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Assessment of Atrazine Distribution in Shiraz Soils, South of Iran

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Abstract: The main objective of this study was focused on determining atrazine residual concentration in agricultural soil in Shiraz and its vicinity. Twenty two sampling fields were selected by grid sampling in Shiraz and its vicinity. Atrazine residual concentrations in 0-20, 20-40 and 40-60 cm soil depths were in the range of 15-550 μg kg^{-1} soil. Data showed that the concentration of atrazine did not exceed the soil quality standard for agriculture which is 22 mg kg^{-1} soil and there was no significant difference between depth and atrazine residual concentration ($p>0.05$). Although, in all sampling regions in Shiraz and its vicinity, the concentration of atrazine did not exceed the soil quality standard for agriculture, atrazine leaching and dissipation rate in soil and risk of atrazine ground water pollution must be determined.

Kay words: Fars, Shiraz, atrazine, soil

INTRODUCTION

Atrazine is a triazine herbicide used to control many broadleaf and some grassy weeds. Because atrazine action is chiefly preemergence, a post emergence broadleaf herbicide is sometimes added to make it more useful in no-till situations (Jones *et al*., 1982). Soil pollution by these herbicides has become a critical issue in today's world. Most of these pesticides are either persistent or are converted into their metabolites some of which are in turn, toxic and persistent. Groundwater may also be contaminated if herbicide or their metabolites leach sufficiently deeply in soil. Although, atrazine application has been banned in Germany since 1991 (Tappe *et al*., 2002) this herbicide is still widely used in agriculture in China and the USA (Huang *et al*., 2003) Atrazine is frequently detected in groundwater and surface water resources (Miler *et al*., 2000). 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 (Capriel *et al*., 1985). Triazines and their environmental behavior have been investigated on short-term time scales under laboratory conditions (Berns *et al*., 2005). The application of 14C-labeled atrazine on long-term time scales (22 years) under outdoor conditions showed that atrazine and its metabolites are biologically active and less than1% of atrazine is mineralized (Jabloniwski *et al*., 2008).

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). Triazine herbicides are also thought to be endocrine disruptors at levels of low exposures (Ren and Jiang, 2001; Hayes *et al*., 2002).

Although, the toxicological effects of atrazine and other triazines on humans is weaker than reported for chlorinated and organophosphorus pesticides, severe environmental problems can result from their persistence in soils and sediments, as well as their runoff to surface and groundwater (Luciana *et al*., 2004). The Maximum Contaminant Level (MCL) for atrazine in drinking water established by the USEPA is 3.0 μg L^{-1} and the European Union requires the MCL below 0.1 μg L^{-1} for a single pesticide in drinking water.

Herweig *et al*. (2001) in his study showed that the interaction between atrazine molecules and clay specific surface was only partly based on reversible mechanisms. Thus, it was possible that atrazine, once adsorbed in the mineral horizon of the soil, persists there over a long period of time and desorbed only gradually, thus being translocated into deeper soil layers and ultimately into the groundwater by the soil leachate (Herweig *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 much more adsorption was attributed to silty loam than the sandy

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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 (Bowman, 1990).

Sadeghi *et al*. (2000) found that leaching potential was more dominant in silty loam soil (because of macro-pore flow in silty loam soil) than sandy soil under non-till system. Sandy soils and soils with low in organic matter were particularly susceptible to leaching of atrazine and other herbicides. Minimizing irrigation levels could retard atrazine transport and leaching through soils (Asara *et al*., 2001). Most of atrazine was bound to clay and then atrazine bound sediment can settle out and accumulate (Barriuso and Koskinen, 1996).

During the last few years, Fars province (in Southern Iran) has achieved the top rank in wheat and corn production in the country. Atrazine is one of the most herbicides which have widely been used in this province to control broad-leafed and grassy weeds and has contaminated soil and water. Therefore, the main objectives of this project are to collect data regarding the consumption of atrazine in Fars province and then determination of atrazine residual concentration in agricultural soils of Shiraz and its vicinity. For this purpose, the city of Shiraz and its vicinity have been chosen as a representative sample of the whole province.

MATERIALS AND METHODS

Reagents: All chemicals were purchased from Merck (Germany). Atrazine standard was supplied by Acqua Standard Europe, Switzerland.

Data collection: Data regarding the consumption of atrazine in Fars province were collected from the plant protection and pest control organization of Shiraz. The amounts of atrazine distribution in Fars province and also in Shiraz and its vicinity were shown in Table 1 and 2. According to data in these Table 1 and 2, the highest amount of atrazine was distributed in Shiraz and its vicinity.

The research has started since June 2004 in Shiraz and its vicinity. The method of study was cross sectional and experimental. Fars is located on the Southern parts of Iran. Shiraz and surrounding is one of the major corn producers in Fars province and the country. Wheat is cultivated in most of the agricultural farms. After wheat harvest, corn is cultivated. Atrazine is one of the most herbicide used in maize farm.

Site selection in Shiraz agricultural fields: Soil samples from 22 farms in Shiraz and its vicinity were selected by grid sampling. Sampling sites were located in Kavar vicinity (4 sites), Zarghan vicinity (6 sites), Kaftark (3 sites), Ghoyom (2 sites), Dehshikh, Khanzenian, Dashetargen, Kohmareh Sorkhi, Sarvestan, Sharifabad and Gharehbagh. The map of 22 sampling sites is shown in Fig. 1. The samples were collected from soil profiles 0-20, 20-40 and 40-60 cm. Then atrazine residual concentration and relative moisture content in soil samples were determined.

Table 1: Distributed atrazine (kg) in Fars province

City	Distributed atrazine (kg)
Abadeh	215
Eghlid	205
Estahban	3000
Arsengan	3780
Bavanat	500
Jahrom	475
Khormbeed	740
Sepidan	4600
Shiraz	11100
Darab	6600
Fasa	9870
Firozabad	4900
Kazeroon	250
Lar	1200
Lamerd	215
Marvdasht	12900
Niriz	2350
Mamasani	300

Table 2: Distributed atrazine (kg) in Shiraz and its vicinities

City	Distributed atrazine (kg)
Zarghan	1635
Kavar	3247
Kharameh	845
Daryon	1475
Seekhdarengon	220
Sarvestan	360
Shiraz suburb	1495

Shiraz suburb is from airport square to Beedzard, from Ghasrdasht to Ghoyom and Ghalat and from Quran gate to Bajgah

Methods

Soil sampling procedure: Disturbed soil samples were collected with a hand-driven soil auger from different points (at least 9 points) of farms in order to have a composite soil sample with all characteristics of the soil region in the corresponding farm. 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 laboratory in zipped plastic bags and were kept frozen at -20°C until they were ready for chemical analysis of atrazine herbicide. The soil samples were air dried in dark in room temperature and screened through a

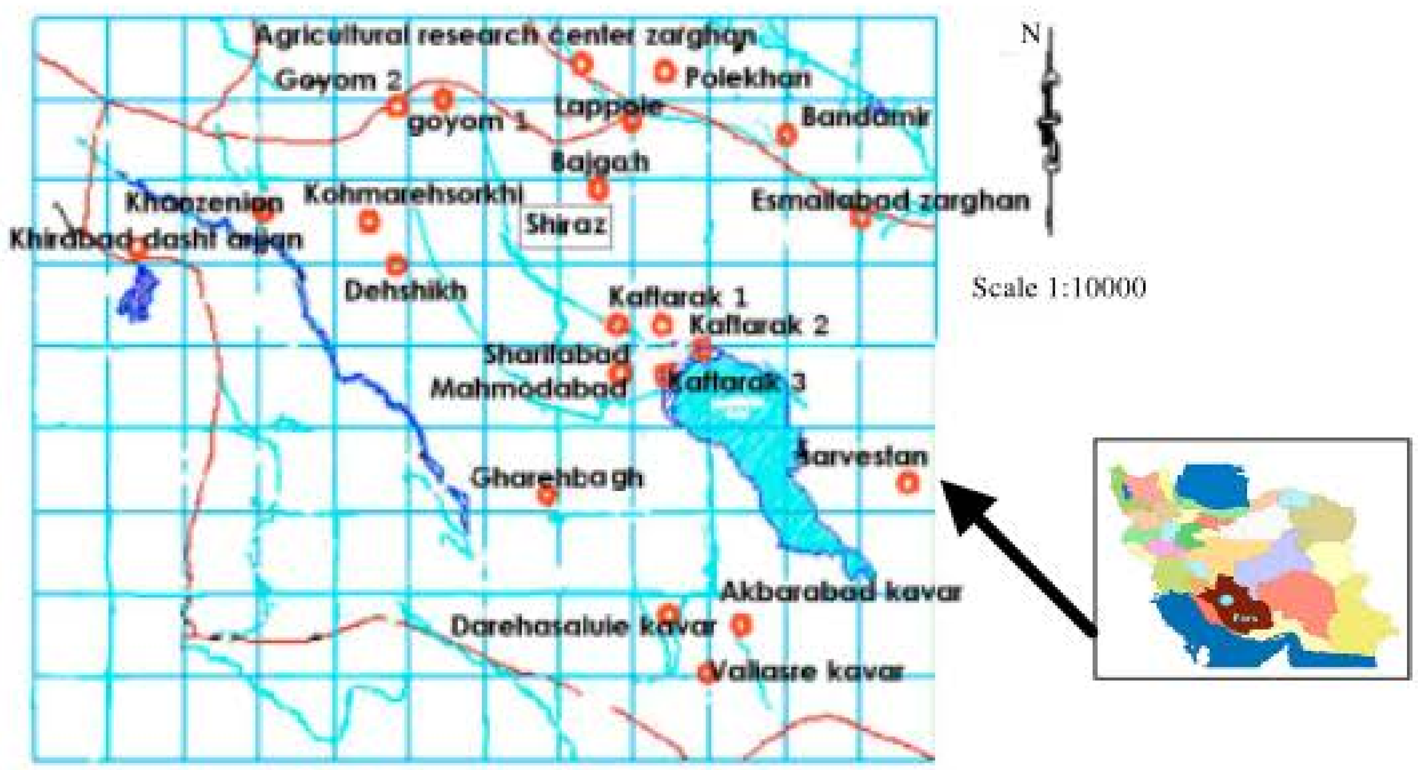

Fig. 1: The map of 22 sampling sites in Shiraz and its vicinity in Iran

2.0 mm sieve for maintaining homogeneity of soil in order to reduce the variability of adsorption data (Sonon and Schwab, 1995).

Soil processing: Soil moisture was determined in atrazine sub-samples by gravimetric methods. Hydrometer was used to determine the soil texture. Other soil characteristics such as soil solution pH (Thomas, 1996), organic matter content (OM) (Darrell and Nelson, 1996) and Cation Exchange Capacity (CEC) (Summer and Miller, 1996) were determined.

Atrazine extraction: Thirty milliliter of dichloromethane was added to 10 g of the soil sample and shaken in reciprocal shaker for 20 min. After filtration, the organic phase was transferred to a separating funnel and then atrazine was back extracted with 20 mL HCl (0.01 N). After that, liquid phase was collected and then transferred to a 15 mL glass vial and stored in a refrigerator prior to electrochemistry analysis. Atrazine recovery percent from soil with this method of extraction was 98%.

Analytical method: Electrochemistry with the Square Wave Voltametric (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 (HMDE) as the working electrode, a platinum rod counter electrode as an auxiliary electrode and an Ag/AgCl electrode as a reference electrode. 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 (0.01 N) at pH = 1.9 (Luciana *et al*., 2004).

RESULTS

Soil physiochemical analysis: The results of physiochemical properties of soil in the 22 different agricultural fields showed that, different soil profiles had an alkaline pH and it was in the range of 7.5 and 7.9. Organic Matter (OM) in soil was between low to medium high and in the range of 3.46-23.85 g kg^{-1} soil, Electrical Conductivity (EC) was from 0.47-2.5 dS cm^{-1}. Cation exchange capacity in soil was between low to medium (13.58-39.13 mole (+)/kg soil). Calcium carbonate in soil was 463.1-637.8 g kg^{-1} soil. Clay content (%) was between 23.3 to 52%. Soil bulk densities in surface layer (0-10 cm) were between 1.2-1.3 g cm^{-3} and in other depths were between 1.35-1.45 g cm^{-3}. Due to plow layer, bulk density in 0-10 cm was low; therefore, porosity in the surface layer of soil was high. Soil textures in these regions were loam, clay loam, silty clay and silty loam. The percent of clay was in the range of 17.06-48.0%.

Atrazine residue in agricultural soil in Shiraz and its vicinity: Atrazine residual concentration, soil moisture and atrazine usage in different soil depths were shown in Table 3. According to Table 3, maximum atrazine residual concentrations in 0-20 and 20-40 and 40-60 cm soil depth were related to the agricultural field which was located near Zarghan research agricultural center. Atrazine residual concentrations in these layers were 550, 360 and 320 µg kg^{-1}soil, respectively. Minimum atrazine residual concentration in 0-20 cm soil depth was 15 µg kg^{-1}soil and was related to the agricultural field near Kaftrak in which atrazine had never been used. Minimum atrazine residual concentration in 20-40 and 40-60 cm soil depth were related to the Kohmareh Sorkhi and Sharifabad fields in which atrazine had never been used. Figure 2-4 showed the counter lines for atrazine residual concentration in 0-20, 20-40 and 40-60 cm soil depths in Shiraz and its vicinity. By using Surfer software, the counter lines were drawn for different depths and sites in Shiraz and its vicinity.

According to regression analysis it can be concluded that in 0-20 and 20-40 cm soil depths whether atrazine was used or not and also in 40-60 cm soil depth in agricultural fields which atrazine was not used, there was no linear relationship and significant difference between atrazine residual concentration and soil moisture ($p>0.05$). According to Scatter diagram there was no other relationship between them either. However, the result of regression analysis showed that in 40-60 cm soil depth in agricultural fields which atrazine was used there was a linear relationship and significant difference between atrazine residual concentration and soil moisture ($p<0.05$). A linear relationship was described by following equation:

$$\text{Atrazine residual concentration} = -257+27.0\times\text{soil moisture}$$

Table 3: Atrazine Residual Concentration, (ARC) μg kg^{-1} soil, Soil Moisture (SM) (%) and Atrazine Usage (AU) in different soil depth in Shiraz and its vicinity

	ARC (μg kg^{-1}soil)			SM (%)			
Sites	0-20	20-40	40-60	0-20	20-40	40-60	AU
Sharifabad	37.5	30	25.5	20.51	17.08	17.59	-
Kohmarehsorkhi	30	33	28	21.22	14.99	12.46	-
Goyom 2	89	40	50.5	21.16	19.69	23.43	-
Kftarak 3	15	43	86	18.99	23.42	19.18	-
Valiasre Kavar	52	56	60	15.27	15.30	14.39	+
Kaftarak 2	81.5	56	30	17.20	16.63	12.38	+
Goyom 1	40	59	74.5	12.35	10.07	7.43	-
Lappoie	32	72	112	15.44	16.23	15.53	-
Bandamir	81.2	73	91	19.85	16.56	16.39	-
Kaftarak 1	15	85	40	8.67	10.60	21.91	-
Akbarabad Kavar	104	89.5	123.2	16.64	17.41	16.08	+
Sarvestan	47.6	94	73	12.54	15.15	14.53	-
Dehshikh	250	160	120	5.48	11.47	25.39	-
Mahmodabad	90	161	82	10.64	11.50	11.48	+
Esmaielabad Zarghan	480	168	105	13.42	14.68	12.41	+
Bajgah	165.7	185	90	12.68	17.76	12.60	-
Khanzenian	445	195	78.5	36.16	38.40	30.54	-
Khirabad Dasht Arjan	75	200	70	13.75	13.57	12.32	-
Darehasaluie Kavar	162.5	213	62	9.73	9.50	10.80	+
Gharehbagh	240	320	175	10.10	9.15	5.39	-
Agricultural research center Zarghan	550	480	240	23.58	19.79	17.55	+
Polekhan Zarghan	550	360	320	16.30	13.21	11.15	+

ARC and SRMC were the mean of three replications; Positive sign (+) means atrazine was used and negative sign (-) means atrazine was not used

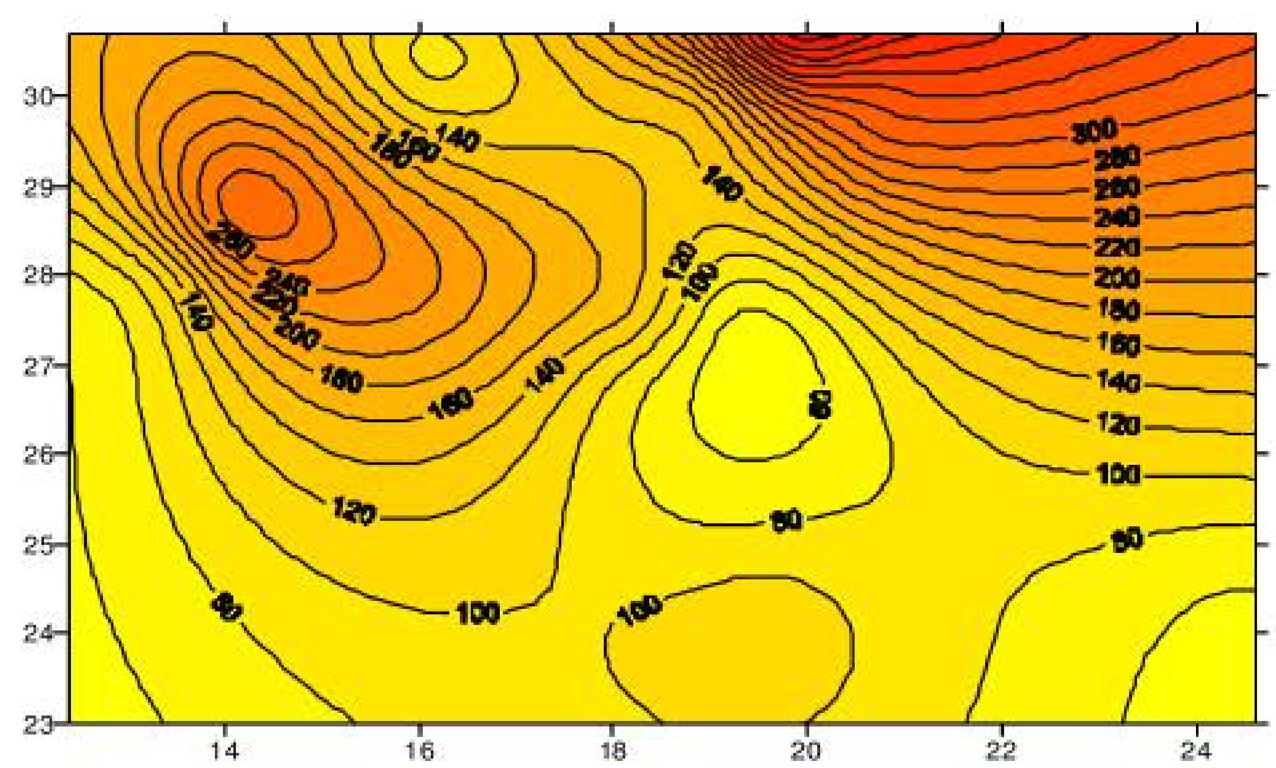

Fig. 2: The counter lines of atrazine concentration in 0-20 cm soil depth in Shiraz and its vicinity

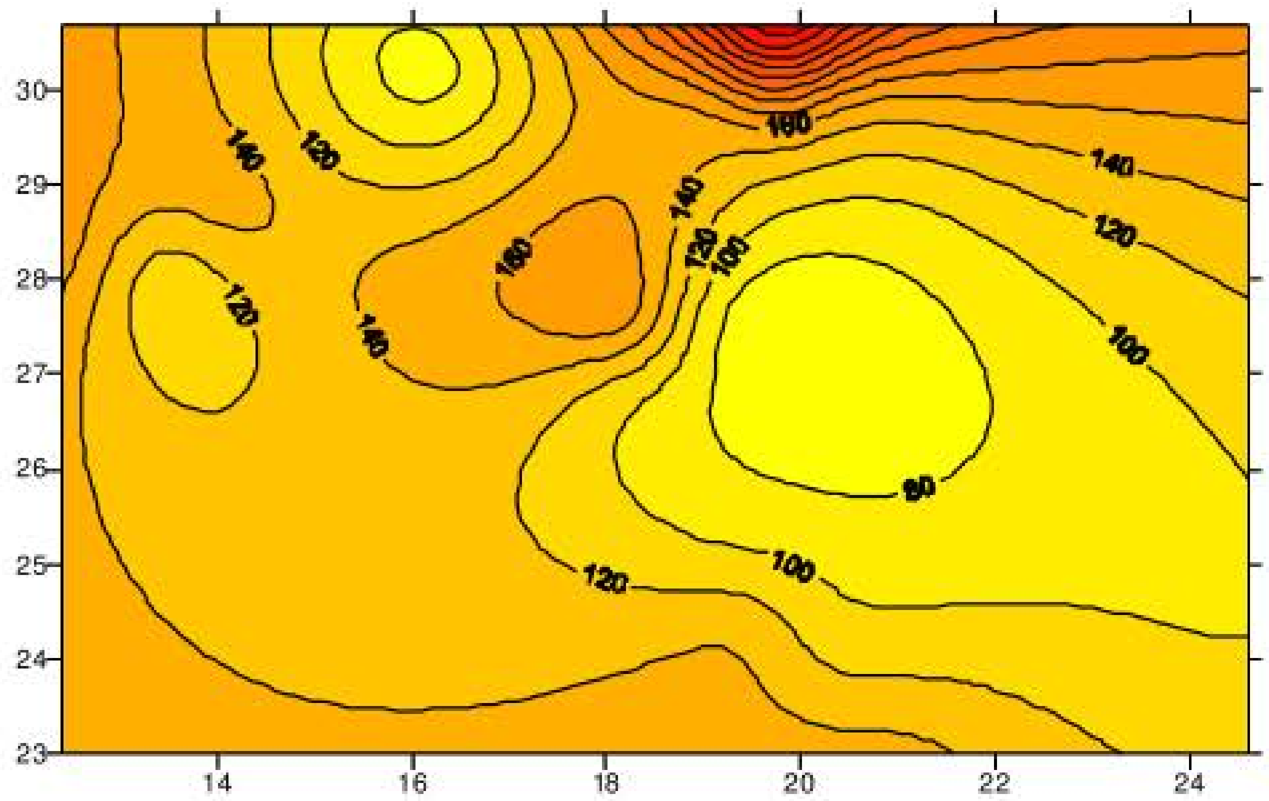

Fig. 3: The counter lines of atrazine concentration in 20-40 cm soil depth in Shiraz and its vicinity

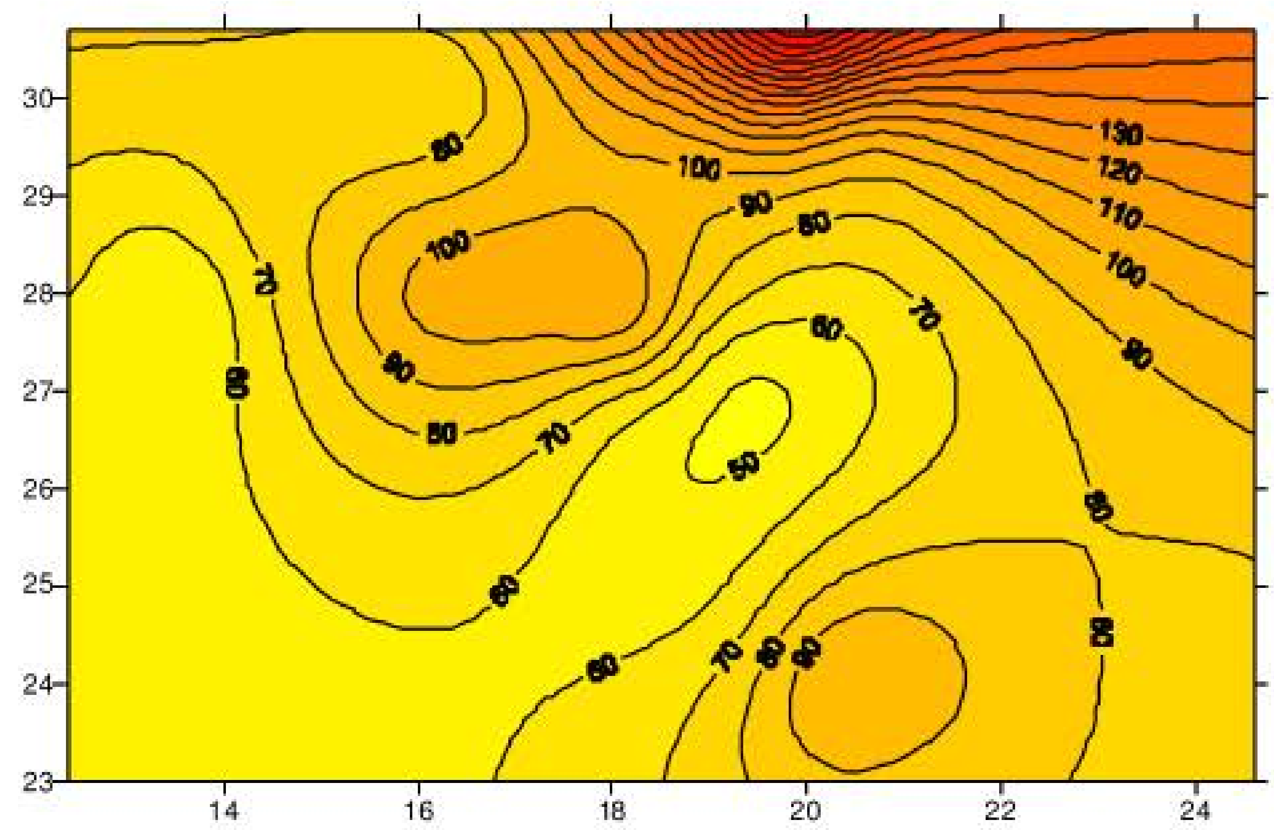

Fig. 4: The counter lines of atrazine concentration in 40-60 cm soil depth in Shiraz and its vicinity

One-way ANOVA test showed that there was no significant difference between soil depth and atrazine residual concentration ($p>0.05$).

DISCUSSION

According to data regarding atrazine residue in agricultural soil in Shiraz and its vicinity, in all sampling regions the concentration of atrazine did not exceed the soil quality standard for agriculture which is 22 mg atrazine kg^{-1}soil. Also data showed that atrazine residual concentration in some sampling regions in which atrazine had never been used was relatively high. Assuming that information given by farmers about using atrazine was correct, the hypothesis would be that atrazine had entered the agricultural soil in some other routh. Atrazine might be transferred via dust wind from the nearby agricultural fields. Due to the low atrazine Henry's law constant, the probability that atrazine evaporates and diffuses into surrounding air is not high. Another main route of atrazine transfer would be irrigation water. Irrigation in these regions was either by ground or surface water. Atrazine leaching to the deeper layers of soil can cause soil and groundwater pollution. Therefore, irrigation by groundwater containing atrazine can cause soil pollution. Surface water was also susceptible to atrazine residual concentration. Atrazine can be washed by rain and finally find its way to surface water.

In a real field, soil had a complex characteristic and many factors influenced the rate of atrazine. The rate of atrazine mineralization in soil is influenced by soil texture.

One study showed that a mineralization of atrazine is 1% after 44 days of incubation. Mineralization increased in the clay sized aggregates up to 6.2% after 23 days. Their data indicated that atrazine and its metabolites are biologically active even after 22 years of aging (Jablonowski *et al*., 2008). Many researchers found that soil texture had a large influence on the temporal variation of atrazine for a particular soil texture. Regarding the soil texture, it should be noted that the clay content has a large effect on adsorption. Herweigh also concluded that atrazine adsorption and desorption in soil is one of the important factor that cause groundwater pollution (Herweig *et al*., 2001). Also, low to medium soil clay content of the soil (17.06-48.0%), caused atrazine leached at a very fast rate. In addition soil textures in these sampling regions were loam, clay loam, silty clay and silty loam. Bowman (1990) and Sadeghi *et al*. (2000) found that atrazine moved deeper in silty loam than sandy soil. Organic matter in the sampling soil was between low to medium high. Due to low organic matter content, atrazine adsorption to organic matter contents was not also high. Present results regarding to the soil pollution are differed from the previous studies because of the soil physicochemical properties including soil texture, organic matter content so the adsorption-desorption rate potential was not the important factor in Shiraz soil pollution. It can be concluded that, due to low organic matter content and soil clay content in the sampling soils, atrazine leaching worked more than degradation processes and therefore, there is a high risk of atrazine pollution in groundwater.

CONCLUSIONS

In all sampling regions in Shiraz and its vicinity, the concentration of atrazine did not exceed the soil quality standard for agriculture which is 22 mg atrazine kg^{-1}soil. Atrazine concentration in water bodies, surface water and especially groundwater, must be determined. Therefore, further study is highly recommended to find the fate of atrazine in water resources. Also, it is very important to determine herbicide in drinking water, because maximum permissible of chemical concentrations in drinking water is very low (<0.1 mg L^{-1}).

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