

Monitoring Malathion Residues in Water of the Gorganrood River Estuary, Iran

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Abstract: This investigation was carried out on surface waters of Gorganrood River Estuary in order to obtain the necessary data and information on the concentration of malathion residues. A seasonal investigation was carried out at three sites along inlet estuary during 2011-2012. There was significant difference between the amounts of Malathion residue in different season. A higher concentration of Malathion was observed in spring with mean levels 88.11 ± 4.40 ($\mu\text{g/l}$). There was a decreasing trend in concentrations of malathion. Mean levels of Malathion residue in other season (winter, summer and fall) were 63.21 ± 8.69 ($\mu\text{g/l}$), 28.44 ± 5.44 ($\mu\text{g/l}$) and 8.58 ± 0.39 ($\mu\text{g/l}$) respectively. In order to reduce the discharge of toxic and bio-accumulative substances into Caspian sea coastal waters, legislative enforcement must be strengthened. Moreover, biological methods could be used for controlling pests and flies instead of pesticides in order to protect the natural environment

Key words: Pesticides Residue • Malathion • Monitoring • Estuary • Water Quality

INTRODUCTION

The aquatic environment is continuously being contaminated with toxic chemicals from industrial, agricultural and domestic activity [1]. Rivers get contaminated with pesticides residues that result from the application of pesticides in agricultural practices. Organophosphate insecticides (OPs) constitute one of the most widely used classes of pesticides being employed for both agricultural and landscape pest control. Use of OPs has increased considerably due to their low toxicity and low persistence in the mammalian system compared to organochlorine pesticides [2].

Malathion is an insecticide with a neurotoxin action that causes insect death by inhibiting the acetylcholinesterase enzyme [3]. Besides their neurotoxin effects, the organophosphate insecticides have other properties such as cytotoxicity, genotoxicity,

mutagenicity and carcinogenicity, which can affect human beings [4, 5]. Monitoring water quality is an important aspect for evaluating temporal variations of river pollution due to natural or anthropogenic inputs of point and non-point sources.

Gorganrood River, with its main branch length of 325 km is one of the largest and most important rivers in the Caspian Sea basin. The importance of Gorganrood River estuary as place for fingerling stocking of valuable fish species (typically sturgeon fish), nursery ground for numerous fish and natural environment for spawning has been well documented. One of the greatest environmental issues in this area is usage of pesticides, chemical fertilizer and discharge of industrial effluents. This study describes the seasonal distribution of malathion residue in surface waters of Gorganrood River Estuary, Golestan province in the north of Iran during 2011-2012.

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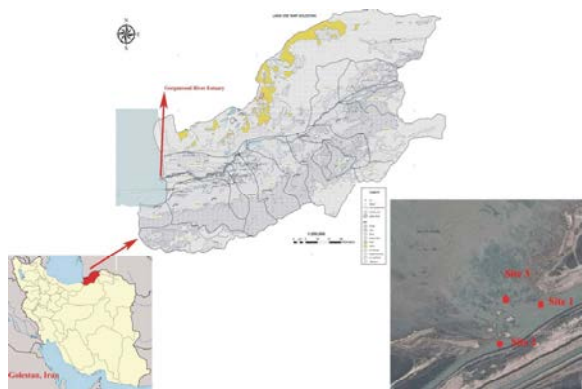


Fig. 1: The location map and the sampling sites of studied area in Golestan province

Study Area Description: Gorganrood River situated in the north of Iran within Golestan Province and this is originated from Narchi Mountains with 1875m height and Bilikoo with 1598m height in 37km distance from Kalaleh and irrigates the North area of Gorgan plain and in Mahichopaghli which nears with Khajehnafas, finally enter to Caspian Sea from the Eastern side of coast. The river water is increasingly deteriorated due to anthropogenic pollution from the rapid economic development. The basin area is 67,000 km² and located between longitudes 48°15' and 52°30' E, latitude 30°17' and 33°49' N. Topography of the area is generally flat, with slopes of 0-1% in East-West and South-North direction. Soil texture varies from silt loam to clay. Annual mean volume which is estimated in Basir Abad hydrometer station for a 20 years period is equal to 450MM. Climate is semi-arid with four distinct seasons. In this study, three monitoring stations located in inlet Gorganrood River estuary were selected for seasonal monitoring of malathion residue (Fig. 1).

Sampling and Extraction: Sampling was done according to the World Health Organization, Manual for Recreational Water and Beach Quality Monitoring and Assessment [6]. For quantify residue of malathion, 36 Water samples (1.5 L) were collected into 2 L cleaned glass bottles from 3 sites of the estuary at approximately 0.3 m depth below the water surface during 1 year. Water samples were pre-filtered through 0.45 μm fiber glass filters (Whatman) to remove debris and suspended materials. These samples were stored on ice on location and then transferred to the laboratory and were kept at 2°C prior to analysis [7]. Sample collection lasted from April 2011 to March 2012.

Table 1: Gas chromatograph mass spectro (GC-MS) condition

Condition	Value
Injection volume	1 μl
Flow rate	3.6ml/min
Injector temperature	250°C
Detector temperature	320°C
Oven temperature program	70°C(2min), 25°C/min to 150°C (0min), 3°C/min to 200°C(0min), 8°C/min to 280°C (7min)
Total time	40 min

Malathion standards with a minimum of 99% purity were purchased from the Accustandard Company of Switzerland. Acetonitrile, Anhydrous magnesium sulphate (MgSO₄) and sodium chloride (NaCl) of analytical reagent grade were purchased from (Darmstadt, Germany). Bondesil-primary secondary amine (PSA; 40 μm) were obtained from Sigma-Aldrich. The sample preparation was adapted from the original QuEChERS (Quick Easy Cheap Effective Rugged Safe) method. In summary, (a) Water samples (50 ml) were filtered first through a 125 mm filter (Fchleicher and Schuell 589.3, Germany); (b) placing a sample of 10 ml of water to 50 ml centrifuge tube; (c) adding malathion in the required concentrations; (d) adding 10 ml of MeCN, 4 g of MgSO₄ and 1 g of NaCl in each tube and centrifuging it at 3,000 rpm for 1 min; (e) For cleanup, transferring 1 ml upper layer in 1.5 ml centrifuge tube with 50 mg PSA and 150 mg MgSO₄ and Vortex for 30 sec; (f) Centrifuge for 5 min; (g) 0.5 ml into sample vial and (g) Inject 1.5 μl into GC/MS [8]. Operating conditions for the GC-MS are shown in Table 1.

Statistical Analysis of Data: All results are expressed as means ± SD. Statistical analyses were carried out using the computerized package SPSS 16.0 for Windows. Data samples were tested for significant differences for variables among different seasons by one-way ANOVA. Mean values were analyzed by the Tukey's test.

RESULTS

Results of seasonal variations in the concentrations of malathion in surface water, from Gorganrood River Estuary are represented in Tables 2 with further illustration in Figure 2. Malathion levels varied significantly among different seasons ($P < 0.05$). As can be seen from these results, higher concentrations of malathion detected in spring and the lowest values were observed in winter. Statistical analysis of data showed that there is a significant relationship between the reductions of pesticide residues with over time.

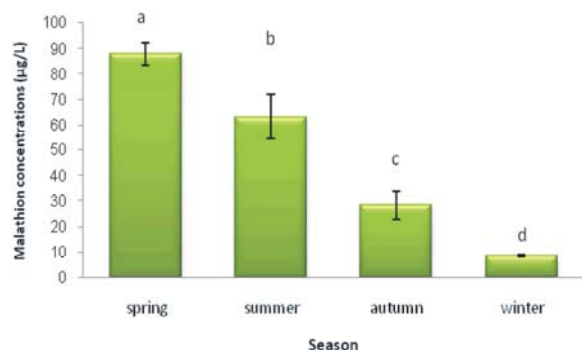


Fig. 2: Seasonal variation in surface water malathion concentration (µg/L) in Gorganrood River Estuary

Table 2: Mean ± SD values of pesticide during four studied seasons

Station	Season			
	Spring	Summer	Autumn	Winter
1	83.33±7.09	65.33±13.05	34.33±5.03	8.23±2.09
2	92.00±17.52	53.66±21.03	27.66±11.23	9.01±2.18
3	89.00±12.00	70.66±28.53	23.33±9.71	8.52±1.52

DISCUSSION

Pesticide degradability depends not only on the capacity for dissolution of the different substances themselves, but also on meteorological conditions (i.e. rainfall) and geological factors (type of rock or sediment present in the water way). Furthermore, the agricultural activity of the area studied may vary considerably from one season to the next [9].

The study recorded highest concentrations of pesticide residue in spring and summer at $p > 0.05$. The mean concentration of pesticide residue for water samples were 88.11 and 63.21 µg/l, this is probably due to their high application at that time. The major inputs of this pesticide into rivers occurred during the spring after their application in agricultural fields, as a result of surface runoff. This observation suggests that rainfall significantly increases pesticide mass loading to the aquatic environment.

The time it takes for malathion to break down to half of the original amount in soil is about 17 days, depending on the soil type. This length of time is known as the half-life. In water, malathion has a half-life between 2 and 18 days, depending on conditions like temperature and pH. Malathion vapor may also move long distances in air or fog. Malathion is highly toxic to bees and other beneficial insects, some fish and other aquatic life. Malathion is moderately toxic to other fish and birds and is considered low in toxicity to mammals [10].

Fish have a wide range of toxicities to malathion, extending from very highly toxic for the walleye (96-hour LC_{50} 64 ppb) to highly toxic for brown trout (101 ppb) and the cutthroat trout (280 ppb), moderately toxic for fathead minnows (8.6 ppm) and slightly toxic for goldfish (10.7 ppm). Various aquatic invertebrates are sensitive, with EC_{50} 's in the 1 ppb to 1 ppm.

Malathion is highly toxic to bluegill sunfish (*Lepomis macrochirus*) and large-mouth bass with 96-hour LC_{50} of 0.10 mg/l and 0.28 mg/l, respectively. It is moderately toxic to the snakehead fish (*Channa punctatus*) and mosquitofish (*Gambusia affinis*) with a 96-hour LC_{50} of 6.60 ppm and a 48-hour LC_{50} of 1.23 mg/l, respectively [11]. Researchers exposed larvae of the estuarine fish red drum (*Sciaenops ocellatus*) to environmentally realistic and sub-lethal levels of malathion at levels of 0, 1 and 10 µg/l up to seven days. No adverse effects were recorded [12].

The obtained results showed that the residual amount of malathion in spring and summer are higher than permissible value for many aquatic species of this river. In addition, detection and permanence of pesticides in water depend on parameters such as the pesticides half-life and solubility in water, the spread and amount of pesticide applications. In order to reduce the discharge of toxic and bio-accumulative substances into Caspian sea coastal waters, legislative enforcement must be strengthened. Moreover, biological methods could be used for controlling pests and flies instead of pesticides in order to protect the natural environment.

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