

ERA: Suitable Method for Estimation of Ecological Effects of Pesticide Contamination on Aquatic Species

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Abstract

An ecological risk assessment (ERA) was conducted for Shadegan Wetland in Iran. The objective of this study was to assess the risk to phytoplankton, zooplankton, invertebrate, insect larvae, and fish affected by pesticide in Shadegan Wetland. Five pesticides (DDT, Aldrine, Dieldrin, Ametryn and Lindane) were assessed to evaluate the impact to aquatic community in the Shadegan Wetland. The risk quotient (RQ) served as calculation in water concentration and toxicant reference values of five pesticides. The results of RQ method showed that RQs for shirbot or large scaled barb (*Barbus grypus*), benni (*Barbus sharpeyi*), golden barb (*Barbus luteus*) and insect larvae (*Chironomus sp.*) were high and the environment at risk of harmful pesticides. It is recommended that proper strategies should be implemented to reduce the risks.

Keywords: ERA, Aquatic species, Shadegan Wetland, Ecological effect, Pesticide, Iran

1. Introduction

Shadegan Wetland comprises the southern portion of the extensive flood plain and delta systems of the Karun, Dez and several other major rivers which rise in the northwest Zagros mountains of western Iran. The sugarcane agro-industrial units have been established northwestern of the freshwater section of the marsh. On average, more than 30 thousand tons of fertilizers and 100 tons of pesticides are annually used within the catchments area (Lotfi et al., 2002). Different studies have been carried out in Shadegan Wetland to assess the pedological, climatological, hydrological, biological and ecological parameters (Lotfi et al., 2002; Arzi et al., 2011). Survey of the

chemical pesticides in the aquatic species of Shadegan Wetland indicated different levels of residues (Arzi et al., 2011). For instance, (Davodi et al., 2010) showed that organochlorine pesticides found in all samples of fishes were in greater concentrations than polychlorinated Biphenyls (PCBs), but ecological risk assessment studies have not been done in this case. There is growing urgency to assess the ecological risk in Shadegan Wetland. For most risk assessments, EPA uses deterministic approach or the risk quotient method to compare toxicity to environmental exposure (EPA, 1998). Therefore, the objective of this study was to use the U.S. Environmental Protection Agency's (USEPA's) Ecological risk assessment paradigm to assess ecological risk of contaminations at various locations

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in the Shadegan Wetland and to rank ecological risk (high to low) for these contaminations. The risk Quotient method was adopted as the screening-level purpose for risk characterization (Bartell et al., 1992; Logan et al., 1995; Kolluru et al., 1996).

2. Material and Methods

Study Area - Shadgan wetland at located in 30°20' N and 48°20' E, in the southwestern part of Iran in Khuzestan province, surrounded by cities such as Abadan, Shadegan and Mahshahr (Fig. 1).



Fig. 1: Sampling locations in Shadegan Wetland, Khuzestan Province, Iran

The region is characterized by its extremely high temperatures, with mean July temperature in excess of 45°C and mean January temperatures in excess 7°C. The average annual rainfall is 146mm, 22% of which falls as winter precipitation, with an abrupt onset in November and more gradual termination in April or May. Shadegan Wetland is listed as a Ramsar convention site of an international importance with almost 400,000 ha, about 296,000 ha of which were established as a wildlife refuge.

Major point sources of contamination in this area include: fertilizers, herbicides and pesticides of sugarcane plantations and agricultural fields in northwestern freshwater marsh and non-point sources consist of hazardous substance residues and particles from refineries and Mahshahr, Bandar Imam and Abadan chemical and petrochemical plants (Davodi et al., 2010). Shadegan Wetland harbors different ecosystems, especially, fresh, brackish and salt waters. For assessing ecological risk; the environmental effect

concentration (EEC) of 5 pesticides (DDT, Aldrin, Dieldrin, Lindane and Ametryn) was measured at 5 locations (Fig. 1) distributed among fresh, brakish (3 locations) and saline waters (two locations). Pesticides were selected as target analytes as they were being widely used in sugarcane plantations in the region and their application in study area.

Although the use of organochlorine pesticides was banned in Iran in 1983, apparently, they are still used under different commercial names (Coke et al., 1999; Hosseini et al., 2008).

Sample collection- Water sampling was performed seasonally for three seasons (in May, September and November 2010) at five sampling locations. Three replicate samples were taken from middepth (0.5 m) using sterile water bottle (Table 1) using QA/QC protocols. Samples were stored at 4°C and analyzed within 48 h.

Table 1. Pesticide residues content (ng/L) in Shadegan Wetland water

	DDT	Lindane	Aldrin/Dieldrin	Ametryn
May	35.6	16.0	3.1	1.8
September	5.6	11.3	8.5	2.0
November	173.0	761.0	744.0	426.0
Average	98.3	263.0	252.0	191.2

Sample Analysis- Analysis of pesticides in water samples were based on the solid-phase micro extraction procedures described in (Hela et al., 2005). Ten (10) ml volume of water samples was placed in 20 ml vials, sealed with hole-caps and PTFE line septa. The samples were stirred at room temperature (25±2°C). After extraction, the fiber was directly exposed to the hot injector of the GC systems for analysis. Thermal desorption of pesticides was carried out for 10 min. After this period, no significant blank values was observed. The quantification was carried out by peak area using the external standard calibration. A detailed description of the methods is given elsewhere (Hela et al., 1998; Hela et al., 2005).

Problem Formulation: Stressor Characteristics

The contamination of Shadegan Wetland mainly originated from agricultural wastewater discharge. With the problem addressed above, the ecological stressors in the Shadegan Wetland are summarized in Table 2.

In the problem formulation phase of this risk assessment, solubility, persistence and bioconcentration potential of contaminant mixtures were weighted as important. It was hypothesized that chemical stressors would contribute the major risk to the aquatic community thus, only chemical stressors (Taiwan Environmental Protection Administration, 1997) was adopted for ecological risk assessment in this study. Ecosystem at Risk- Since toxicological data were limited for some local species, this study relied on available toxicity data of 9 species.

Therefore, the valued ecosystem components were selected in Table 3. The valued ecosystem components were biological indicators of ecological conditions and represented the whole aquatic

community in Shadegan Wetland. In addition of being indicators of ecosystem structure, the valued ecosystem components were selected as the assessment endpoint because they exhibited marked sensitivity to stressors, and changes in populations (Davodi et al., 2010).

Assessment Endpoints- Assessment endpoints are the link between scientifically measurable endpoints and the objectives of the stakeholders and resource managers (Barthouse et al., 1987; Suter, 1991; Suter, 1993). The assessment endpoints in this study were the survival of aquatic species in Shadegan Wetland. Representative aquatic species from five major trophic levels were chosen as endpoints in order to complete an ecosystem-level analysis.

Table 2. Summary of stressors to aquatic species in the Shadegan Wetland

Ecosystem element	Stressor	Risk
Fish	Sedimentation, suspended solid, flow rate, construction and change of river channel, toxic substances, nutrients, dissolved oxygen, exotic species	Reduction in species richness or abundance, inhibit respiration rate, reduction of habitats, destruction of microhabitats, reduction in species richness or abundance, increased mortality, change of dominant species
Benthic organisms	Sedimentation, Flow rate, construction, toxic substances, dissolved oxygen	Reduction in production of benthic community, reduction of habitats, destruction of microhabitats, reduction in species richness or abundance or increased bioaccumulation effect, increased mortality
Aquatic insects	Sedimentation, flow rate, construction, toxic substances, dissolved oxygen	Reduction in production of aquatic insect, reduction of habitats , destruction of microhabitats, reduction in species richness or abundance or increased bioaccumulation effect, increased mortality
Algae	Suspended solids , flow rate, toxic substance, nutrients	Reduction of photosynthesis rate, reduction in species richness or abundance, eutrophication

Table 3. The valued ecosystem components listed in the Shadegan Wetland

Phytoplankton	Zooplankton	Invertebrate	Insect	Fish
Blue-green algae.	<i>Daphnia pulex</i>	<i>Tubifex tubifex</i>	<i>Chironomus</i> sp	
Green algae		Oligochaeta	<i>Barbus grypus</i> <i>B. Luteus</i> <i>B. Sharpeyi</i>	

Analysis: Characterization of Exposure- Exposure data were used in conjunction with effects data to characterize risk. The exposure analysis for pesticides considered use rates, sources, loading, chemical properties, and a spatial/temporal scale of measured concentrations. The data was applied to determine the expected environmental concentration (EEC).

Characterization of Ecological Effects - Ecological effects were determined on the basis that measurement endpoint was correlated to assessment Endpoint. In this study, toxicological end point concentration (LC50) of 9 aquatic species were obtained from the pesticide action network (PAN) pesticide data base (www.pesticideinfo.org), pesticide toxicity index for fresh water aquatic organisms and others were from literature validated toxicological data (Munn and Gilliom., 2001; Hela et al., 2005; Davodi et al., 2010; PAN pesticide database, 2010).

Toxicant reference values of different selected species in Shadegan Wetland are presented in Table 4. Risk Characterization- Risk Quotient Method (RQ)- In the deterministic approach, RQ is quotient of measured or estimated environmental concentration (exposure) divided by a toxicant reference values (TRV), the RQ single pesticide (i) was calculated using:

$$(RQ_i) = \text{EXPOSURE} / \text{TOXICITY} = \text{MEC}_i / \text{TRV}_i = \text{MEC}_i / \text{LC}_{50} \text{ or } \text{EC}_{50} \quad (1)$$

Where, MEC_i = measured environmental concentration of pesticide i (or EEC estimated in field sampling)

TRV_i = toxic reference values or LC_{50} or EC_{50}

(LC_{50} - half lethal concentration for the 50% of the population of tested species) of pesticide (i)

LC_{50} or EC_{50} was estimated quantitatively from pesticide action network (PAN) pesticide database or (Munn and Gilliom., 2001; Hela et al., 2005; Davodi et al., 2010; PAN pesticide database, 2010).

For a mixture of (n) kinds of pesticides, the risk quotient of mixture (RQ_m) was calculated as the addition of RQ_i for mixture components: $\text{RQ}_m = \sum_{i=1}^n \text{RQ}_i = \sum_{i=1}^n \text{MEC}_i / \text{TRV}_i \quad (2)$

3. Results and Discussion

The Risk Quotients were calculated by dividing the environmental concentration in Table 1 and the toxicant values in Table 4 using Equation (1). The sum of Risk Quotients of each detected pesticide is shown in Figure 3.

The risk quotients of the representative species in Shadegan Wetland ranged from 0.06 to 3.40. Comparing to literature reported levels of concern (i.e., $\text{RQ} \geq 1$ high risk, $0.1 \leq \text{RQ} < 1$ medium risk, $0.01 \leq \text{RQ} < 0.1$ low risk) (Sanchez-bayo et al., 2002). It is clear that pesticide posed higher risk to lower creatures and lower risk to higher animals. The total ecological risk of (*Chironomus sp.*) and *B. grypus* was the highest in the wetland ecosystem, whereas phytoplanktons were faced with low risk level. As a result, insect larvae and (*Barbus sp.*) should be chosen as the key protection objectives of the ecosystem in Shadegan Wetland. The relative contributions of pesticides to the total ecological risk were calculated to identify pesticides that posed higher risk to a specific organism (as shown in Figure 4).

Table 4. Selected toxicant reference values ($\mu\text{g/L}$) for different organisms in Shadegan Wetland

Pesticides	phytoplankton		zooplankton		invertebrate	insect	fish		
	Green algae (LC_{50} 7-14d)	Blue-green algae	<i>Daphnia pulex</i> (LC_{50} -48 h)	<i>oligochaeta</i> (LC_{50} -48-96 h)	<i>Tubifex tubifex</i>	<i>chironomus .sp</i> (LC_{50} 24-48 h)	<i>B.grypus</i>	<i>B. Sharpeyi</i>	<i>B.Luteus</i>
DDT	8500	22000	105	130	4000	65	410	105	345
Aldrin	20000	15000	28	-	6710	280	0.05	-	-
Diieldrin	20000	1000	251	-	-	560	-	-	-
Ametryn	-	-	40000	-	-	-	2500	2500	2500
Lindane	2500	-	3800	5660	3900	41.4	105	76	320

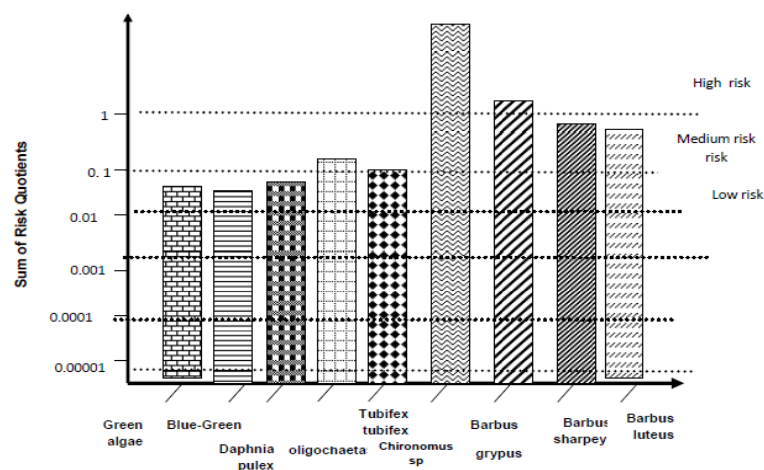


Fig. 3: Combined ecological risks based on RQ method

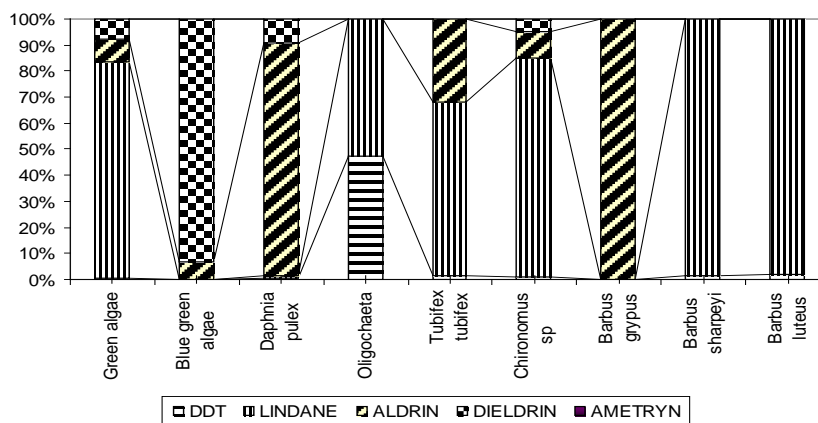


Fig. 4: the contribution of detected pesticides in total ecological risk

Lindane, Aldrin and Dieldrin were the greatest hazards to the species in the wetland. In general, phytoplanktons (algae and blue-green algae) are exposed in Lindane (82%) and Dieldrin (93%), respectively. Risk posed to algae and blue green algae were all caused by Lindane and Dieldrin, which acted strongly on photosynthesis. Green algae account for a significant portion of (*Barbus* sp.) diet. For oligochaeta, *T. tubifex*, (*Chironomus* sp.), *B. sharpeyi* and *B. luteus*, the highest risks were posed by Lindane, whereas toxicity for *D. pulex* and *B. grypus* was mainly determined by Aldrin. Since Lindane and Aldrin occurred commonly in the Shadegan Wetland, the need to focus on removing of Lindane and Aldrin from the ecosystem was serious.

In view of the additional effects of the detected pesticides as determined by ERA and the RQ method, it

is concluded that the detected pesticide levels exert a significant pressure on the Shadegan Wetland, especially in acute effect levels. Comparing this study with another study (Chen and Haung., 2010) showed that although both studies consisted of similar groups of species (phytoplankton, zooplankton, benthos, fish and insect larvae) and the fact that both studies have reported Lindane and DDT in noticeable quantities in the wetland ecosystem, RQ method in Shadegan Wetland for *B. sharpeyi*, *B. luteus*, *B. grypus* and (*Chironomus* sp.) revealed greater importance. Firstly, RQ in (*Chironomus* sp.) was at high level (RQ=3.40) and in other fishes, respectively, but in findings of Chen and Haung., 2010, RQ quantity was lower (RQ=0.9). Therefore, it is very likely ecosystem is vulnerable to damage and the the unique biodiversity of the wetland at great risk of loss.

4. Conclusion

Agricultural wastewater in Shadegan Wetland has degraded the quality of water and the functioning of some organisms. This study proposed a methodology by integrating ecological risk assessment (ERA) and risk quotient method. The risks of 5 pesticides in Shadegan Wetland were assessed. The assessment indicated that, DDT was the primary pesticide affecting the quality of water in the wetland. DDT caused the most ecological risk to the entire ecosystem followed by Lindane and Aldrin. (*Chironomus* sp.) and *B. grypus* are the primary species at risk. Therefore, it seems that the international wetland is suffering from high load of pesticides. The results of this study can contribute to the risk management and the restoration efforts that have been conducted during the last years in the wetland by the local authorities. A more complete assessment of the risks posed to the ecosystem of Shadegan Wetland will require, in addition to data on the concentrations of pesticides, a more complete set of toxicological information especially of endemic species and for the chronic- effect level. Finally, it is necessary to obtain more environmental data pertaining to temporal and spatial variations to characterize the total ecological risk of the whole Shadegan Wetland ecosystem.

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References

Arzi, A., Hemmati, A.A. and Nazari khurasgani, Z., 2011. Determination and comparison of the organochlorine pesticide residue levels among

- benni fish of shadegan, mahshahr and susangerd cities, khuzestan province in Iran, *Jondishapur journal of natural pharmaceutical products*.6: 24-31.
- Barnhouse, L.W., Suter II, G.W., Rosen, A.E. and Beauchamp, J.J., 1987. Estimating responses of fish populations to toxic contaminants, *Environmental Toxicology and Chemistry* .6: 811–824.
- Bartell, S.M., Gardner, R.H. and O'Neill, R.V., 1992. *Ecological Risk Estimation*, Lewis, Chelsea, Michigan.
- Coke, L., Karakaya, A.E. and Afkham, B.L., 1999. Organochlorine pesticide contaminants in human milks samples collected in Tabriz (Iran), *Bulletin Environmental Toxicology* .63: 44-45.
- Chen, W. C.S. QU, J.B.I. and Haung, F.Y.L.I. L., 2010. Ecological risk assessment of pesticide residues In Taihu Lake Wetland, China. *Ecological Modelling* .
- Davodi, M., Esmaili-sari, A. and Bahramifarr, N., 2010. Concentration of polychlorinated biphenyls and organochlorine pesticides in some edible fish species from the Shadegan marshes (Iran), *Ecotoxicology and Environmental Safety* .7: 2-3.
- Hela, D. and Albanis, T., 1998. Pesticide determination in estuarine and marine sediments, using gas chromatography with FTD and MSD, *Fresenius Environmental Bulletin* .7: 704-709.
- Hela, D.G., Lambropoulou, D.A., Konstantinu, I.K. and Albanis, T.A., 2005. Environmental monitoring And ecological risk assessment for pesticide contamination and effects in Lake Pamotives, northwestern Greece, *Environmental Toxicology and Chemistry*. 24: 1548-1556.
- Hosseini, S.V., Behrouzi rad, B., Esmaili-sari, A., Bahramifar, N., Hosseini, S.M., Tahergorabi, R., Hosseini, S.F. and Feas, X., 2008. Contamination by organochlorine compound in the edible tissue of Four sturgeon species from the Caspian Sea (Iran), *Chemospher*.73: 972-979.
- Kolluru, R.V., Bartell, S.M., Pitblado, R.M. and Stricoff, R.S., 1996. *Risk Assessment and Management Handbook*, McGraw-Hill, New York.

- Logan, D.T. and Wilson, H.T., 1995. An ecological risk assessment method for species exposed to contaminant mixtures, *Environmental Toxicology and Chemistry* .14: 351–359.
- Lotfi, A., Savri, A., Behrouzi rad, B., Ghaffari, H. and Kavousi, K., 2002. Shadegan Wetland Environmental management project, report 2, 76: 44-48.
- Munn, D.M. and Gilliom, R.J., 2001. Pesticide toxicity index for fresh water aquatic organisms, U.S. geological survey, Water resources report.
- PAN pesticide database, pesticide action network, North America, 2010. www.pesticideinfo.org.
- Sanchez-Bayo, F., Baskaran, S. and Kennedy, I.R., 2002. Ecological relative risk (ECORR): another approach for risk assessment of pesticides in agriculture, *Agriculture Ecosystem Environment*. 91: 37-57.
- Suter II, G.W., 1991. Screening level risk assessment of off-site ecological effects in surface waters downstream from the U.S. Department of Energy Oak Ridge Reservation, ORNL/ER-8, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Suter II, G.W., 1993. *Ecological Risk Assessment*, Lewis, Boca Raton, Florida.
- Taiwan Environmental Protection Administration, 1997. Investigation of pollution source and benthic biota in Keelun River. EPA-86-G103-03-20, Taipei, Taiwan.
- U.S.environmental protection agency., 1998. *Guidelines for ecological risk assessment* .U.S Environmental protection agency, Washington, D.C, EPA/630/R-95/002F.