FATE OF ATRAZINE IN THE AGRICULTURAL SOIL OF CORN FIELDS IN FARS PROVINCE OF IRAN

[1]S. Nasseri, *[2]M. Dehghani , [3]S. Amin, [1]K. Naddafi, [4]Z. Zamanian

[1]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran
[2]Department of Environmental Health Engineering, School of Public Health, Shiraz University of Medical Sciences, Shiraz, Iran
[3]Department of Water Engineering, Shiraz University, Shiraz, Iran
[4]Department of Occupational Health, School of Public Health, Shiraz University of Medical Sciences, Shiraz, Iran

ABSTRACT

Atrazine, a herbicide widely used in corn production, is frequently detected as pesticide in water resources. In this research, four agricultural fields with a long history of atrazine application in Shiraz and its vicinity in Fars province of Iran, have been studied to determine the fate of atrazine through the passage of time. These four farms were cultivated under a crop rotation (corn-wheat) during the past 10 years. Samples were collected from four soil profiles of 0-10, 10-20, 20-40, and 40-60 cm soil depth at different times. The time intervals for soil sampling started before atrazine application and continued until no atrazine was detected. According to the general linear model, there was no significant difference between atrazine residual concentrations and the soil moisture and depth ($p \geq 0.05$). But, significant difference between atrazine residual concentrations and the sampling regions was observed ($p < 0.001$). Based on the data, atrazine leaching and dissipation rate in different soil profiles in the four sampling regions were high and significant. Therefore, there is a high risk of atrazine pollution in groundwater resources of the region.

Key words: Atrazine, Soil, Shiraz, Dissipation rate, Pesticide fate

INTRODUCTION

Atrazine is a triazine herbicide used to control many broad leaf and some grassy weeds (Dossantes *et al*., 2004). Atrazine is frequently detected in groundwater and surface water resources (Putnam, 1997). Atrazine is moderately persistent in the environment with the half-life of one to twelve months. However, the herbicide has been reported to persist in soils for up to a decade. In fact, it was the second most frequently detected pesticide in the EPA's national in drinking water well survey (Dossantes *et al*., 2004).
Atrazine has recently been reported to have

long-term reproductive and endocrine-disrupting effects (Colborn *et al*., 1993). Atrazine is a probable human carcinogen (Van Leewen *et al*., 1999). International Agency for Research on Cancer (IARC), 1991 has concluded that there is inadequate evidence in human and limited evidence in experimental animals for the carcinogenicity of atrazine (Group 2B). The maximum contaminant level (MCL) for atrazine in drinking water established by the USEPA is 3.0 µg/L and the European Union requires the MCL below 0.1 µg/L for a single pesticide in drinking water.

*Corresponding Author: E-mail:

Although the toxicological effects of atrazine on humans is weaker than the other chlorinated herbicides, severe environmental problems emerged due to their persistence in soils, as well as their runoff to surface and groundwater (Dossantes *et al*., 2004). According to the national environmental board soil quality standards for habitat and agriculture should not exceed 22 mg atrazine per kg soil.

The fate of atrazine in soil depends upon many different factors including sorption to soil component, uptake by plants, transport via runoff and leaching, biodegradation, photodegradation, volatilization, and chemical degradation. (Swann and Eschenroeder, 1983). Although, herbicide mobility and leaching process in soil are very gradual process, the leaching rate can be very rapid due to irrigation and soil texture. Since the mobility of a herbicide through soil is the indicator of the potential for contamination of groundwater, therefore, study the herbicide residue in soil is a very important issue.

Chai has investigated the leaching of pesticides such as atrazine in humid tropical soils at different depths (Chai *et al*., 2009). All the soils investigated are acidic clay soil with high organic matter contents. Atrazine was moderately leached beyond 15 cm soil depth at the first heavy rain. The general low to moderate tendency for the pesticide to leach in the investigated soils might partly be attributed to the high content of organic matter throughout the soil profile. However, leaching of atrazine at low to average rain was observed in clay soils, whereas in sandy soil. The pesticide was rapidly transported to 40 cm soil depth regardless of its sorption property, suggesting that leaching was caused by preferential flow.

Adsorption-desorption behaviors of atrazine in soil were studied in Darehasaluie Kavar corn field in Fars Province. Sorption kinetics showed an immediate rapid sorption followed by a slow sorption process. Desorption of atrazine was similar to its adsorption, but at a very slower rate. The adsorption-desorption rate was positively related to the amount of applied atrazine and the time required for equilibration (Dehghani *et al*., 2005).

During the last few years, Fars province (in southern Iran) has been the first in wheat and corn production in the country. Shiraz city and its surrounding are the major corn producers in Fars province and the country. Wheat is cultivated in most agricultural farms in Fars province especially Shiraz city and surrounding. After wheat harvest, corn is cultivated. Atrazine is one of the most herbicide used in maize farm. Therefore, Shiraz city and its surrounding were selected as the region with the highest history of atrazine consumption. Case studies for determining the atrazine soil pollution were done in agricultural soil of this city. Therefore, the objectives of this research was to determine the temporal variation of atrazine residual concentration in four different soil profiles in four agricultural corn fields with long history of atrazine consumption.

MATERIALS AND METHODS
Reagents
All chemicals used were of analytical grade and purchased from Merck Co. (Germany). Atrazine standard was supplied by Acqua Standard Europe, Switzerland. A stock solution of 1000 µg mL^{-1} atrazine analytical grade was prepared by dissolving 5 mg solid standard of atrazine (100% purity) in methanol. Working solutions were prepared by diluting appropriate volume of this stock solution in distilled deionized water. Hydrochloric acid (0.01N) was used for pH adjustment. The standard solid and solution were stored in freezer at -20°C.

Site selection of agricultural fields
The sites with a long history of atrazine consumptions in the map of Shiraz and surrounding areas were determined by the data collected from the Plant Protection and Pest Control Organization of Shiraz. To determine the fate of atrazine with time, four different farms with a long history of atrazine application in Shiraz and its vicinity were selected including 2 sites in Kavar (Old Kavar Corn Field (OKCF) and Norozan Kavar Corn Field (NKCF)), 1 site in Zargahan (Polekhan Zarghan Corn Field (PZCF)) and 1 site in Bajgah (Bajgah Agricultural Corn Field (BACF)). Selected field characteristics in Shiraz and its vicinity are shown in Table 1. The native soil characteristics at different sites are summarized in Table 2.

Table 1: Selected field characteristics in Shiraz and its vicinity

Site code	Area (ha)	Watertable (m)	Atrazine (kg/ ha)	Cultivation rotation	Sampling method
OKCF	23	40	2.5	Corn - Canola	Disturbed & non-disturbed
NKCF	20	150	2.5	Corn - Wheat	Disturbed & non-disturbed
PZCF	12	3	0.6	Corn - Wheat	Disturbed & non-disturbed
BACF	10	30	3.3	Corn - Wheat	Disturbed & non-disturbed

OKCF=Old Kavar Corn Field; NKCF=Norozan Kavar Corn Field; PZCF=Polekhan Zarghan Corn Field; BACF=Bajgah Agricultural Corn Field

Table 2: Native soil characteristics at different sites

Sampling site	Characteristic
Kavar	Fine loamy, mixed, thermic Typic Haploxerepts
Zarghan	Fine loamy, mixed, thermic Typic Xeroflouvents
Bajgah	Fine loamy, mixed, thermic Typic Calcixerepts

Soil physiochemical characteristics

The general physiochemical characteristics of soil were determined. Hydrometer was used to determine soil textures using Guelph method. Soil texture in this method was determined in 0-60 cm soil depth in 20 cm increments. Other soil characteristics such as soil solution pH (Thomas, 1996), organic matter content (OC) (Darrel and Nelson, 1996), Cation Exchange Capacity (CEC) (Summer and Miller, 1996), $CaCO_3$ content (Richards, 1954) and electrical conductivity (Rhoades, 1996) were determined. Soil moisture was determined in atrazine sub-samples by gravimetric methods (Fig1).
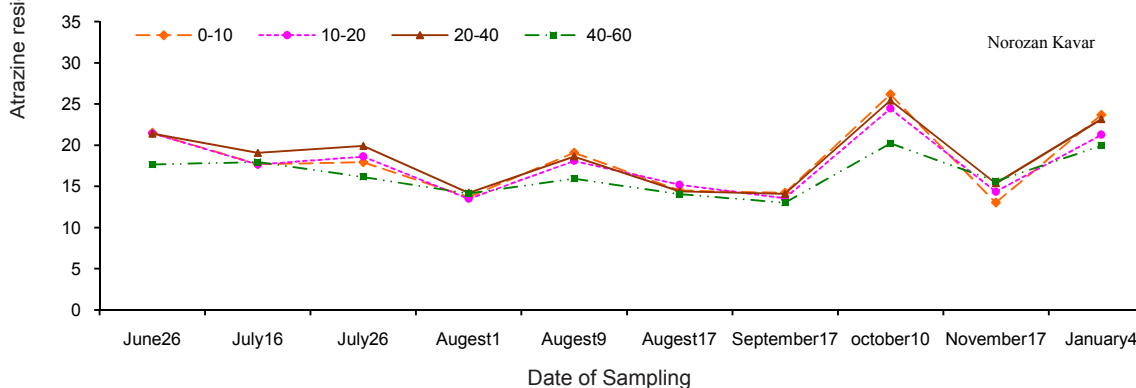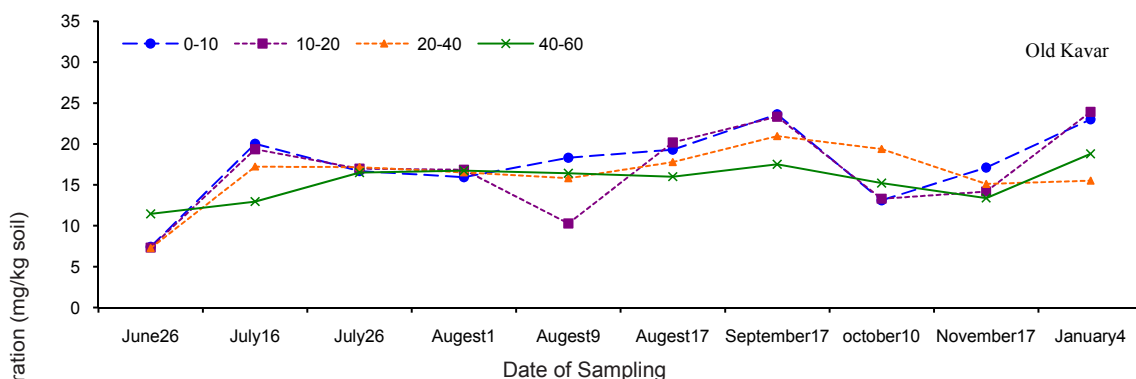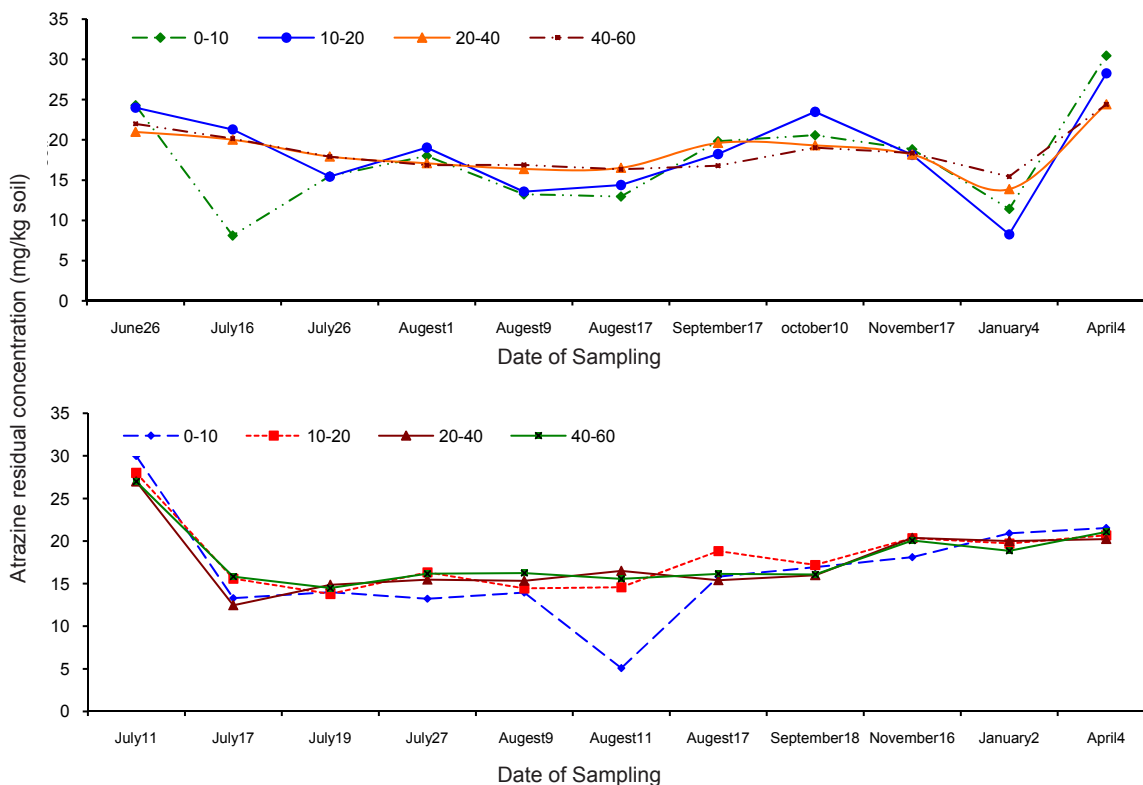
Fig1: Variation of soil moisture in different soil depths in diffrent corn fiels

Soil sampling procedure

Soil samples were collected with a hand-driven soil auger from different points (5 samples per ha) of farms in order to have a composite soil sample with all characteristics of the soil region in the corresponding farm (Amin, 1982). To obtain soil density in those regions, undisturbed soil samples were collected with core samplers. To determine atrazine percent recovery, soil samples were collected from area near farms mentioned before. These areas did not have any history of atrazine consumption in the past few years.

The soil samples were transported to the laboratory in zipped plastic bags and were kept frozen at -20°C until chemical analysis. The soil samples were thawed and air-dried at dark at room temperature, and screened through a 2.0 mm sieve for maintaining homogeneity of soil in order to reduce the variability of adsorption data

(Sonon and Schwab, 1995).

To study atrazine residual concentration in 0-60 cm soil depth the first two layers were sampled in a 0-10 cm increment, (0-10 and 10-20 cm soil depth) due to the high variation of atrazine residual concentration in the upper layer of soil the next two layers were in a 0-20 cm increment, (20-40 and 40-60 cm soil depth). Therefore, in order to have a better picture of atrazine presence in agricultural soil, the samples were collected from soil profiles 0-10, 10-20, 20-40, and 40-60 cm at different times. Immediately after applying atrazine to soil, rapid leaching in soil is seen. Therefore, in order to monitor its behavior we needed sampling with shorter intervals. A month later, atrazine leaching in soil showed a lower pace, needing sampling with longer interval (Noshadi, 2002). Therefore, the

time intervals for soil sampling from four high atrazine consumption agricultural farms were as follows: before atrazine application, one day after application, one week after application, two weeks after application, and then, every month until atrazine residual concentration did not change or was almost constant. Some dates of soil sampling were postponed due to problems such as farm irrigation at the time of soil sampling or heavy rain. Actually, soil sampling continued until the electrochemistry analysis did not detect any atrazine. Atrazine residual concentration and soil moisture were determined in those four farms.

Atrazine extraction and electrochemistry analysis

The following method was used for extraction of atrazine from soil for electrochemistry analysis. 30mL of dichloromethane was added to 10g of the soil sample and shaken in a reciprocal shaker for 20 minutes. After filtration, the organic phase was transferred to a separating funnel and then atrazine was extracted with 20mL HCl (0.01N). Afterwards, the liquid phase was collected and transferred to a 15mL glass vial and stored in a refrigerator prior to electrochemistry analysis (Dehghani *et al*., 2005). Atrazine recovery percent from soil with this method of extraction was 98%.

Electrochemistry with the Square Wave Voltammetric (SWV) was used in this study to determine atrazine residual concentration in soil samples. The electrochemical with three-electrode configuration was used comprising a Hanging mercury drop electrode (Micro Auto Lab type II analyzer equipped with Metrohm VA STAND 663 and GPES 4.9 software) as the working electrode, a platinum rod counter electrode as an auxiliary electrode, and an Ag/AgCl electrode as a reference. Under optimized conditions for high sensitivity, the SWV experiments were carried out scanning the potential from -0.5 to -1.2 V versus Ag/AgCl using the pulse height of 25 mV and frequency of 10 HZ, with a potential increment of 1.95 mV. The voltammograms were obtained in HCl (0.01N) at pH=1.9 (Luciana *et al*., 2004).

RESULTS

The results of physicochemical properties of soil in the four regions at different soil depths of 0-20, 20- 40, and 40- 60 cm are shown in Table 3. The variations of soil relative moisture contents for soil profiles of 0-10, 10-20, 20-40, and 40-60 cm at stimulated time intervals in each soil sampling region are shown in Fig 1.

Temporal variations of atrazine residual concentrations of 4 different soil profiles for each replication in are shown in Figs 2-5. All Figures are based on the mean of three replications.

Table 3: The physiochemical properties of soil in the four agricultural fields

Site code	Soil depth cm	pH	EC* ds/cm	OC** g/kg soil	CEC*** mole (+)/kg soil	CaCO₃ g/kg soil	Particles sand distribution (%)				Texture
							Sand	Coarse silt	Fine silt	Clay	
OKCF	0-20	7.7	1.41	23.85	39.13	540.3	16.7	40.0	6.0	37.3	Silty-clay-loam
	20-40	7.7	1.05	17.02	13.58	570.2	18.7	33.3	10	38.0	Silty-clay-loam
	40-60	7.6	1.29	13.62	28.26	520.4	12.7	34	6.0	43.3	Clay
NKCF	0-20	7.6	2.18	13.62	15.76	495.5	16.7	39.3	8.0	36.0	Silty-clay-loam
	20-40	7.6	1.21	10.21	26.08	540.3	8.7	40	4.0	47.3	Silty-clay
	40-60	7.6	0.47	17.03	35.32	530.4	18.7	19.3	10	52.0	Clay
PZCF	0-20	7.5	2.5	20.43	16.84	515.4	26.7	31.3	6.0	36.0	Clay-loam
	20-40	7.6	1.90	13.62	36.41	463.1	16.7	42	4.0	37.3	Silty-clay-loam
	40-60	7.9	0.89	3.46	25.54	483.1	14.7	40	4.0	41.3	Silty-clay
BACF	0-20	7.7	0.8	17.02	32.24	495.5	22.7	44	2.0	31.3	Clay-loam
	20-40	7.7	0.77	17.2	15.21	637.8	26.7	39.3	6.0	28	Loam
	40-60	7.7	0.5	6.81	36.41	577.7	28.7	44	4.0	23.3	Loam

*Electrical Conductivity
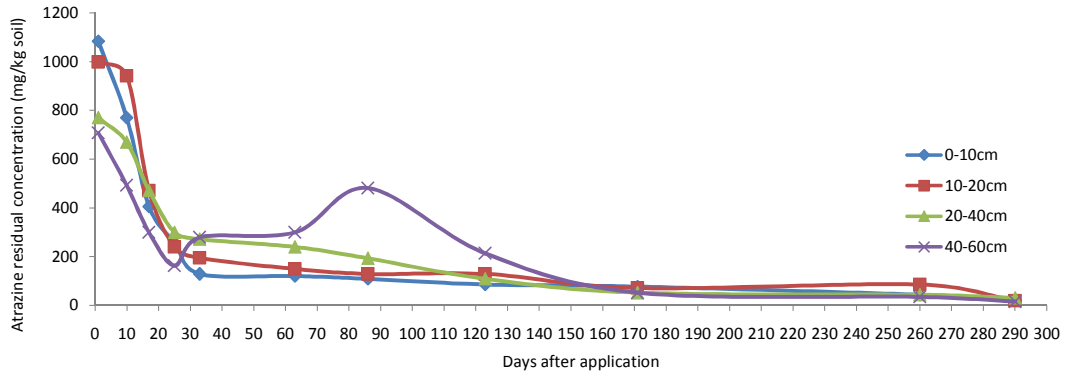** Organic matter Content
*** Cation Exchange Capacity

Fig2: Atrazine residual concentration in different soil depths Old Kavar corn field
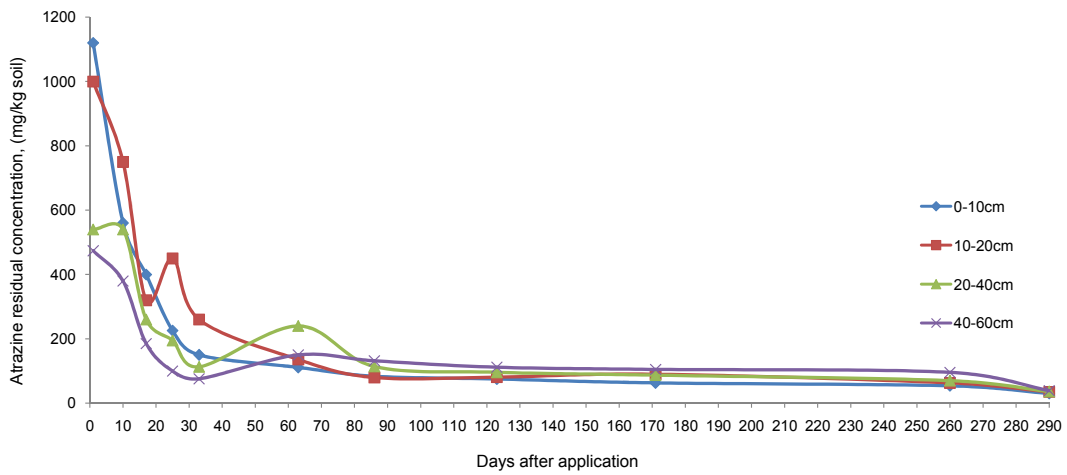

Fig3: Atrazine residual concentration in different soil depths Norozan Kavar corn field
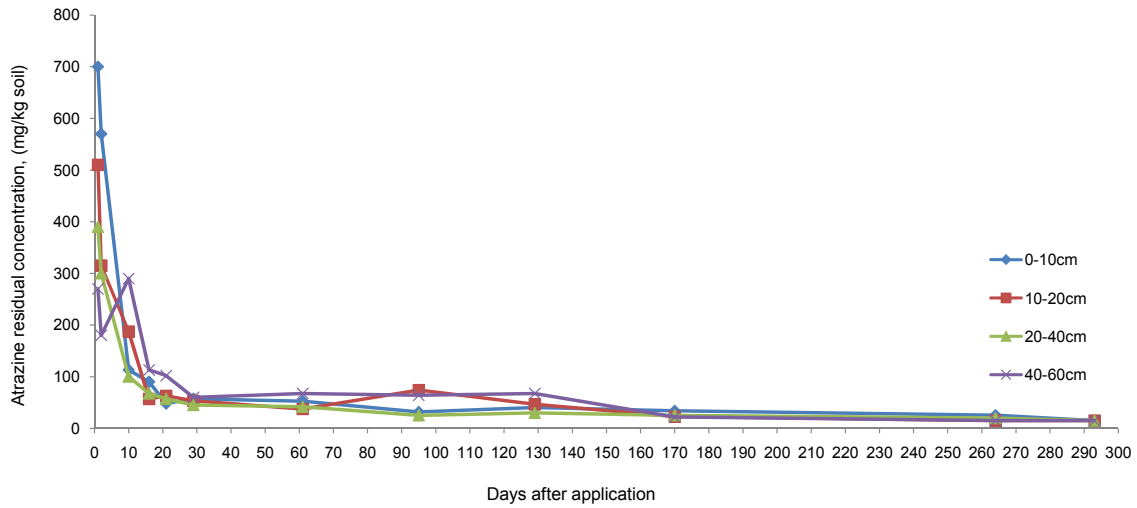
Fig4: Atrazine residual concentration in different soil depths in Polekhan Zarghan corn field
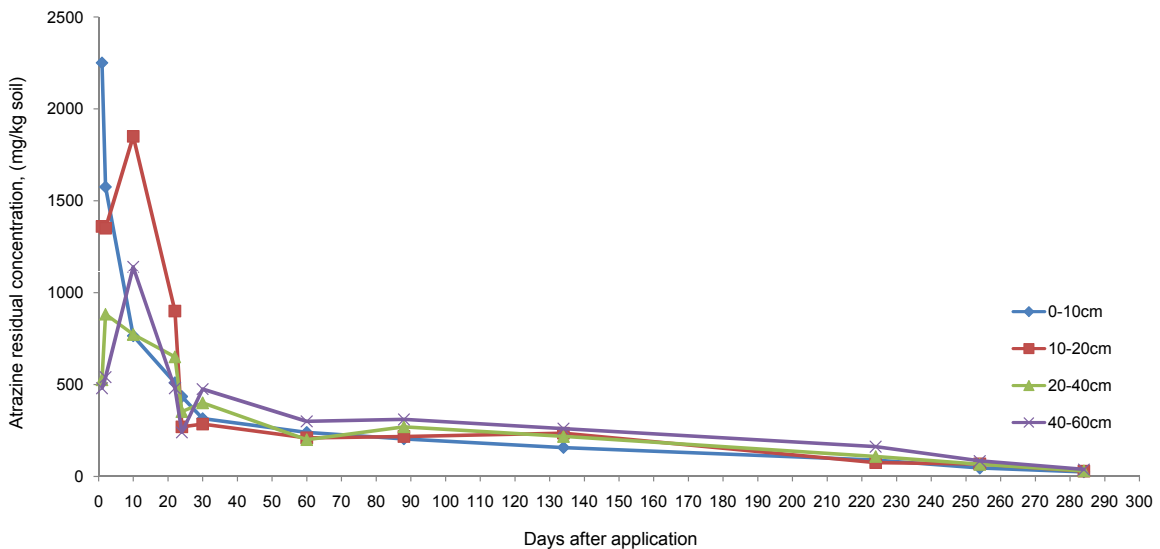

Fig5: Atrazine residual concentration in different soil depths in bajgah agricultural corn field

Data regarding the physiochemical properties of the soil (Table 3) showed that in the upper layer of the soil, the organic matter content (OC) was moderate due to the fertilizer amendment, but in 40-60 cm soil depth, the OC was low. Therefore, the effect of organic matter on adsorption in deeper layers (40-60 cm soil depth) was low or negligible. Regarding the soil texture, it should be noted that the clay content has a large effect on adsorption. The effect of clay content on adsorption was between medium to high.

General linear model showed that there was no significant difference between the soil moisture and atrazine residual concentrations ($p \geq 0.05$).

According to interaction plot, as the soil depths increased, atrazine residual concentrations decreased at a very slow rate (almost constant). However general linear model showed that there was no significant difference between atrazine residual concentrations and soil depth (p>0.05). However, based on this model, there was a significant difference between atrazine residual concentrations and the sampling regions (p<0.001).

DISCUSSION

Data regarding the temporal variation of atrazine in four agricultural corn fields with a long history of atrazine consumption showed that atrazine dissipation and leaching were the main reason for atrazine reduction in these fields.

Although general linear model showed that there was no significant difference between soil moisture and atrazine residual concentrations (p>0.05), but the data showed that atrazine concentration in deeper soil layer increased at a very fast rate due to the high soil moisture corresponding to irrigation or heavy rainfall. Thus, downward flux had a major role in atrazine leaching. Atrazine was present more in the dissolved phase compared to the solid phase, even though the solubility of atrazine was not considered high. In addition, low soil clay content at the surface layer, caused atrazine leaching at a very fast rate. Due to the increasing atrazine concentration at deeper soil depths after the first day of atrazine application, leaching was the dominant process, compared to degradation. In a real field, the soil has complex characteristics and many factors influence the fate of atrazine. Although Canny (1995) showed that atrazine contents of the top layer of soil decreased slowly after atrazine spreading, he concluded that degradation was more important than leaching for this decrease.

Tillage could be another reason for rapid leaching of this herbicide. Gish *et al*. (1986) reported much less leaching of atrazine through the soil profiles of the non-till fields. They suggested that the interaction of tillage and soil texture had a large influence on the temporal variation of atrazine for a particular soil texture.

General linear model showed that there was no significant difference between atrazine residual concentrations and soil depth (p>0.05). During the first month after atrazine application, variation of atrazine concentration in deeper layers had a descending trend. In other words, higher atrazine concentration was observed in surface (0-10 and 10-20 cm soil depths) compared to subsurface soil (20-40 and 40-60 cm soil depths). However, after one month, this trend changed. Thus, atrazine concentration in subsurface soil was higher than in surface soil and had an ascending trend. The main reason for the change in this trend from descending to ascending was the high rate of dissipation and leaching of atrazine in surface layer. Therefore, through the passage of time, more atrazine was left in subsurface soils. This caused higher atrazine concentration in deeper layers and atrazine leached deeper layers of soil. Therefore, a high risk of atrazine pollution exists for groundwater resources of the region. Indeed, it is important to note that atrazine metabolites as products of atrazine degradation processes, have high leaching potential and therefore, there is a high risk to contaminate groundwater.

The clay content has a large effect on adsorption. The effect of clay content on adsorption was between moderate to high. Herweigh in his study also showed that the interaction between atrazine molecules and clay specific surface was only partly based on reversible mechanisms. He concluded that atrazine once adsorbed in the mineral horizon of the soil, it may persist there for a long period of time and then it desorbed gradually. Therefore, the feasibility of the occurance of atrazine pollution in groundwater due to the soil leachate is very high (Herweigh *et al*., 2001). Bowman (1990) found that atrazine moved deeper in silty loam than sandy soil, even though the silty loam soil had higher organic matter content and therefore, much more adsorption was attributed to silty loam than the sandy soil. Greater leaching in the silty loam was due to the higher water-holding capacity and slower infiltration rate, allowing atrazine more time to desrobe and move with water through soil. Chai (2009) found that atrazine was moderately leached in the soil with high organic matter content. Leaching of atrazine was observed in clay and sandy soil (Chai *et al*., 2009).

Regarding the data, atrazine dissipation rate in

surface soil was greater than subsurface soil. In deeper soil depths atrazine adsorption and leaching processes became significant. Due to low organic matter content in lower depths, atrazine adsorption to organic matter contents was not high. But its adsorption by clay colloids became important. When adsorption phenomenon was occurred, atrazine bioavailability became less and therefore, atrazine biodegradation occurred at lower rates. As the adsorption rate of atrazine in soil increased, the amount of atrazine which was available for dissipation decreased. Ultimately, atrazine was desorbed and leached towards deeper soil layers and caused groundwater pollution. Dehghani (2005) reported that the adsorption-desorption rate of atrazine was positively related to the amount of applied herbicide and the time required for equilibration (Dehghani *et al.*, 2005).

To conclude, Data regarding the temporal variation of atrazine in four agricultural corn fields with a long history of atrazine consumption showed that atrazine dissipation rate is high in surface soil especially during hot weather conditions. High soil moisture due to irrigation at the time which atrazine is applied to soil is one of the major causes for atrazine mobility and leaching process. High atrazine leaching and dissipation processes in different soil profiles in the four different sampling regions were the main reason for atrazine reduction in these fields. Therefore, there is a high risk of atrazine pollution in groundwater.

REFERENCES

Amin, S. (1982). Modeling phosphorus transport in surface runoff from agricultural lands. Ph.D. thesis, Purdue University, Lafayette, 157.

Bowman, B. T. (1990). Mobility and persistence of alachlor, atrazine and metolachlor in Plainfield sand, and atrazine and isazofos in Honey wood silt loam, using field lysimeters. *Environ. Toxico. Chem.* **9**, 453-461.

Canny, C. (1995). Equation of atrazine transfer from agricultural land to surface water. *Physics and Chemistry of Earth*. **2** (3- 4): 359- 367.

Rhoades, J. D. (1996). Salinity electrical conductivity and total dissolved solids. In. *Methods of soil analysis.* Sparks, L. D. (Ed). SSSA BOOK Series. **5**: 417- 436.

Chai, L. K. (2009). Fate of pesticides in the humid tropics application to insecticides used in vegetable crops. Ph.D. thesis, University of Copenhagen, 35.

Colborn, T., Vomsaal, F. S., and Soto, A. M. (1993). Developmental effects of endocrine disturbance chemical in wild life and humans*,* Environ, Health Perspectives, **101**: 378- 384.

Darrell, W. N., and Nelson, L. E. (1996). Total organic carbon and organic matter. In. *Methods of soil analysis.* Sparks, D. L. (Ed). SSSA Book Series 5: 982- 991.

Dehghani, M., Nasseri, S., Amin, S., Nadafi, K., Taghavi, M., Yunosian, M., Maleky, N. (2005). Atrazine adsorption-desorption behavior in Darehasaluie Kavar corn field soil, *Iran J. Environ. Health Sc. Eng.,* **2** (4): 221-228.

Dossantes, L. B. O., Abate G., and Masini, J.C. (2004). Determination of atrazine using square wave voltammetry with the Hanging Mercury Drop Electrode (HMDE). *Talanta***. 62**: 667-674.

Gish, T. J., Helling, C. S., and Kearney, P. C. (1986). Chemical transport under no-till field conditions. *Geoderma*. **38**: 251-259.

Herweigh, U., Klumpp, E., Narres, H., and Schwuger, M. J. (2001). Physicochemical interactions between atrazine and clay minerals. *App. Clay Sci.* **18**: 211-222.

International Agency for Research on cancer (IARC). Occupational exposures in insecticide application, and some pesticides, Lyon. 1991 441-446 [IARC Monographs on the evaluation of carcinogenic risk to human, (531)].

Luciana, B. O., Gilberto, A. J. C, and Masini, J. C. (2004). Determination of atrazine using square wave voltammetry with the Hanging Mercury Drop Electrode (HMDE)*.* Talanta, **62**: 667- 674.

Noshadi, M. (2002). Evaluation of PRZM-2 model with herbicides field data on a silty clay soil in College of Agricultural. Ph.D. Thesis. Shiraz University.

Putnam, J.E., (1997). Occurrence of phosphorus, other nutrients, and triazine herbicides in water from the Hillsdale Lake Basin, Northeast Kansas, May 1994 through May 1995. US Geological Survey, Water-Resources Investigations Report. 97- 4019.

Rhoades, J. D. (1996). Salinity electrical conductivity and total dissolved solids. In. *Methods of soil analysis.* Sparks, L. D. (Ed). SSSA BOOK Series. **5**: 417- 436.

Richards. L. A. (Ed). (1954). Diagnosis and improvement of saline and alkali soils. USDA Handbook No. B. U. S. GOV. Print. Office. Washington D. C.

Sonon, L. S., and Schwab, A. P., (1995). Adsorption characteristics of atrazine and alachlor in Kansas soils. *Weed Sci.* **43**: 461- 466.

Rhoades, J. D. (1996). Salinity electrical conductivity and total dissolved solids. In. *Methods of soil analysis.* Sparks, L. D. (Ed). SSSA BOOK Series. **5**: 417- 436.

Summer. M. E., and Miller, W. P. (1996). Cation exchange capacity and exchange coefficient. In. *Methods of soil analysis.* Sparks, D. L. (Ed). SSSSA Book Series **5**: 1205-1230.

Swann, R. L., and Eschenroeder, A. E. (1983). Fate of chemicals in the environment. *American Chemistry Symposium. Series 225. American Chemistry Society*, Washington, D.C.

Thomas, G. W. (1996). Soil pH and soil acidity. In. *Methods of Soil Analysis.* Sparks. L. D. (Ed). SSSA Book Series. **5**: 457- 490.

Van leeuwen, J. A., Waltner-Toews, D., Abernathy, T., Smith, B., and Shokri, M. (1999). Associations between stomach cancer incidence and drinking water contamination with atrazine and nitrate in Ontario (Canada). Agro ecosystems. 1987- 1991. *Int. J. Epidemiol.* **28**: 836- 890.