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Evaluating concentration, distribution, and risk assessment of organophosphate pesticides in paddy fields of Sepidrud River watersheds, Rudbar county, Guilan Province, Iran

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ABSTRACT
Organophosphate pesticides are widely used in agriculture fields as an effective method against pests. However, concerns about the toxicity effects of these compounds on the non-target organism have grown in recent years. The aims of the present study were to assess the concentration, distribution, and biological risk of organophosphate pesticides in the paddy rice of Guilan Province in the Northen Iran. For these purposes, paddy samples were taken from 12 stations and 36 paddy fields in the watershed of Sepidrud River in the precinct of Rudbar County. Samples were analyzed to assess the concentration, distribution, and risk assessment of Diazinon and Malathion as famous commercial formulations of organophosphate pesticides. Results of the present study showed that the average residual Diazinon and Malathion concentrations in samples were 1.226 ± 0.71 and 0.422 ± 0.06 ppb, respectively. In addition, the health risk index (HRI) was 0.08. According to the results, the average concentration of organophosphate pesticides and the health risk for rice consumption was lower than the standard of Plant Protection Organization in Iran and may not be a serious hazard for people who eat rice regularly. However, due to a significant correlation between the consumption of these pesticides by elevating their residual in paddy fields production, it is necessary to monitor and management organophosphate pesticide application in paddy fields. The results of the present study can be considered as a basic information for future environmental studies and health risk management of agricultural produce.

Keywords: Environmental risk assessment, Residue, Pesticides, Agriculture, Organophosphate.
Article type: Research Article.

INTRODUCTION
Pesticides are widely used in agriculture as an effective method against pests (Vajargah *et al*. 2013a). According to the Food and Agriculture Organization (FAO), about 3.8 million tons of pesticides were used in agricultural lands in 2012 (Abdi & Sobhan Ardakani 2019). Pesticides can disturb the ecological balance, since their widespread use can increase the water, soil, and crop pollution, thereby elevating environmental and health risks (Aktar *et al*. 2009). The average use of pesticides in Asia has the highest statistic where insecticides are used in the range of 6.5 to 60 kg per hectare (Pan *et al*. 2018). Organophosphate pesticides are a group of phosphorus-containing chemicals that due to their significant efficiency, shorter half-life than chlorine pesticides, and solubility in water, are used to control a wide range of pests in the agricultural sector, and the application of these pesticides is currently expanding in the world (Vajargah *et al*. 2013b). According to the Official Annual Statistics, about 40% of all commercially produced and used pesticides in the world belong to this category (Yousefi-

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Porshokouh *et al.* 2019). Organophosphates have gradually replaced Organochlorine pesticides, because of their easily-degradation in the environment and significant economic benefits (Nicolopoulou-Stamati *et al.* 2016). Organophosphate pesticides can block acetylcholinesterase (AChE) activity and disrupt the functioning of the nervous system (Liang *et al.* 2019). Minor chemical changes within the molecular structure of organic phosphorus of these chemical compounds often cause a large change in its toxicity from one type to another (Smulders *et al.* 2004). Rice is one of the favorite nutrients in Iran and has second place among the most vital foods list after wheat (Karizakil 2016). Rice consumption per capita for Iranian people is 40 kg annually (Nemati *et al.* 2014). Northern provinces of Iran (including Guilan, Mazandaran, and Golestan provinces) are known as the pole of rice production in Iran (Saadat *et al.* 2019). According to official reports, over 85% of about 2.5 million tons of rice in Iran during 2015 was produced in the Mazandaran, Guilan, and Golestan provinces (Nabavi-Pelesaraei *et al.* 2018). Sepidrud River plays influential role in the sustainable agriculture in Guilan Province. Its branches supply the required water for many paddy farms in this province (Tohidifar *et al.* 2016). Climate of Rudbar County in South Guilan is semi-arid based on the De Martonne classification method (Mohamadi *et al.* 2018). The average annual temperature and rainfall are 16.1 °C and 535 mm, respectively (Modarres & Sarhadi 2011). Rudbar has about 3300 hectares of paddy fields (Karimzadegan *et al.* 2022). According to official reports, Diazinon and Malathion were the most used pesticide in the paddy field of Guilan from 2019 to 2021 (Nozari *et al.* 2023). The present study was designed and implemented due to the potential toxicity of organophosphate pesticides to non-target organisms and the importance of consumer health.

MATERIALS AND METHODS

Sampling and analysis of samples

The study area included 12 stations on the shores of the Sepidrud River from Gelevarz to Sheikhali-Touse with a total area of 2000 ha (Fig. 1). In addition, the number of samples was estimated by the $n = (\delta/\delta/3)^2$ formula with a confidence of 95 % and a precision of 1.1 standard deviations (Arjmandi *et al.* 2010). The number of samples was 3 for each station according to the scale of 1×1 km (Galani *et al.* 2020). Samples of each station (paddy rice samples) were mixed together and were evaluated in the form of a single sample from each station. The samples were kept at 4 ℃ in the refrigerator for further analysis (Horvat *et al.* 2003).

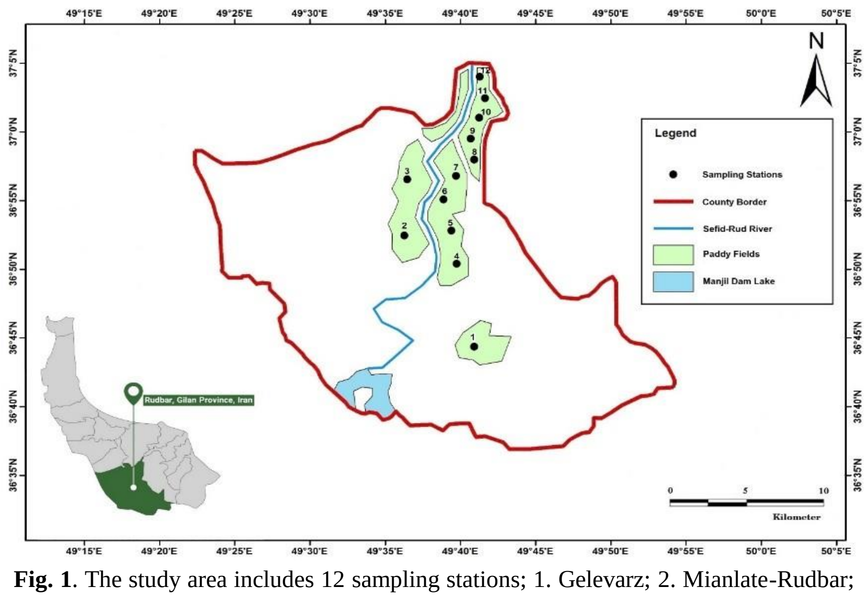

Fig. 1. The study area includes 12 sampling stations; 1. Gelevarz; 2. Mianlate-Rudbar; 3. Rud-Abad; 4. Khereshk; 5. Shahran; 6. Halimejan; 7. Bragour; 8. Shahre-Bijar; 9. Mirzagolband A; 10. Mirzagolband B; 11. Sheikhali-Touse A; 12. Sheikhali-Touse B.

Residual concentration of Diazinon and Malathion were characterized using Gas Chromatography (7890A GC, Agilent Co., CA, US) in the Ariya Chemistry Sharif Laboratory (Fahmideh town, Karaj, Iran).

Statistical processing and data analysis

All analyses were performed using SPSS software (SPSS Statistics V20, IBM Co., New York, US) in the Windows platform (Win. 7 ultimate × 32, Microsoft Inc., New Mexico, US). Significant differences between residual average concentrations of paddy rice samples were determined through the one-way analysis of variance (ANOVA) with a 95% confidence. Finally, the Health Risk Index (HRI) was assessed through the US Environmental Protection Agency's recommended guidance as follows (Darko & Akoto 2008; Ghanbari *et al.* 2021):

(1) EADI $= \frac{RPC \times FCR}{BW}$

EADI (mg kg^{-1} day^{-1}) = Estimated average daily intake (EDI)
RPC (mg day^{-1}) = Residual pesticide concentration
FCR (kg day^{-1}) = Food consumption rate
BW (kg)= Body weight

(2) HRI $= \frac{EDI}{ADI}$

ADI (mg kg^{-1} day^{-1}) = Acceptable daily intake

RESULTS AND DISCUSSION

There was a significant difference between the Diazinon residue concentrations in different stations ($p < 0.05$). The highest and lowest concentrations (1.70 and 0.01 ppb) were related to Gelevarz and Rud-Abad stations, respectively (Fig. 2a). In addition, the highest and lowest concentrations of Malathion (0.51 and 0.31 ppb) were measured in Gelevarz and Khereshk stations, respectively (Fig. 2b).

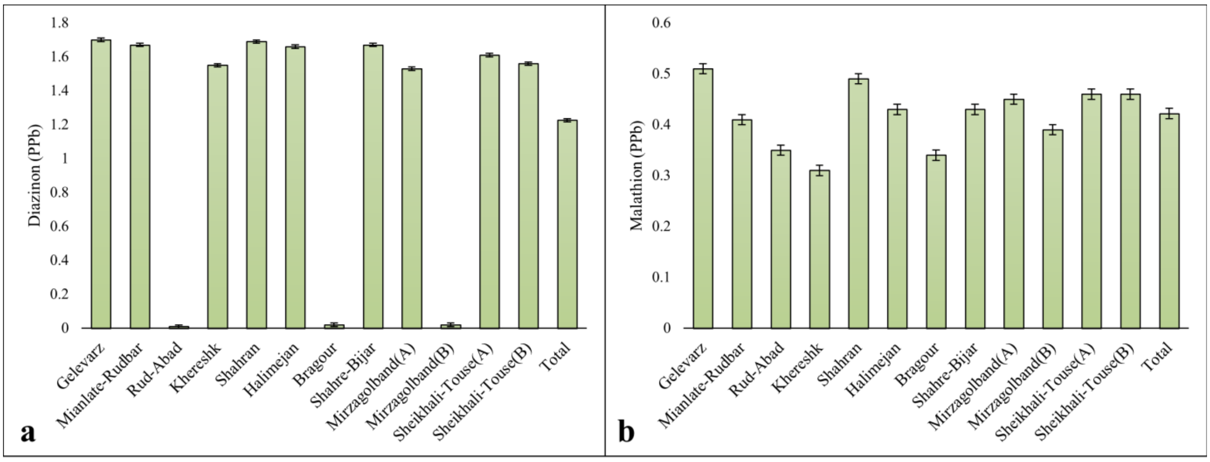

Fig. 2. The residual concentration of organophosphates pesticides (a: Diazinon and b: Malathion) in paddy samples of Rudbar County fields.

In the present study, the average health risk index (HRI) in 12 stations was 0.08 ppb kg^{-1} day^{-1}. The Diazinon HRI values for the 12 stations were as follows: Gelevarz 0.07, Mianlate-Rudbar 0.02, Rud-Abad 0.11, Khereshk 0.09, Shahran 0.03, Halimejan 0.10, Bragour 0.06, Shahre-Bijar 0.08, Mirzagolband A 0.14, Mirzagolband B 0.11, Sheikhali-Touse A 0.09 and Sheikhali-Touse B 0.07 ppb kg^{-1} day^{-1}, respectively (Fig. 3a). In addition, The HRI values of Malathion residue for the 12 stations were as follows: Gelevarz 0.03, Mianlate-Rudbar 0.01, Rud-Abad 0.06, Khereshk 0.04, Shahran 0.02, Halimejan 0.05, Bragour 0.02, Shahre-Bijar 0.03, Mirzagolband A 0.07, Mirzagolband B 0.04, Sheikhali-Touse A 0.05 and Sheikhali-Touse B 0.01 ppb kg^{-1} day^{-1}, respectively (Fig. 3b). The highest Diazinon and Malathion residual concentrations in the paddy rice samples among all the stations were found at Gelevarz Station, where exhibited the highest residual Diazinon and Malathion concentration among the 12 stations in the study area. The lowest were recorded in Rud-Abad and Khereshk stations, respectively. The overall mean residual Diazinon and Malathion concentrations in the paddy rice samples in Rudbar were 1.226 and 0.422 ppb, respectively, which were less than the Maximum Residual Limit (MRL) for Diazinon (200 ppb) and Malathion (8000 ppb) set by the Plant Protection Organization of Iran (PPOI) in 2022. The low Diazinon and Malathion concentrations in the paddy rice samples of all stations compared to the MRLs in Iran indicate that although the consumption of pesticides does not have the same pattern, however, a smaller level of this pesticide is used in Rudbar paddy fields. Therefore, the pesticide residues in paddy rice and their long-term use in paddy fields may lead to chronic diseases (Čuš *et al.* 2010).

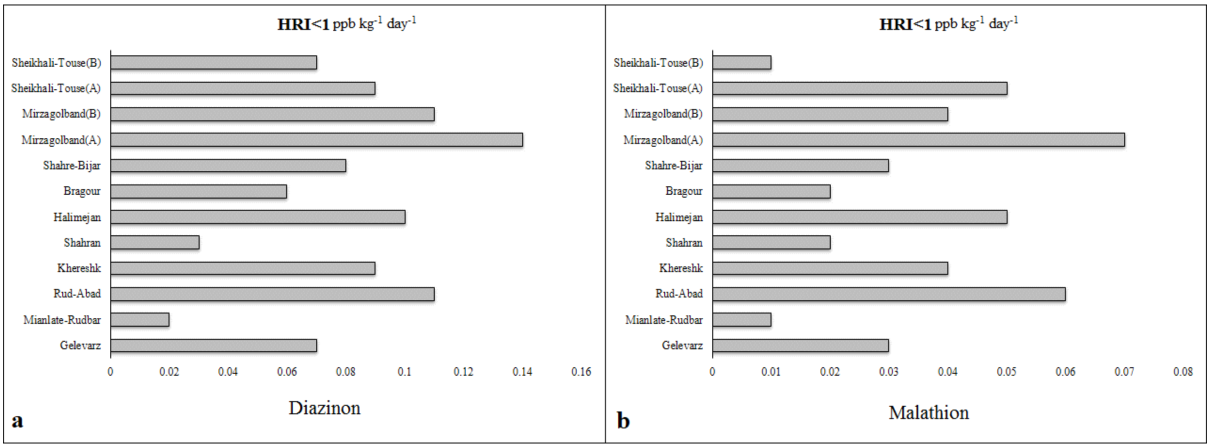

Fig. 3. The HRI values of Diazinon (a) and Malathion (b) residue in paddy rice for the 12 stations of Rudbar County fields.

Ghanbari *et al.* (2021) studied the residual concentrations of Diazinon in produced Rice in Rasht county (Guilan province, Iran) reporting that it was 0.4 mg kg^{-1} and HRI was higher than 1. In addition, Arjmandi *et al.* (2010) studied the Diazionon residue in paddy fields of Mazandaran Province, Northern Iran, reporting that its levels varied from 0.01 to 1.14 mg kg^{-1}. The results of the present study confirmed the presence of organophosphorus residues in rice paddy (0.422 ppb for Diazinon). However, its concentration was lower than the previous concepts. Hence, it can be concluded that there are no potential health risks for rice consumers according to the standards of Plant Protection Organization in Iran (PPOI; HRI < 1). The findings of a study in China on organophosphorus pesticide residues in milled rice (*Oryza sativa*) indicated that 9.3% of the samples contained detectable residues of chlorpyrifos, dichlorvos, omethoate, methamidophos, parathion-methyl, parathion, and triazophos. The total averages of these pesticides were between 0.011 and 1.756 mg kg^{-1}, very lower than the maximum residue limit (Chen *et al.* 2012). In addition, Jaipieam *et al.* (2009) studied residual concentration of organophosphate pesticides in Thailand fields, reporting that 85.18 % of rice samples were contaminated with carbamate and organophosphate pesticides. A comparison of the results of the present study with those obtained by Jaipieam *et al.* (2009) exhibited that there is a significant correlation between the application of pesticides and their residual concentration. However, there was a significant different ($p < 0.05$) in HRI index (HRI < 1) between our study and that of Jaipieam *et al.* (2009; HRI > 1). The latter reported a high risk of developing cancers or non-cancer diseases. Islam *et al.* (2021) evaluated the human health risk from residual pesticides in Bangladesh paddy fields reporting that the residual concentrations of the studied pesticides (dimethoate, fenitrothion, chlorpyrifos, quinalphos, diazinon, and malathion) were above than European Union Maximum Residue recommended Levels. According to its standards, an acceptable HRI value is less than 1. Similarly, the HRI index in the present study was in acceptable level (0.8). Guilan Organization of Agriculture has reported per capita rice consumption of 48 and 45 kg $year^{-1}$ in Guilan Province and Rudbar County, respectively, which is seven times less than the amount determined for adults (Mohamadi *et al.* 2018). This is while the per capita consumption of rice in Iran is 36 kg (Shariatifar *et al.* 2009). Although cases of chronic diseases were reported in the study area, however, further studies should be conducted on the relationship between pesticide residues in rice crops and the occurrence of chronic diseases to define the health risks of pesticide residues for rice consumers in the study area. These approaches, combined with proper diet management and creating public awareness of potential health risks resulting from chronic exposure to pesticides in rice, could play a key role in risk reduction.

CONCLUSION

Despite the minimal risk of the studied crop for consumers, chemical pesticides or poisons are recommended to be replaced by other methods. Management in the application of pesticides, the reduced using of low-cost pesticides, employing parasitoids and biological control instead of chemical methods are some of the issues that need to be considered in this study area. Given that diazinon and malathion residues in paddy rice samples are at the threshold of ADI and RfD values, necessary research is suggested in the study area to minimize the adverse effects of these pesticide application in rice fields for consumers.

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