Assessment of Atrazine Distribution in Shiraz Soils, South of Iran

1M. Dehghani, 2S. Nasserri, 3S.A. Amin and 4Z. Zamanian

1Department of Environmental Health Engineering, Shiraz University of Medical Sciences, Shiraz, Fars, Iran
2Department of Environmental Health Engineering, Tehran University of Medical Sciences, Tehran, Iran
3Department of Water Engineering, Shiraz University, Shiraz, Fars, Iran
4Department of Occupational Health Engineering, Shiraz University of Medical Sciences, Shiraz, Fars, Iran

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.

Key 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 precurrence, 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 (Berner 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 than 1% of atrazine is mineralized (Jablonowski 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
soil. Greater leaching in the silty loam was due to the higher water-holding capacity and slower infiltration rate, allowing atrazine more time to desorb 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 (Barrios 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-leaved 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, Khanenian, 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.

**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
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 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 (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 52.8. 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 ploy 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 Kafrak 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>
<thead>
<tr>
<th>Sites</th>
<th>ARC (µg kg⁻¹ soil)</th>
<th>SM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-20</td>
<td>20-40</td>
</tr>
<tr>
<td>Sharifabad</td>
<td>37.5</td>
<td>30</td>
</tr>
<tr>
<td>Kohmareh Sorkhi</td>
<td>30</td>
<td>33</td>
</tr>
<tr>
<td>Goyom 2</td>
<td>89</td>
<td>40</td>
</tr>
<tr>
<td>Kfarak 3</td>
<td>15</td>
<td>43</td>
</tr>
<tr>
<td>Valsaste Kavar</td>
<td>52</td>
<td>56</td>
</tr>
<tr>
<td>Kafarik 2</td>
<td>81.5</td>
<td>56</td>
</tr>
<tr>
<td>Goyom 1</td>
<td>40</td>
<td>59</td>
</tr>
<tr>
<td>Lappole</td>
<td>32</td>
<td>72</td>
</tr>
<tr>
<td>Bandamar</td>
<td>81.2</td>
<td>73</td>
</tr>
<tr>
<td>Kafarik 1</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>Akbarabad Kavar</td>
<td>104</td>
<td>89.5</td>
</tr>
<tr>
<td>Sarvestan</td>
<td>47.6</td>
<td>94</td>
</tr>
<tr>
<td>Dehshikh</td>
<td>250</td>
<td>160</td>
</tr>
<tr>
<td>Mahmodabad</td>
<td>90</td>
<td>161</td>
</tr>
<tr>
<td>Esmaeilabad Zaghan</td>
<td>480</td>
<td>168</td>
</tr>
<tr>
<td>Bagh</td>
<td>165.7</td>
<td>185</td>
</tr>
<tr>
<td>Khazanian</td>
<td>445</td>
<td>195</td>
</tr>
<tr>
<td>Khirabad Dasht Arjan</td>
<td>75</td>
<td>200</td>
</tr>
<tr>
<td>Darakehlek Kavar</td>
<td>162.5</td>
<td>213</td>
</tr>
<tr>
<td>Gharehbagh</td>
<td>240</td>
<td>320</td>
</tr>
<tr>
<td>Agricultural research center Zaghan</td>
<td>550</td>
<td>480</td>
</tr>
<tr>
<td>Poleghan Zaghan</td>
<td>550</td>
<td>360</td>
</tr>
</tbody>
</table>

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.
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 route. 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 (Jablonsowski 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. Herweig also concluded that atrazine adsorption and desorption in soil is one of the important factors 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).

ACKNOWLEDGMENTS

The authors would like to thank Tehran University of Medical Sciences for its financial support, as well as providing facilities and excellent technical assistance at the Department of Chemistry, Water Engineering and Soil Sciences in Shiraz University are highly appreciated.

REFERENCES


