

Full Length Research Paper

Aquatic ecosystem contamination and ecological effects of agricultural sewage in the Caspian Sea watershed

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Accepted 6 October, 2014

The existing system of management and development of irrigation and drainage without consideration of the ecological danger have led to disruption of the ecosystem balance and change its function. The existence of many rivers draining into the Caspian Sea, and uncontrolled utilization of pesticide toxicants, are one of major concern regarding the water resources in the north provinces of Iran. A study has been done for measuring of Organochlorine and Organophosphorus pesticides in nine rivers of the Caspian Sea basin in Mazandaran and Golestan Provinces which include Haraz, Babolroud, Talar, Tajan, Siahroud, Gharahsoo, Nekaroud, Gorganroud and Atrak from April 2005 to March 2006. Samples analyzing revealed that Phosphorous toxin are observed frequently in aquatic ecosystems especially in summer and autumn. Diazinon as a phosphorous pesticide almost was found in all rivers during the year and its concentration is somewhat more than others. On the other hand, chlorinated pesticides are observed frequently in spring and especially in summer, but are not found in winter at all. Due to the vast expansion of agricultural fields in the study area, these contaminants are leached by rainfall, irrigation and drainage activities and then are conducted to the rivers and finally into the Caspian Sea.

Key words: Caspian sea, pesticides, Mazandaran, Golestan.

INTRODUCTION

The Iranian coast of the Caspian Sea stretches for nearly 900 km from Azerbaijan in the west to Turkmenistan in the east. This coastline is now becoming increasingly polluted with massive loads of contaminants discharged into the Caspian Sea from various anthropogenic sources. The areas of river mouths, water areas near human settlements and agricultural fields are the most heavily polluted areas.

Data of the toxicological survey of bottom sediments obtained during the expedition conducted under the Caspian Environmental Program (CEP) indicated the increased content of different compounds of

Organochlorine pesticides near the coast of Azerbaijan and Iran which attributed to their application in agriculture, rice growing in particular (Kajiwara et al., 2003). Motavalli (1999) reported that the World Bank estimated that a million cubic meters of untreated industrial wastewater is discharged directly into the Caspian Sea. The report by Neville (2006) mentioned scientific estimates of annual averages of 24,000 tones of sulfites, and 400,000 tones of chlorine. Sea currents transport and circulate the entrapped pollutants along the Iranian coast of the Caspian Sea. The chemicals and pesticides are threats to the flora and fauna.

One example of detrimental impacts on aquatic life could be found in the account given by Energy Information Administration (2003) which reported that thousands of seals that live in the Caspian Sea had died since 2000 because of the consequence of pollution that

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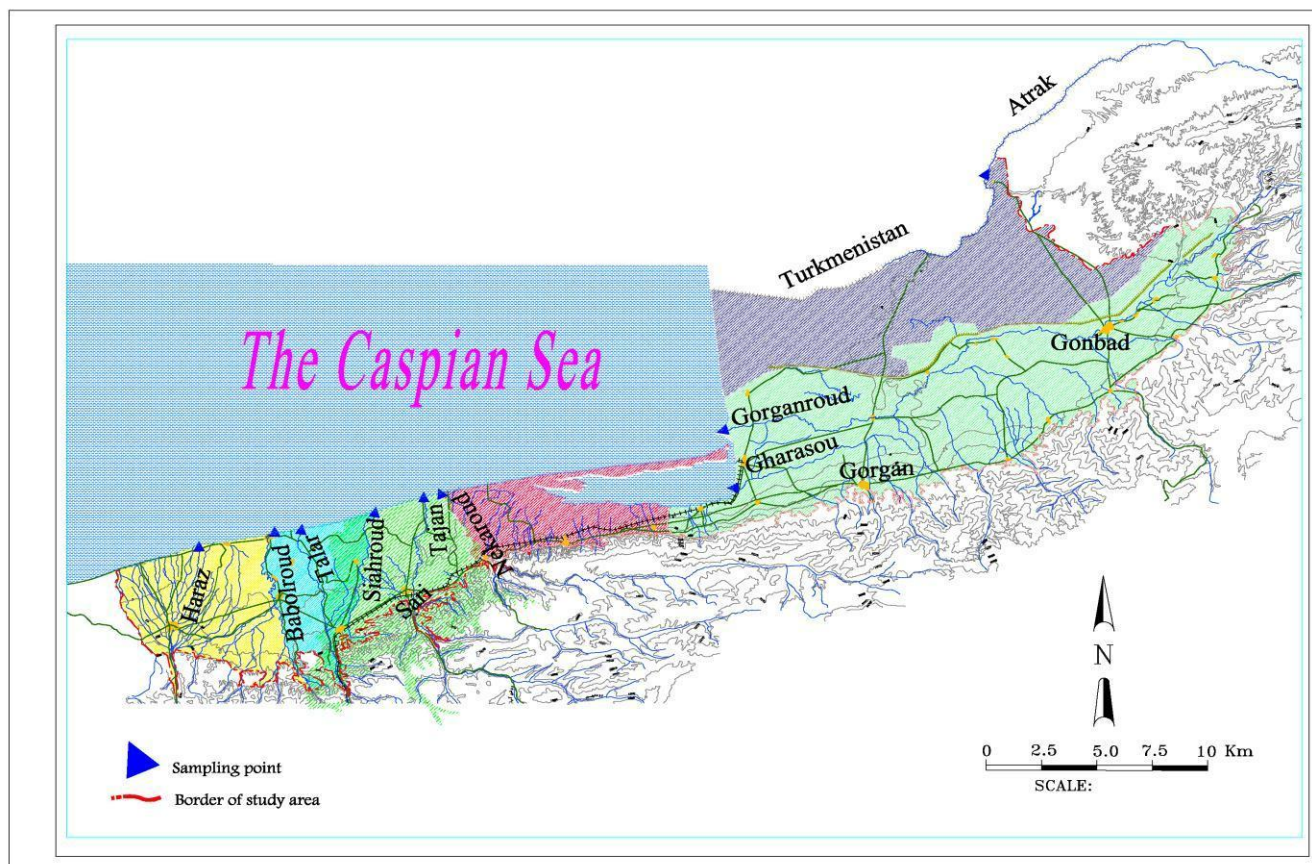


Figure 1. Border of study area and sampling points.

affected their immune system. According to the Caspian Environmental Program (CEP), sturgeon landings have decreased from 30,000 tons in 1985 to only 5,672 tons in 1995 (Parizanganeh et al., 2007). The existing and potential problem facing aquatic and human life as a result of toxic pollutants, therefore, requires the investigation of the current concentration of contaminants in the studied area.

MATERIALS AND METHODS

We have categorized the study area to 6 subareas including Haraz, Talar, Tajan, Neka, Gorgan and Gomishan (Figure 1). Haraz subarea includes Haraz and Babolroud River, Talar includes Talar and Siahroud River, Tajan includes Tajan River, Neka includes Nekaroud River, Gorgan includes Gorganroud and Gharasou River and Gomishan includes Atrak River. This study was done for measuring organophosphorus and organochlorine toxins in Mazandaran and Golestan Rivers since April, 2005 to March, 2006. All stations were chosen near estuary at the end of farm and agriculture fields in order to establish an equal condition in sampling.

Sampling was being done monthly and sampled from middle across and depth of the rivers. Two samples were always gotten in each station to avoiding the shortage of sample volume, and were sent to laboratory for analyzing immediately. Both groups of pesticides were measured by specific method and instrument. Organochlorine pesticides were analyzed by means of Flame

ionization detector (FID) and gas chromatography and Organophosphorus pesticides were analyzed by means of nitrogen-phosphorus detector (NPD) and gas chromatography. Identification and measurement of organochlorine and organophosphorus pesticides were done by standard stop time toxicants and calibration curve graph. However, we also measured total DDT concentration of four fish species (Barb, Pike, Mullet and Carp) in Siahroud River concurrently in summer.

RESULTS

In this research we have studied two groups of toxins including organophosphorus and organochlorine pesticides. Organophosphorus pesticides include Diazinon, Chloropyrifos, Ethion, Endifenphos, Azinphos-methyle and organochlorine pesticides include δ -HCH (gamma-hexachlorocyclohexane), Dieldrin, 2-4DDE, 4-4DDE, 2-4DDT and 4-4DDT (Esmaili, 2002). These pesticides are mainly used as fungicides, insecticides and herbicides throughout agricultural lands. Both pesticides are used for different products including rice, orange, orchard and etc (Figure 2).

Diazinon is an organophosphorus which was observed in all rivers during the year and its concentration is more than EPA (Environmental Protection Agency, www.epa.gov) standard in all stations. This toxin is used throughout the year, but maximum concentrations are

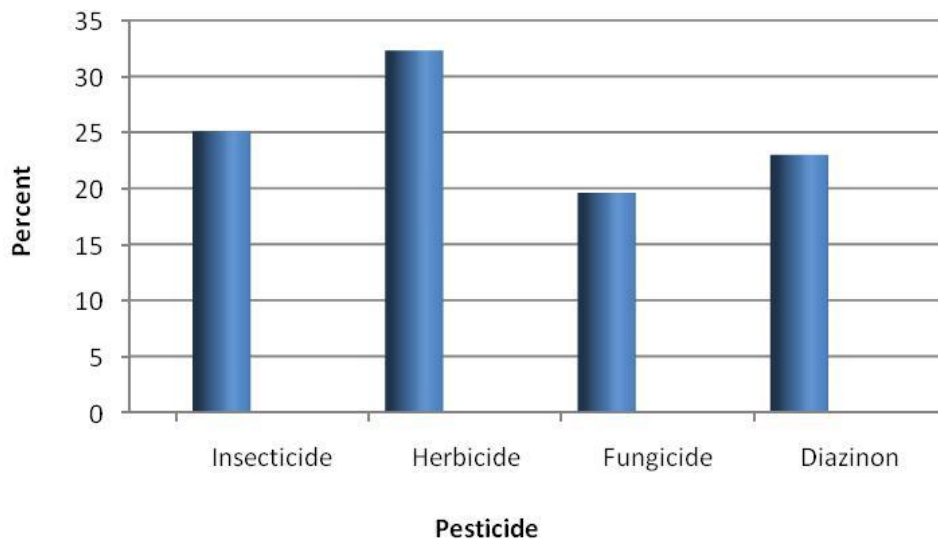


Figure 2. Percent of different distributed pesticides in Mazandaran and Golestan Provinces in 2009.

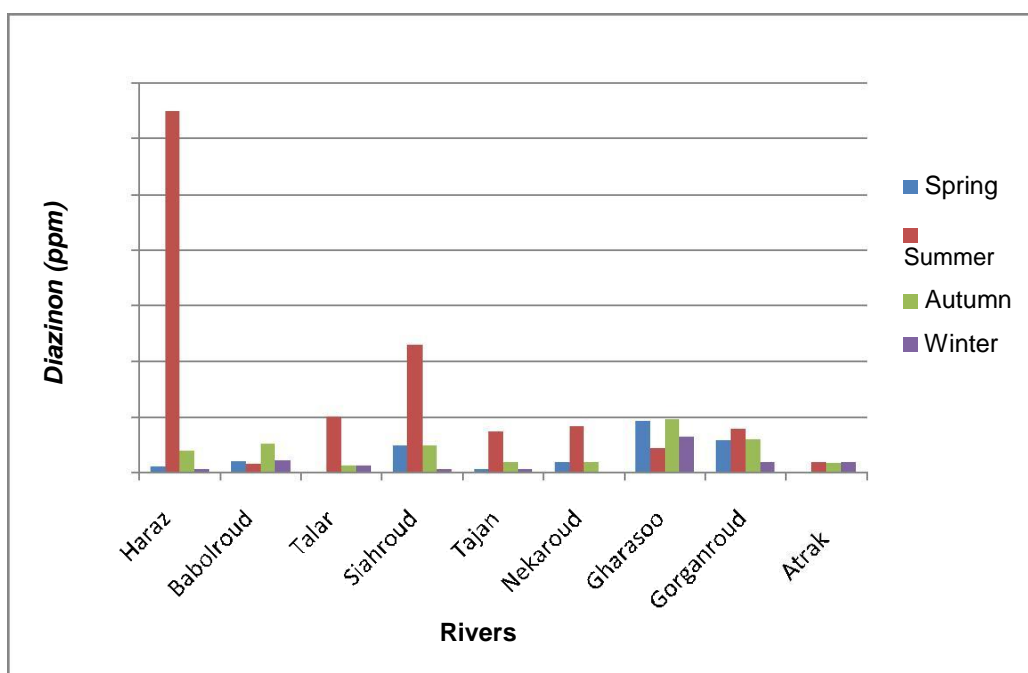


Figure 3. Seasonal diazinon concentration in different rivers.

usually observed in summer. For instance, in Haraz River, Diazinon concentration in summer is 16 times of autumn; but we can observe relatively steady concentration in Atrak River during the year (Figure 3). Winter and spring have low values in comparison with summer and autumn seasons. These differences reflect diversity of land use. Other organophosphorus including Ethion, Chloropyrifos and Endifenphos had less frequency than Diazinon respectively. Nevertheless, Azinphos-methyle was not observed in any sample at all.

DDT (Dichlorodiphenyltrichloroethane) has different

derivatives such as DDD (Dichlorodiphenyldichloroethane) and DDE (Dichlorodiphenyldichloroethylene). Among DDT group, 2-4DDE and 2-4DDT have maximum and minimum frequency in samples respectively. DDT concentration is varied in terms of season and rivers. Studies have shown the amount of DDT to be high in summer and low in winter, generally. Our study, however, indicates Haraz, Tajan and Siahroud have more concentration than others (Figure 4). Haraz and Tajan have highest values in summer and autumn, while Babolroud show maximum

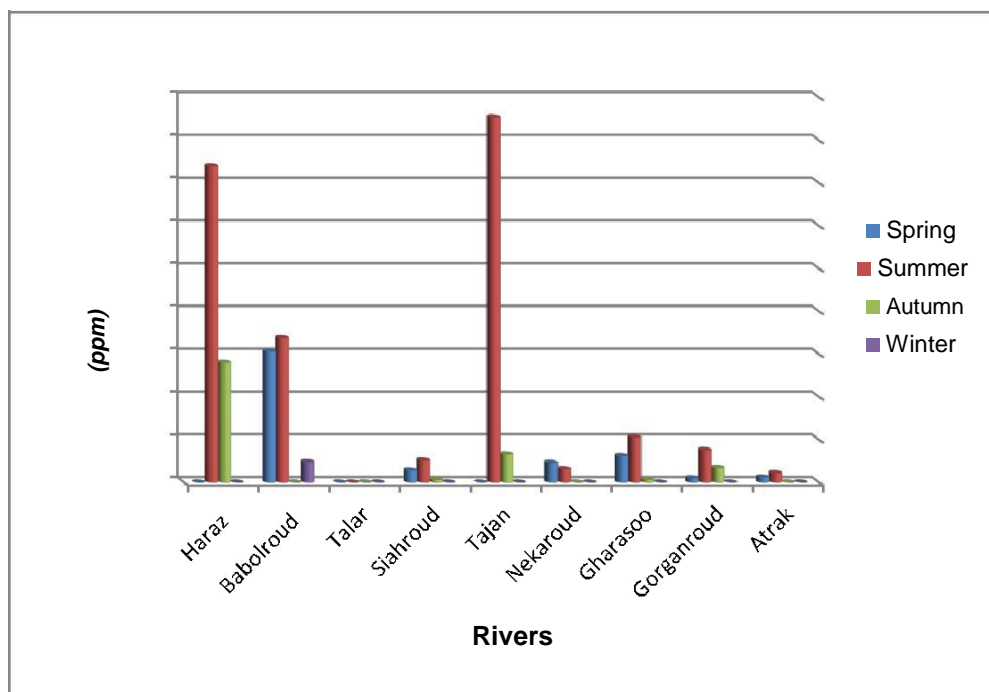


Figure 4. Seasonal total DDT concentration in different rivers.

concentration in spring and summer. Other rivers have no high variations throughout the year. In fact, eastern rivers (Golestan Province) apparently experience low amount of DDT in comparison with Mazandaran Province Rivers. As we mentioned previously, total DDT concentration of four fish species (Barb, Pike, Mullet and Carp) in Siahroud River measured concurrently in summer showed 0.5, 0.16, 0.14 and 0.39 mg/L respectively.

DISCUSSION

DDT is a lipophilic compound and accumulates in fat tissues of plants and animals. DDT usage has been banned since 1985 in Iran, but it is still observed in the environment due to its high residence time. Moreover, this pesticide is smuggled into the country as ant toxin.

In summer, Diazinon concentration is more than in other seasons due to more usage in rice paddy. During this study, we observed maximum concentration of Diazinon in Haraz River due to the fact that this region is mainly designated for rice paddy. In a region such as Haraz where the main product is rice, the amount of Diazinon usage is naturally high since it is used as a form of rice pesticide. Finally, these pollutants are discharged into water bodies, including surface and even underground reservoir. For instance, a study conducted by Yousefi (2008) on pesticides in 12 city of Mazandaran Province has shown underground water in Amol (adjacent Haraz River) had a higher level of Diazinon than others. During rice harvesting, this pesticide is used for the spraying of orange and orchards pest again.

A study conducted by Nazari (1996) showed that a wide variety of organochlorine pesticides are used

throughout Mazandaran and Golestan Provinces from April to May in contrast with January to February by the least application. Mixed vapor with DDT in agricultural fields can remain for 6 months in atmosphere. Most DDT in sprayed areas are deposited in the soil and logarithmic decrease is observed at the pollution source. DDT is transported more by air and can be carried to thousands of kilometers, reaching the ground again via rainfall.

Rice growing is a common product in area and varied pesticides are used in different stages of its growth. For example, Diazinon and δ -HCH are mainly used for annihilating of rice pests. It is obvious that climate condition, quality and quantity of water are main effective factors in forming of crop pattern. For instance, by moving from Haraz to eastern part of the area, water quantity decreases but in Gorganroud and Atrak, there is a major shortage of water. This phenomenon has important impact on crop pattern. About 97% Lands adjacent of Haraz and Babolroud contain rice paddy field and only 3% allocated to non-paddy (Figure 5). Whereas in Atrak and Gorganroud, the eastern part of study area, 90% of lands is allocated to non-paddy products such as cotton, bean, soya, wheat, tobacco and so on. In comparison with rice paddy fields, these products have less water requirement.

Similar to Diazinon, organochlorine pesticides have maximum level in summer and winter has minimum level so far as we observed ND concentration in all rivers. Among the rivers, maximum and minimum organochlorine pesticides were measured in Tajan and Talar respectively. During this study, all organochlorine measurements were ND in Talar River.

The residence time of total DDT in the environment is relatively short ($t_{1/2} = 3$ to 5 years), so at least 75 to 80%

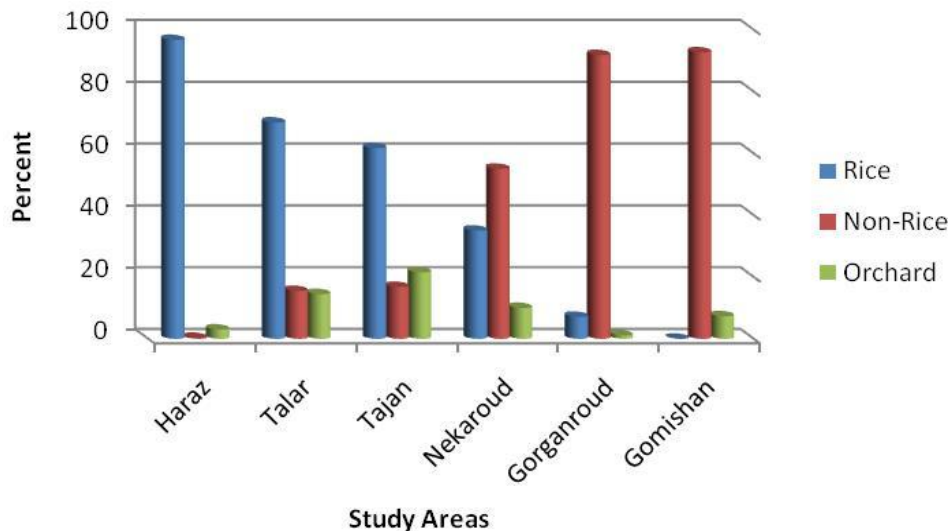


Figure 5. Percent of various cropping patterns in different parts of the study area.

of the current total DDT should be in the form of DDE or DDD if it was introduced into the environment before the 1985 ban. Values of Henry's law constant indicate that these compounds can reach the troposphere as vapor. These vapors are little absorbed by airborne particulate matter and represent the major component in atmospheric chlorinated hydrocarbon levels. DDT concentration in surface water is a function of soil and rainfall. Thus, vapor movements of these pollutants suggest that restrictions and regulations operating in the more technically advanced countries could only be partially effective on a worldwide basis. In contrast to organochlorine, organophosphorus pesticides have not long residence and decay after 20 to 25 days of spraying. Residence time of organophosphorus is less than organochlorine, but their toxicity is more acute for biota. For example, according to EPA standard, maximum concentration of 4,4-DDT and 2,4-DDT is 0.1 ppm and 0.113 to 0.8 mg/L respectively, but maximum allowable level of Diazinon is determined 0.001 ppm. Although Diazinon has a low residence time, when discharged into aquatic ecosystem, it can cause acute effect in short-time. For instance, LC50 of DDT and Diazinon are 250 and 125 mg/L for Carp respectively. The lethal effect of Diazinon is 2 times of DDT for Carp.

As organochlorine pesticides were used in past time, we conclude they can transfer to fish bodies by means of food chains and their concentrations always are more than their surrounding environment. At the same time, DDT concentration was 0.026 mg/L in water which reflected bioaccumulation factor (BAF) about 19, 6, 5 and 15 times in the aforementioned species respectively.

Concentration of organochlorine pesticides including Dieldrin, Aldrin and DDT was measured in muscle tissues of stellate sturgeon (*Acipenser stellatus*) of southern

coasts of the Caspian Sea by Keshavarzi (2008). Comparison of measured concentrations with maximum residue limit (MRL) established by FAO/WHO showed that the average concentration of DDT in samples from Bandare Turkman (Gorganroud River Estuary) exceeded the MRL value.

On the other hand, a study by Kajiwara et al., (2008) showed that DDTs were the predominant contaminants that ranged from 3.1 to 560 $\mu\text{g/g}$ in the blubber of Caspian seals, which died during an outbreak of canine distemper virus in 2000 and 2001. The levels of pesticides in Caspian seals, however, comparable to those in other aquatic mammals that have suffered from epizootics, might pose a risk of immune suppression.

Finally, the use of environmentally harmful pesticides in small-scale farming along the Caspian coastline and river deltas has been identified as a serious threat to aquatic biodiversity in the region. In order to reduce the discharge of toxic and bio-accumulative substances into coastal waters, legislative enforcement must be strengthened. As suggested earlier, the sale and use of DDT has been legally prohibited in Iran for 2 decades but the supply is still abundant throughout the area. To better enforce the ban on DDT, regional control functions need to be strengthened and local officials must be given the necessary resources to control local market supply and sale. The feasibility and effectiveness of improved legislative enforcement are expected to be high since forbidden chemicals are easy enough to identify and confiscate. Responsibility for improved enforcement should be given to local and municipal authorities. A recommended parallel measure is to provide local farmers with economically viable alternatives to DDT. This could be done by reducing import taxes on modern and less environmentally harmful pesticides. Modern

pesticides are generally more expensive than DDT on the local markets and, therefore, cannot compete with traditional products. Tax reductions could reduce the prices of modern pesticides substantially, but it is unlikely that prices can drop enough to compete with the very cheap chemicals currently in use. The short-term effectiveness of a state-driven substitution of obsolete pesticides is hence expected to be fairly low. This measure is however still recommended as a long-term policy. Since, the public awareness of the ecological consequences of the use of toxins is rather low in the region, educational efforts would complement the 2 top down measures suggested previously. Special training, lectures, and educational TV programs need to be developed and offered both to authorities and local communities in the region. A better public understanding of the ecological vulnerability of the Caspian waters can in the long run increase local engagement in the regional environment.

Educational policies are hence recommended on a broad scale in all 5 littoral countries. So that the Caspian Sea cannot be divided into separate compartments; what affects one part of the sea may affect all parts, since all parts are linked. The sea itself is a unique body of water which is of global significance. Concerted action in marine monitoring and management therefore has the potential to deliver the greatest benefits to all participating states.

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