground water by movement and also it could be absorbed by soil [25].

These toxins and their products made by their degradation found in water, soil and microorganisms. Atrazine is one of the triazin components, which is identified as a human carcinogen and causes trouble for cardiovascular and reproduction. Furthermore, consume polluted water with the amount more than the atrazine MCL level in short time creates heart and lung congestion, kidney damage, muscle spasms, weight loss, tremors and paralysis in organs, breathing problem, high temperature of the body and damage to the adrenal glands. And long-term consumption of polluted water with the amount higher than the MCL level cause weight loss, cardiovascular damage, retinal and some muscle damage and ultimately, cancer [26].

According to some reasons such as the characteristics of three mentioned pesticides and extensively used of those in agricultural regions of Kermanshah especially in Mahidasht (the rate of 2,4-D, Alachlor and Atrazine in Kermanshah were 500, 60 and 12 tons in 2005-2008, respectively) [27] existence many deep wells in this area (supplying the drinking water of Mahidasht district) [28] and importance the protecting of aquifers as the significant resources of available drinking water without required any treatment, the purpose of present study was monitoring the drinking water resources to identify the quality and pollution condition in term of widely using of herbicides in this area.

## MATERIAL AND METHODS

This study was a cross-sectional, descriptive-analytical investigation. Initially, the data about the area was collected to identify and selected the villages where the farm lands were around and above the water wells in Mahidasht district. Then the wells which were represented the whole aquifer of the region were selected. Totally, 5 water wells were chosen in four corners and middle of a region to sampling.

Therefore, 5 places ( Mahidasht district, villages such as Namivandoliya, AabasAabad, Rizevand and ZalkehAabasGholi ) have been chosen. A total number 120 samples were taken from June, 2010 to May 2011, twice a month. All samples were stored at 4°C and transferred to the research laboratory of public Health faculty of Kermanshah University of Medical Sciences for analyzing 2,4-D, atrazine and alachlor toxin residues. All analyzing and sampling were carried out according to standard method [29].

**Analyzing:** The samples were analyzed using dispersive liquid-liquid micro extraction method (DLLME) which was a new and the exact method. So, 5cc of filtered water (0.2µ filters) was taken and poured into conical tubes then 3µ of strong HCl was added till the pH reached 3. Then 1 ml of this solution injected into a conical tube and the turbid solution was obtained, which was due to the distribution of extractor solvent particles into aqueous solution. After that conical tube contain sample centrifuged with 5000rpm (round per minute) for 3-5 minutes in order to deposit chlorobenzene in bottom of conical tubes. Then the precipitated chlorobenzene draw out and transferred to a clean tube, and the chlorobenzene was vaporized by pure nitrogen gas till the volume reached 1ml.

This residue was re-dissolved in 50µL mobile phase (mobile phase consists of water and Acetonitrile with ratio 30 to 70) then the obtained solvent was injected to HPLC.

**Preparation stock Solutions and Instrument calibration:** To draw the calibration curve of each toxin, daily stock solution (dissolved toxins with 99.99% concentration in 1000 ppm methanol) was prepared, all toxic material purchased from Sigma-Aldrich Company, Germany.

**Concentrations Reading:** Toxins Measurement include, 2,4-D, atrazine and Alachlor carried out by the DLLME method [30] and HPLC. For reading the concentration of study toxins use liquid chromatography with high efficiency with 254nm wave length and UV detector, purchased from Knauer company, Germany. The using column inside the instrument was H5-ODSC18 with 15cm length, 4.6 mm diameter and particle size of 5µm made of Anachem company, England. The carrier phase included water and acetonitrile with ratio 30 to 70 and flow rate 0.5 ml/min.

**Enrichment Factor:** The standard curve of direct injection has been applied to achieve the enrichment factor and extraction efficiency. In order to, the standard solutions of toxins with concentrations of 0.5, 1, 1.5, 2 and 2.5 µg/ml in methanol were prepared. Then 30µL of each standard were injected to HPLC.

The concentration of compounds in sedimentation phase was obtained by draw calibration curves. The enrichment factor and The extraction efficiency were calculated using equation 1,2 [31].

$$E.F. = \frac{C_{sed}}{C_o} \quad (1)$$

EF=Enrichment factor

C<sub>sed</sub>=Concentration in sediment phase

C<sub>o</sub>=Initial concentration of analyst in aqueous solution

$$R\% = \frac{C_{sed} \lambda V_{sed} \lambda 100}{C_o \lambda V_{aq}} \div E.F. \lambda \frac{V_{sed}}{V_{aq}} \lambda 100 \quad (2)$$

=Percentage of extraction efficiency R%

V<sub>aq</sub>, V<sub>sed</sub> Volume of sediment and aqueous phase, respectively

(The detection limit for these 2 toxins has been calculated up to a concentration of 50 ng/l.)

**Method of Calibration Curve preparation in DLLME:**

To prepare a calibration curve, the extraction and analyzing of 6-7 standard solutions with different concentration from 0 to 300ppb have been carried out by HPLC instrument. then The calibration curves were drawn using under peak area of compounds against the standard concentrations of each compound.

The correlation coefficient (r<sup>2</sup>), linear range of the calibration curve (LR), limit of detection (LOD) (the LOD was achieved from 3 times to signal noise) for each toxin was obtained.

**RESULT**

The calibration curve result of toxins include 2,4-D, atrazine and Alachlor showed that there was a direct relationship between the concentration of toxins and under peak area of the curve (Fig. 1, 2, 3).

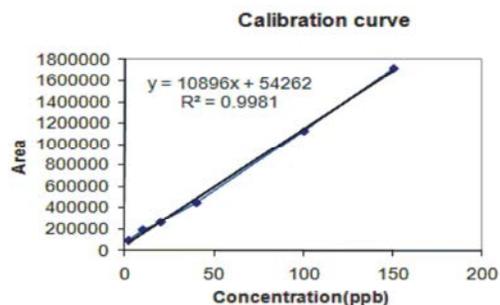


Fig. 1: Calibration curve for 2,4-D

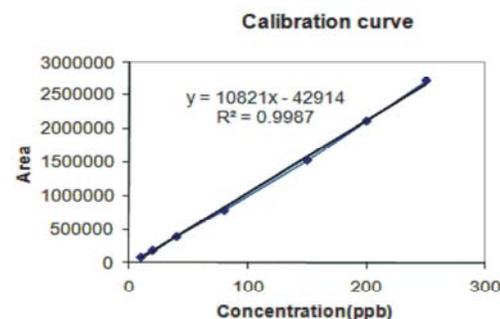


Fig. 2: Calibration curve for atrazine

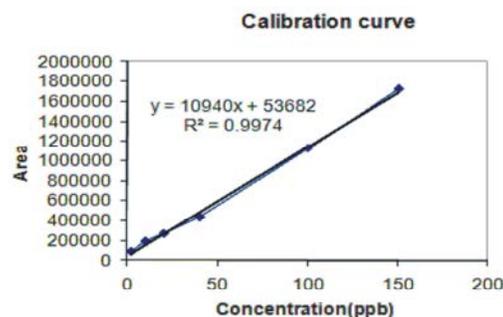


Fig. 3: Calibration curve for Alachlor

Table 1: Quantitative results of HPLC-UV and DLLME for determination of 2,4-D, atrazine and Alachlor in water samples

| Compounds | RSD <sup>1</sup> % (n=7) | EF <sup>2</sup> | ER <sup>3</sup> (%) | LR <sup>4</sup> (ppb) | (r <sup>2</sup> ) <sup>5</sup> | LOD <sup>6</sup> (ppb) |
|-----------|--------------------------|-----------------|---------------------|-----------------------|--------------------------------|------------------------|
| 2,4-D     | 6.2                      | 70.3            | 42.2                | 150-10                | 0.9981                         | 5.00                   |
| Atrazine  | 7.1                      | 63.8            | 38.3                | 250-20                | 0.9987                         | 10.0                   |
| Alachlor  | 5.6                      | 72.5            | 43.5                | 150-10                | 0.9974                         | 5.00                   |

<sup>1</sup>Relative standard deviation

<sup>2</sup>Enrichment factor

<sup>3</sup>Extraction recovery

<sup>4</sup>Linear range

<sup>5</sup>The Correlation Coefficient

<sup>6</sup>Limit of detection

Table 2: Values of monitoring toxins in Mahidasht region

| No. | Toxin    | (Mean) | (S.D)  | Maximum calculated value (ppb) | Minimum calculated value (ppb) |
|-----|----------|--------|--------|--------------------------------|--------------------------------|
| 1   | 2,4-D    | 3.97   | 11.033 | 58.2                           | 0                              |
| 2   | Alachlor | 2.081  | 5.643  | 26.7                           | 0                              |
| 3   | Atrazine | 0      | 0      | 0                              | 0                              |

Table 3: Obtained results from analysis of study toxins in Mahidasht due to place of sampling

| Name of well   | Parameter | Unit | Maximum | Minimum | Mean  | (SD)  | Standard no.1053 Iran, |                        |                                     |
|----------------|-----------|------|---------|---------|-------|-------|------------------------|------------------------|-------------------------------------|
|                |           |      |         |         |       |       | ( maximum level)       | EPA <sup>7</sup> (MCL) | WHO <sup>8</sup> (MCL) <sup>9</sup> |
| Mahidasht      | 2,4-D     | µg/l | 58.2    | 11.3    | 19.38 | 21.4  | 30µg/l                 | 70µg/l                 | -                                   |
|                | Alachlor  | µg/l | 26.7    | 0       | 7.70  | 10.01 | 20µg/l                 | 2µg/l                  | 20µg/l                              |
|                | Atrazine  | µg/l | 0       | 0       | 0     | 0     | 2µg/l                  | 3µg/l                  | 2µg/l                               |
| Upper Namivand | 2,4-D     | µg/l | 0       | 0       | 0     | 0     | 30µg/l                 | 70µg/l                 | -                                   |
|                | Alachlor  | µg/l | 0       | 0       | 0     | 0     | 20µg/l                 | 2µg/l                  | 20µg/l                              |
|                | Batrazine | µg/l | 0       | 0       | 0     | 0     | 2µg/l                  | 3µg/l                  | 2µg/l                               |
| Abas Abad      | 2,4-D     | µg/l | 0       | 0       | 0     | 0     | 30µg/l                 | 70µg/l                 | -                                   |
|                | Alachlor  | µg/l | 0       | 0       | 0     | 0     | 20µg/l                 | 2µg/l                  | 20µg/l                              |
|                | Atrazine  | µg/L | 0       | 0       | 0     | 0     | 2µg/l                  | 3µg/l                  | 2µg/l                               |
| Rizevand       | 2,4-D     | µg/l | 0       | 0       | 0     | 0     | 30µg/l                 | 70µg/l                 | -                                   |
|                | Alachlor  | µg/l | 0       | 0       | 0     | 0     | 20µg/l                 | 2µg/l                  | 20µg/l                              |
|                | Atrazine  | µg/l | 0       | 0       | 0     | 0     | 2µg/l                  | 3µg/l                  | 2µg/l                               |
| ZalkeAbasgholi | 2,4-D     | µg/l | 26.5    | 7       | 5.56  | 7.81  | 30µg/l                 | 70µg/l                 | -                                   |
|                | Alachlor  | µg/l | 11      | 0       | 2.70  | 4.18  | 20 µg/l                | 2 µg/l                 | 20µg/l                              |
|                | Atrazine  | µg/l | 0       | 0       | 0     | 0     | 2 µg/l                 | 3 µg/l                 | 2µg/l                               |

Table 4: Values of monitoring toxins in Mahidasht according to seasons

| No. | Toxin    | Season | (Mean) | (S.D)  | Median | Maximum measured value (ppb) | Minmum measured value (ppb) |
|-----|----------|--------|--------|--------|--------|------------------------------|-----------------------------|
| 1   | 2,4-D    | Spring | 9.383  | 9.683  | 8.4    | 33.1                         | 0                           |
|     |          | Summer | 0      | 0      | 0      | 0                            | 0                           |
|     |          | Fall   | 2.363  | 6.747  | 0      | 33.2                         | 0                           |
|     |          | Winter | 14.288 | 11.842 | 11.95  | 58.2                         | 0                           |
| 2   | Alachlor | Spring | 2.6    | 5.286  | 8.1    | 25                           | 0                           |
|     |          | Summer | 0      | 0      | 0      | 0                            | 0                           |
|     |          | Fall   | 0.48   | 2.745  | 0      | 18.5                         | 0                           |
|     |          | Winter | 3.63   | 6.154  | 8.8    | 26.7                         | 0                           |
| 3   | Atrazine | Spring | 0      | 0      | 0      | 0                            | 0                           |
|     |          | Summer | 0      | 0      | 0      | 0                            | 0                           |
|     |          | Fall   | 0      | 0      | 0      | 0                            | 0                           |
|     |          | Winter | 0      | 0      | 0      | 0                            | 0                           |

Table 5: Results of one-way ANOVA for comparing average value of toxins in wells and in different seasons

| Toxin    | P <sub>value</sub> |
|----------|--------------------|
| 2,4-D    | 0.0117             |
| Alachlor | 0.0057             |
| Atrazine | -                  |

<sup>7</sup>US Environmental Protection Agency

<sup>8</sup>World Health Organization

<sup>9</sup> Maximum Concentration Level

Quantitative results of DLLME and HPLC-UV for determination of 2,4-D, atrazine and Alachlor indicated a high regression coefficient (Table 1, 2, 3).

The following tables show the maximum, minimum, mean, median and standard deviation of studied toxins based on the seasons. Thereby, within the measurement period, no amount of Atrazine pesticide was detected (Table 2). The highest residue concentration of 2,4-D and Alachlor were 58.2 and 26.7 ppb, respectively, which have been observed in the winter months.

## DISCUSSION AND CONCLUSION

For data analysis, Comparison the average concentration of 2,4-D and alachlor between the wells based on the seasons and place of sampling carried out by One-Way ANOVA indicated that there was a significant difference between these average concentrations of toxins ( $P$  value  $< 0.05$ ). Whereas this result was consistent to those results of organophosphate and organo chlorine toxin study in Mazandaran eastern, Iran and Turkey, respectively [18, 32].

According to obtained results of all monitored toxins the minimum concentration was equal zero, whereas the maximum concentrations of 2,4-d, alachlor and atrazine were 26.7, 58.2 and 0 ppb ( $\mu\text{g/L}$ ), respectively, in this study.

The maximum value of 2,4-D and Alachlor in Mahidasht was higher than the newest standard recommended by WHO and the industrial and research institute standard of Iran (30 and 20 for 2,4-d and alachlor, respectively) [33, 34].

However, the results revealed that the level of 2,4-D and alachlor value in wells of Zalke-abasgholi and Mahidasht villages were higher than the other wells due to hydraulic gradient from northwest to Southeast in Mahidasht region.

The 2,4-D and alachlor toxins were easily measured in Mahidasht area wells rather than atrazine toxin due to widely used of these toxins to control weeds, though no atrazine was found in the samples. Therefore, it confirms the relationship between level of toxins usage and their levels in groundwater. The rate of 2,4-D and Alachlor of some studied samples in Mahidasht region wells were higher than the limited level recommended by industrial and research standard of Iran ( $58.2 \mu\text{g/L} > 30 \mu\text{g/L}$  for 2,4-D and  $26.7 \mu\text{g/L} > 20 \mu\text{g/L}$  for alachlor. (Muhsin KONUK *et al*

showed that the value of organochlorine in drinking water of Afionkarahisar (Turkey) was more than limited level [32]. Renato Zanella *et al* reported that the amount of Alachlor, atrazine, metolachlor, permethrin, propanil and simazine were more than the other toxins in drinking water [35].

All toxins found in water samples during the rain fall seasons (from November 15, 2010 to May 2011) was due to the transfer of pesticides sprayed on the soil and plants by the seasonal rainfall into groundwater. Soleimani *et al*, study showed that the concentration of fenitrothion and butachlor in Anzali lagoon was maximum in February and Jun [36].

In fact, in rain fall seasons due to lack of sunlight to photolysis toxins and also immediate washout of pesticides by rainfall after spraying pesticides provided condition for entered toxins to underlying soils and groundwater. While, in seasons of low rain fall according to lack of sufficient water to wash out the pesticides, photolysis and analysis of pesticides, the toxins wouldn't enter ground water. Therefore, the highest amount of toxins was found in ground water in the area during high rainfall seasons. Khara *et al*, investigation indicated that the butachlor pesticide concentration of water samples in winter was more than other seasons [37].

Although, other pesticides such as Thribenuron, Paraquat, oxyfluorfen, butachlor, methyl Sethoxydim, ethalfluralin, metribuzin, glyphosate, 2,4-D+M.C.P.A. ecosynil, fenoxaprop - p -ethyl, Sulfosulfuron are also used in the areas and they have not been considered in this study. And there is a possibility to polluted water with these toxins in the region.

Regarding to obtaining results it can be concluded that the leakage of toxins into the drinking water resources will increase the concentrations risk of water resources in the future and to protect the existing water resources a few appropriate solutions must be provided.

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