A WATER QUALITY STUDY WITH EMPHASIS ON PESTICIDES IN SHIROUD RIVER CATCHMENT IN SOUTHERN PART OF CASPIAN SEA, IRAN

by

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LIST OF ABBRIVIATION

ADB	Asian Development Bank
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
BHC	Benzene Hexa-Chloride
BOD	Biochemical Oxygen Demand
CACAR	Canadian Artic Contamination Assessment Report
CAG	Cancer Assessment Group
CARC	Cancer Assessment Review Committee
CRAVE	Carcinogen Risk Assessment Validation Effort
CV	Coefficient of Variation
DA	Discriminant Analysis
DDE	1,1-Dicholoro-2, 2′ -bis (*p*-chlorophenyl)Ethylene
DDT	dichloro-diphenyl-trichloroethane[2, 2′ -bis(p-chlorophenyl)-1, 1, 1,-trichloroethane]
DHEW	United States Department of Health, Education and Welfare
DO	Dissolved Oxygen
DUSACE	Department of the US Army Corps of Engineers
DWD	Drinking Water Directive
EC	European Community
EC	Electrical Conductivity
ECD	Electron Capture Detector
ECETOC	European Chemical Industry, Ecology and Toxicology Center
EEC	European Economic Community
EECD	European Economic Community Directive

EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agriculture Organization
FA	Factor Analysis
FCH	Farm Chemicals Handbook
FDA	Food and Drug Administration
ha	Hectare
HCB	Hexa-Chloro-Benzene
HCH	1,2,3,4,5,6-Hexachlorocyclohexane
HIARC	Hazard Identification Assessment Review Committee
IARC	International Agency for Research on Cancer
IFRO	Iranian Fisheries Research organization
IMI	Industrial Ministry of Iran
IMO	Iranian Meteorological Organization
IPCS	International Program on Chemical Safety
IPM	Iranian Power Ministry
IRPTC	International Register of Potentially Toxic Chemicals
JPPA	Japan Plant Protection Association
JSA	Japan Statistic Association
MAC	Maximum Admissible Concentration
MJAI	Ministry of Jahade Agriculture of Iran
mm	millimeter
MRC	Malaysian Rivers Classification
OC	Organo-Chlorine
OCI	Organo-Chlorine Insecticide

OCPs	Organo-Chlorine Pesticides
OECD	Organization for Economic Co-operation and Development
OPP	Office of Pesticide Programs
PBOM	Programming and Budget Organization of Mazandaran
PCB	Poly-Chlorinated Biphenyls
PCA	Principal Component Analysis
POP	Persistent Organic Pollutant
SPSS	Statistical Package for Social Science
TDS	Total Dissolved Solids
TWAS	Third World Academy of Science
USDA	U.S. Department of Agriculture
USEPA	United States Environmental Protection Agency
UNEP	United Nations Environment Program.
WHO	World health Organization
WRI	World Resources Institute

KAJIAN KUALITI AIR MENUMPU PADA RACUN SERANGGA PEROSAK DI LIMBANGAN SUNGAI SHIROUD DI BAHAGIAN SELATAN LAUT CASPIAN – IRAN

Abstrak

Kajian kualiti air telah dijalankan ke atas Sungai Shiroud di Iran. Sungai ini terbentang sejauh 32 km bermula dari gunung Albourz dan berakhir di bahagian selatan Laut Caspian. Pemantauan telah dijalankan secara berkala selama setahun (Julai 2003 sehingga Jun 2004) untuk parameter fiziko-kimia (16) dan sebatian racun serangga organoklorida (OCPs) (15). Sebanyak lapan stesen telah dipilih untuk kajian di tiga bahagian sungai (3 di bahagian gunung, 4 di bahagaian dataran dan 1 di muara). Parameter fiziko-kimia diukur menggunakan kaedah ASTM sementara racun serangga organoklorida (OCPs) dianalisa menggunakan GC-ECD mengikut prosedur US-EPA (508). Matriks data kompleks (31 x 96) telah menggunakan teknik statistik multivariat seperti analisis faktor (FA) dan analisis diskriminan (DA). Parameter fiziko-kimia telah dianalisa dengan FA dan keputusan menunjukkan terdapat enam faktor yang mempengaruhi sehingga 74.17% daripada keseluruhan variasi dalam kualiti air. Keputusan untuk OCPs juga menunjukkan terdapat enam faktor yang mempengaruhi sehingga 73.39% variasi keseluruhan kualiti air. DA telah dijalankan untuk memahami peranan stesen (ruangan) and variasi musim (temporal) ke atas kualiti air sungai tersebut. DA memberikan empat parameter (suhu air, konduktiviti,kedalaman purata sungai dan oksigen terlarut) dengan 86% ketepatan diperolehi ke atas stesen yang sama untuk analisis ruangan. Manakala lapan parameter (suhu air, oksigen terlarut, silikat, ion kalsium, jumlah kekerasan, jumlah pepejal terlarut, ortofosfat dan nitrat) memberikan lebih daripada 93% ketepatan diperolehi bagi analisis temporal. DA memberikan sembilan sebatian (α -BHC, δ -BHC, DDE, heptachlor, dieldrin, γ-BHC, endrin, β-endosulfan and endrin aldehid) dengan 80%

ketepatan diperolehi untuk analisa ruangan, manakala lima sebatian (δ -BHC, β -endosulfan, α -BHC, endosulfan sulfat and endrin aldehid) dengan 76% ketepatan diperolehi untuk analisa temporal. Oleh itu, DA membolehkan pengurangan daripada segi dimensi untuk set data yang besar; dengan memberikan beberapa parameter petunjuk yang bertanggungjawab ke atas variasi yang besar. Variasi kualiti air ini disebabkan oleh suhu, penggunaan racun serangga yang berbeza di kawasan pertanian, aktiviti biokimia dan penggunaan nutrisi oleh akuatik ekosistem sungai tersebut. Bilangan sebatian yang dikesan daripada 15 sebatian OCPs untuk empat musim ialan (14 sebatian dengan variasi maksimum daripada γ-BHC (60µg/L) sehinggaα-endosulfan (5.2 µg/L)) semasa musim bunga, (10 sebatian dengan variasi maksimum DDT dan DDE (25µg/L) sehingga endosulfan sulfate (3.6µg/L)) semasa musim panas, (6 sebatian dengan variasi maksimum aldrin (38 µg/L) sehingga endrin (4.2 µg/L)) semasa musim luruh dan (11 sebatian dengan variasi maksimum daripada heptachlor epoksida (50.8 µg/L) sehingga dieldrin (3.2 µg/L)) semasa musim sejuk. Walaubagaimanapun, mengikut peratusan bahan-bahan kimia ini berdasarkan lapan stesen dari hulu ke hilir sungai boleh dikelaskan sebagai: (i)sederhana tercemar (33 – 40% bahagian), (ii) tercemar (47 – 54% bahagian), dan (iii) sangat tercemar (60 – 80% bahagian). Variasi OCPs pula disebabkkan oleh penggunaan bahan-bahan kimia di kawasan pertanian atau daripada air larian tanah akibat hujan yang masuk ke sungai. Kepekatan sebatian OCPs (5.2 to 60.0µg/L) dalam air Sungai Shiroud adalah sangat tinggi dibandingkan dengan piawaian kepekatan OCPs dalam air permukaan daripada negara-negara Eropah dan US-EPA (sebatian individu tidak melebihi 0.1µg/L dan jumlah semua racun serangga < 0.5 µg/L).

A WATER QUALITY STUDY WITH EMPHASIS ON PESTICIDES IN SHIROUD RIVER CATCHMENT IN SOUTHERN PART OF CASPIAN SEA, IRAN

Abstract

Shiroud River of Iran was chosen in this study to monitor its water quality. The river has a span of 32 km starting from Albourz mountainous and end up at the southern part of Caspian Sea. The monitoring was done regularly over a period of one year (July 2003 to June 2004) for different physico-chemical parameters (16) as well as organochlorine pesticides (OCPs) compounds (15). A total of eight stations were selected for observation in three different regions of the river (3 on the mountainous, 4 in plain and 1 in estuary). The physico-chemical parameters were measured by ASTM method while organochlorine pesticides (OCPs) were analyzed by GC-ECD according to US-EPA (508) procedure. The complex data matrix (31×96) was treated with multivariate statistical techniques such as factor analysis (FA) and discriminant analysis (DA). The physico-chemical parameters were analyzed by FA and it was observed that there are six factors explaining up to 74.17% of the total variation in water quality. Six factors were observed for OCPs which account for 73.39% of the total variation in water quality. DA was done to understand the role of the stations (spatial) and seasonal variation (temporal) on water quality of the river. DA gave four parameters (water temperature, conductivity, mean river depth and dissolve oxygen) affording more than 86% correct assignations (return to the same station) in spatial analysis, while eight parameters (water temperature, dissolved oxygen, silicate, calcium ion, total hardness, total dissolved solids, orthophosphate and nitrate) to afford more than 93% correct assignations in temporal analysis. DA showed nine compounds (α -BHC, δ -BHC, DDE, heptachlor, dieldrin, γ-BHC, endrin, β-endosulfan and endrin aldehyde) affording more than 80% correct assignations in spatial analysis, while five

compounds (δ -BHC, β -endosulfan, α -BHC, endosulfan sulfate and endrin aldehyde) to afford 76% correct assignations in temporal analysis. Therefore, DA allowed reduction in dimensionality of the large data set, defining a few indicator parameters responsible for large variations. The variations of water quality are due to temperature, usage of different types of fertilizer in agricultural lands, bio-chemicals activities and nutrients consumption by aquatic in the river ecosystem. The number of compounds detected out of 15 OCPs components during four seasons were 14 compounds with maximum fluctuation of γ-BHC (60μg/L) to α-endosulfan (5.2 μg/L) in spring, 10 compounds with maximum fluctuation of DDT and DDE (25μg/L) to endosulfan sulfate (3.6μg/L) in summer, 6 compounds with maximum fluctuation of aldrin (38 μg/L) to endrin (4.2 μg/L) in autumn and 11 compounds with maximum fluctuation of heptachlor epoxide (50.8 μg/L) to dieldrin (3.2 μg/L) in winter. However, according to the percentage of these chemicals were distributed in eight stations from upstream to downstream classified as; (i)- moderate polluted (33 to 40%), (ii)- polluted (47 to 54%), and (iii)- highly polluted (60 to 80%) regions. The variation of OCPs caused by usage of chemicals in agricultural lands or by washed out of land soils from rainfall discharged to the river by runoff. The OCPs compounds concentrations (5.2 to 60.0μg/L) in Shiroud River water were compared with European countries and US-EPA standards for OCPs concentration in surface water (individual compound should not exceed 0.1μg/L and sum of all pesticides <0.5μg/L) were considered very high.

CHAPTER 1

INTRODUCTION

1.0 Introduction

There are more than 10 main rivers in the Mazandaran province (north of Iran) which discharge their waters into the southern part of the Caspian Sea. Shiroud River is one of the main rivers and it located in west of Tonekabon city. The total land area of Shiroud River basin is about 200 km^2 (Figure 3.2). It discharges approximately 47 millions m^3 of water annually into Caspian Sea.

The water quality of Shiroud River is very important for the continual existence of the ecosystem in general, particularly the aquatic life forms. Over the last four decades, this river has been one of the main sources for the breeding, growth and the natural propagation of fish including *Rutilus frisiii kutum* one of the main commercial species. However, in recent decades, this river has been facing various environmental problems such as the discharge of solid and liquid wastes from industrial and residential areas around the river basin. These wastes and effluents as well as agrochemicals (fertilizer and pesticides) from run off and drainage has seriously polluted the river. The ecosystem of the river is further affected by other anthropogenic activities too. One such activity is the removal of huge amounts of sands and gravels as raw materials for producing asphalt for building construction from the river bed by a nearby asphalt making factory.

In recent years, there has been a persistent use of organic chemical by farmers to achieve better yields for different types of agricultural products. As a result high concentration of pesticides in aquatic life and in the water of the river been detected and it poses a main hazard to the life and health of human beings, animals and plants.

Generally, these organo-chlorine pesticides (OCPs) are used in paddy fields, tea farms, horticultures and orchards in Shiroud River basin to control weeds and pests. These chemicals can stay for long periods in the soil because they are un-degradable and have a long half life. OCPs discharged after heavy rainfall have also been washed into the river by land run off and have had effect on the quality of freshwater in the river. In this study, a total of fifteen OCPs compounds and sixteen physico-chemicals parameters of water quality are studied to determine the effect of pesticides contamination on water quality and on aquatic life in Shiroud River ecosystem.

1.1 Climatology

Climate is usually defined as the statistical description in terms mean and variability of temperature, humidity, precipitation, evaporation and wind direction over a period of time ranging from months to years. The climates of the west part of the Mazandaran province (including Shiroud River basin) is more humid than that of eastern part. This province likes other provinces in the whole country have four seasons. The upper of Shiroud River is located in mountainous areas and has a slightly different climate than that of the down stream areas. The other parameters of climate such as air temperature, mean relative humidity, precipitation and evaporation in Shiroud River basin are elaborated as follow:

1.1.1 Air Temperature

The air temperature of Shiroud River basin is measured by the Iranian Meteorological Organization (IMO) whose station is located in a suburb of Ramsar city. The latitudes and longitudes of Ramsar IMO station are 36° 54′ N and 52° 40′ E respectively. The elevation of this station is minus twenty (-20) meters from world sea levels. The data spanning a 25 years period indicate that the variations and differences of air temperature between the four seasons ranged between 9-7°C [appendix 1(a) as reported by IMO (2004)].

1.1.2 Mean Relative Humidity

The mean relative humidity of Shiroud River basin as measured by the Ramsar station between 1980-2004 indicate that there was a 34 % fluctuation between the maximum and minimum range by IMO (2004). These fluctuations were particularly pronounced during 1990 to 1999 period (appendix 1(b)).

1.1.3 Precipitation

Precipitation has a main role in controlling other parameters such as air temperature, mean relative humidity, evaporation and even the flow rate of a river. As such, precipitation data recorded by the IMO station during the 25 years is very useful in analyzing other parameters related to this matter. The data indicates that over the past 25 years, precipitation fluctuated by as much 1000 mm (more data on appendix 1(c)) with the annual maximum precipitation being 1825 mm in 2001 (IMO, 2004). The maximum percentages of precipitation within 25 years period were 24 and 49 percents related to October and fall season. The minimum percentages of precipitation within 25 years period were 12 % in spring and 3 % related to June and August.

1.1.4 Evaporation

Evaporation was measured by over a period of 14 years from 1991-2004. In climatology, evaporation is directly related to air temperature. Usually in summer the amount of evaporation is much higher than during the other seasons due to higher air temperatures. The data for the 1991 -2004 period indicate that evaporation with respect to precipitation was 2 and 1.6 times more in spring and summer seasons, respectively. However, in the fall and winter seasons, the amount of evaporation in relation to precipitation was less (appendix 1(d)).

1.2 River Flow Rate

The fluctuation of flow rate between maximum and minimum was 21.5m^3/sec in October 1967. During the last two decades (1966-1988), the annual average volume of water discharged from Shiroud River into the Caspian Sea as measured by the regional water authority of the Mazandaran province was more than 100 Millions m^3 (IPM, 2003). The annual average volume of water discharged into the sea in the recent decade, have decreased to less than 50 millions m^3. This reduction of water flow can affect different parameters of water quality and ecosystem of the river. In addition to this, the highest fluctuation in flow rate was 21.5m^3/sec in October 1969 (appendix 1(e)).

1.3 Agriculture

Agriculture is one of the main sources of revenue and occupation of the local population in the Mazandaran province. By this, the average annual precipitation (1150 mm) is higher in this province in comparison to that in other parts of the country which has an annual average of 240-250 mm (IMO, 2004) and this favors the cultivation of agricultural products such as rice, tea, horticulture and fruits. Most of these agricultural produce are cultivated in residential areas and villages around the riverine lands of Tonekabon city and its suburb.

1.3.1 Cultivation and Land Use

The total area under cultivation in the Mazandaran province during the 2002-2003 periods was about 352289 ha. Almost 61.8 percents of these lands were under wet cultivation of irrigation causing irrigation systems while the reminder 38.2 percents was developed to dry farming. The total area under the two types of cultivations (irrigation system and dry farm) in the Tonekabon city and its suburbs were 15072 ha. Lands used under paddy cultivation, orchards products, tea farms and kiwi fruit in the Shiroud River basin totaled approximately 913, 705, 100, and 88 ha, respectively (MJAI, 2004).

1.3.2 Various Types of Cultivation and Their Products

The main agricultural produce of this area is rice which is the predominant cereal crop and the main staple foods for the people in the north of Iran. The total production of paddy in Mazandaran province during the 2002-2003 periods was 896792 tons whereas in Tonekabon city and its suburb, the total production amounted to 48000 tons only (MJAI, 2004). In Shiroud River basin and surrounding lands paddy is the main crop followed by oranges, tea and various kinds of fruits. In fact, the total output of rice from this region amounted to 2300 tons. Overall, 66.05 percents of cereals products (out of 1680000 tons cereal products in the Mazandaran province) were cultivated using irrigation systems while the remaining 33.95 percents were obtained via dry farming (MJAI, 2004).

1.4 Industry Activities and Agricultural Products

Mazandaran province is a major producer of agricultural produce due to its fertility and intensive cultivation methods. To preserve the environment and the agricultural lands of this province, the government has banned the establishment of large scale industries such as oil and gas industries and automobile manufacturing. In spite of this, there are small scale industries producing different kinds of products in all the 15 cities of the Mazandaran province. 2992 industrial units have been activated in different type of industry products (IMI, 2004). Nevertheless, agriculture based industries are more active in all the cities of the province. For example, in Tonekabon city and its suburbs, there are 222 industrial units and the majority of their products are related to agricultural activities. Almost 10% of Tonekabon city industrial units are located in Shiroud River basin and its residential areas. [(4 factories for tea process, 14 factories for rice and food products and rest of it are active in asphalt preparation and wood processing (appendix 1(f))].

1.5 Population and Residential Areas Along on the River

Tonekabon City and its suburbs measuring approximately 2140 km^2 are divided into two main parts namely called the central and Abbas Abad sectors. Based on the 1996 census, the population of Tonekabon city and its suburb was almost 200000. Shiroud River basin located in the central sector consists with 33000 people living in 135 residential area and villages (PBOM, 1996). More than 30 of these villages are sited very close to Shiroud River and thus have a direct effect on its water quality. The residential areas and villages around Shiroud River are:

BalaShiroud, LazarBon, BeRamsar, Tokeleh, LatKenar, MianRoud, Amoghim Mahalleh, Solaiman Abad, Darreh Welab, KondaSarak, Akhond Mahalleh, Kabod Kelaieh, Kashkoh, Akher Mahalleh, Rostam Peshtah, SangSera, RezaPet, Akhond Malak, KeratChal, Paltan, Terang Peshteh, GondaSar, ShoaibKelaieh, Paein Kheshkeroud, Bala KheshKeroud, Godeh, Takish, Nesameh, Shalandan, and KarKu.

1.6 Sources of Pollution

A number of sources can pollute surface water. They include run off, rainfall, soil erosion, agricultural waste, industrial waste, domestic waste and waste from other anthropogenic activities. In this case of Shiroud River, it is more likely to be affected by pollution of its more exposed and accessible nature. Therefore, three sources of pollutions such as non-point, point and domestic wastes of pollutions are discussed follows:

1.6.1 Non-Point Source of Pollution

The main non-point sources of pollution in the environment are related to different activities such as agriculture, silviculture, atmospheric, urban and suburban run off. Nevertheless, it is difficult to identify the sources of pollution and their points of discharge into the surface water. Since a researcher is in the dark about the chemicals used in agricultural activities by farmers to control weed and pests. These are classified as non-point source of pollution. Therefore, most non- point sources of pollution in Shiroud River basin are OCPs components which are made by artificially synthesized substances and their properties are generally toxic to both humans and wildlife. Generally, these pesticides are used by farmers in paddy fields during agricultural activities.

1.6.2 Point Source of Pollution

There are different types of general activities in residential areas along the river banks whose waste and effluents could cause pollution. They are called point sources of pollutions. These activities could be categorized into industry, agricultural products and municipality activities. In Shiroud River basin, activities related to agriculture and the local municipalities are the main point sources of pollution. There are many rice mills factories, tea and food processing plant along Shiroud River basin. These industries discharge their waste into the river which plays a major role in transporting chemicals into coastal water ecosystem.

1.6.3 Causes of Pollution

As explained earlier in pages 5 and 6, different kinds of agricultural produce are produced in lands around Shiroud River basin. In order to get better yields and protection of their products from weeds and pests, farmers usually use different types of chemicals. In general, the pollution causes can be summarized as follows:

1. Different types of fertilizers are used during agricultural activities every year. Portions of these chemicals such as phosphates and nitrogen are used by plants and soils while the rest are washed away by run off into the river.
2. Each year, different types of pesticides are used for protecting crops from weeds and pests a large portion of these chemicals remain un-adsorbed by plants and remain in soils before being gradually released into the river ecosystem via variety of ways.
3. In industrial zones, factories dump their wastes and effluents into various kinds of resources such as rivers, water reservoirs and surface waters. The major pollutants released from industries may contain both organic as well as inorganic compounds.
4. There are residential areas along the river which use water for different purposes in daily activities, wastewater from such activities are discharged into the river system without being treated. These wastes usually contain huge amount of dangerous substances which re harmful to both human and animals.

1.7 Biotic Description

Phytoplankton, zooplankton, benthic insects and various species of fish play a major role in the assessment of aquatic life and water quality of Shiroud River ecosystem. These water quality parameters and biological characterization have been studied in 1992 and 1998 by IFRO (2000), and are elaborated as follow:

1.7.1 Fish Population

In Shiroud River, there are two types of population for fish that called native and non-native into the river. Also, there are numerous varieties of fish from different families that live in this river where the aquatic life and ecosystem of Shiroud River is totally different in comparison to the other major rivers in west part of the Mazandaran province. Currently, thousands of *Rutilus frisiii kutum* fish migrate from the Caspian Sea into the river mouth for spawning and natural propagation. Governmental departments usually use these fish species for artificial propagation in order to produce finger link fish that are released into the river mouth for stocking. In total, six families of fish (*Petromyzonidae, Cyprinidae, Cobitidae, Gobiidae, Salmonidae* and *Mugilidae*) live in Shiroud River as reported by IFRO (2000).

IFRO (2000) reported on the diversity of native fish in two studies (1992 and 1998) conducted in Shiroud River basin. The total native fish populations caught within the two periods were 64 and 77 percents, respectively. In the second study (1998) there was 13% increase in the amount of native fish population over that of first study (1992). A few species of native fish where identified within the two periods of studies namely *Capoeta capoeta gracilis, Barbus lacerta cyri, Barbus mursa, Alburnoides bipunctatus, Alburnus alburnus, Chalcalburnus chalcoides, Cyprinus carpio, and Reodeus seriseus* (*Cyprinidae* family), *Cobitis taenia* (*Cobitidae* family), *Liza aratus*

(*Mugilidae* family), *Neogobius fluviatilis, Neogobius kessleri* (*Gobiidae* family) and *Salmo trutta fario* (*Salmonidae* family).

1.7.2 Benthic Population

The classification of river benthic population and their diversity in Shiroud River are explained in terms of order and the family of benthic insects as well as their abundance in the river bed. They are described briefly as follows:

In Shiroud River bed, nine orders of benthic insects were identified such as Diptera, Ephemeroptera, Tricoptera, Coleoptera, Pelecoptera, Gastropoda, Odonata, Arachoidaida, and Polychaeta (IFRO, 2000). During study in 1998, 24 family of benthic insects were identified in Shiroud River namely *Simullidae, Ragonidae, Chironomidae, Ceratopogonidae, Diptera(p), Ephidridae(l), Tipulidae, Tabanidae*, *Dixidae (Diptera* order*), Caenidae, Baetidae, Hexagenidae, Epheridae(pup),* Heptagenidae (Ephemeroptera order), Hydropschidae, Tricoptera(l)**,** *Perlodidae (Tricoptera* order*), Hydrocaphidae(l), Elmidae, Coleoptera(l), Dytiscidae (Coleoptera* order*), Plecoptera(p)* in *Pelecoptera* order*, Limnidae* in *Gastropoda* order*, Nereis* in *Polychaeta* order*, Gomphidae* in *Odonata* order, and *Arachoidaida* as an order (IFRO, 2000).

In general, the average weight and abundance of insects in benthic samples of last study (1998) in Shiroud River were 2.41g/m^2 and 179 insects /m^2, respectively. The average insects that collected per sample was 13 during one year (IFRO, 2000).

1.7.3 Phytoplankton

The category and classification of phytoplankton in Shiroud River are explained by the data were collected from IFRO technical report (2000). The total number of phytoplankton division, genera and species identified in the river were 5, 55 and 165 respectively, and explained in detail as follows:

In general, five divisions of phytoplankton were identified namely Chrysophyta, Chlorophyta, Cyanophyta, Pyrophyta, and Euglenophyta. The numbers of genera for these five divisions of phytoplankton over a period of one year were 19, 12, 8, 6 and 4, respectively. While the numbers of species for the five divisions of phytoplankton over one year were 84, 40, 17, 10 and 9, respectively. Chrysophyta (Diatoms) was dominated by parameters such as accumulation, the biomass and various species of other phytoplankton phyla. The accumulation and biomass of Chrysophyta was covered 80-90 percents and 49-86 percents, respectively while the rest of phylum was covered by only 10-20 percents (IFRO, 2000).

1.7.4 Zooplankton

The total number of zooplankton diversity identified in class, genera and species were 5, 28 and 20, respectively and is summarized as follows:

In general, five classes of zooplankton were identified in Shiroud River namely protozoa, rotatoria, copepoda, cladocera and zoobenthos. The percentages of genera were 28, 39, 11, 3 and 18, respectively. Between the four seasons, the maximum and minimum number of genera plus species in all classes during summer and winter were 27 and 21, respectively (IFRO, 2000). The maximum genera and species in the five classes of zooplankton were identified in all samples of the four seasons belonged to rotatoria.

1.8 Problem Statement

At present, Shiroud River is suffering from pollution by anthropogenic pollutants due to agricultural activities. This river is famous in Iran due to the migration of commercial species of fish (*Rutilus frisiii kutum*) during the spawning season form the Caspian Sea to the river estuary. Furthermore, the socio-economic status and occupations of more than twelve thousands fishermen in Gilan, Mazandaran and Golestan provinces are dependant on this fish stock. Unfortunately in recent decade, the usage of fertilizers and chemicals for controlling of pests and weeds has increased in Shiroud River basin due to intensive paddy cultivation, horticulture and the proliferation of tea farms. The basic problems for the accomplishment of rivers studies are the lack of reliable data for confirming the magnitude of OCPs residues that contribute to the contamination of the river and its potential effect on water quality.

1.9 Objectives of Study

The objective of this study is outlined as follows:

1. To study the pollution status of water quality in Shiroud River by evaluating the effect of organochlorine pesticides (OCPs) components and physico-chemical parameters on water quality in the river.
2. To identify the main sources of pollution in terms of point source and non-point source of Shiroud River.
3. To stusy the temporal and spatial variations based on OCPs components and physico-chemical of water quality parameters.
4. To recommend the necessity and usefulness of multivariate statistical techniques for evaluation and interpretation of large complex data with a view to get better information about the water quality and the design of a monitoring network for the effective management of water resources and the control of water pollution.

1.10 Thesis Organization

This thesis covers six chapters and appendices. A brief introduction about the river location, climate, flow rate, land use, agricultural products, cultivation, industry activities, population along the river basin, point and non-point sources of pollutions, and a short description of biological situation of the river are given in Chapter 1 (Introduction). This chapter also includes the problem statements related to areas of current research and the objectives of the present study.

Chapter 2 (Literature Review) A brief causes of diseases by pesticides, OCPs residues in human milk, lipid accumulation, usage of pesticides in the world, movement of pesticides, leachabitiy, monitoring of OCPs in different countries, EU standard, classification, generation, half-lives and properties of pesticides. A short description is given about the effect of OCPs on vital and non-target organisms, chemicals fertilizers, pest resistibility, freshwater shortage and water diseases. Also a brief review is included on statistical techniques used as a tool for data management.

Chapter 3 (Materials and Methods) This chapter provides a brief overview about location Shiroud River and full description of sampling stations, methodology of pesticides analysis (preparation, separation, cleanup and dehydration, re-concentration of sample process), standard and reagents, gas chromatographic conditions and methodology water quality parameters (temperature and pH measurement, dissolved oxygen, biochemical oxygen demand (BOD), total dissolved solids (TDS), Orthophosphate, total phosphorus, alkalinity, ammonia-nitrogen, nitrite-nitrogen, nitrate-nitrogen, total hardness, calcium ion, electrical conductivity, and silica) as well as methods of statistical analysis.

Chapter 4 (results and discussion) In this chapter two sets of data are applied for the analysis of water characteristics parameters and organochlorine pesticides (OCPs) compounds collected from surface water samples. A brief explanation about descriptive statistics (Maximum, minimum, mean, standard deviation and coefficient of variation) and their relationships, correlation between parameters and compounds and finally the main part and framework for results and discussion of data sets are included in this chapter. The procedure and methods are used for the analysis of data are factor analysis (FA) and discriminant analysis (DA) for both water characteristics parameters as well as organochlorine pesticides (OCPs) compounds.

Chapter 5 (Conclusions) concludes the findings of the current studies. To avoid confusion, contents of this chapter are arranged according to the sequence of their appearance in Chapter 4.

Chapter 6 deals with recommendations for future study in the related field made from an understanding of the issue. These recommendations are given their due significance and importance of the river ecosystem for further research works in this area in the near feature.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

Water is the major component of all living being and plays a prominent role in life. The usage of water by human being is based on their life style and economical status. Nowadays, the life style for water usage is totally changed when compared to that half a century ago. The demand of water in modern society is rapidly increased due to the usage of municipal, agricultural, domestics and industrial purposes. Therefore, by huge water utilization creates a volume of effluents and freshwater reserving is facing a lot of pollution problems.

In this chapter, a brief explanation is given about causes of diseases, OCPs residues in human milk, lipophilicity, usage of pesticides in the world, movement of pesticides, leachabitiy, monitoring of OCPs in different countries, EU standard, classification, generation, half-lives and properties of pesticides. A short description is given about the effect of OCPs on vital and non-target organisms, chemicals fertilizers, pest resistibility, freshwater shortage and water diseases. Also a brief review is included on statistical techniques used as a tool for data management.

2.1 Organo-Chlorine Pesticides (OCPs) Effects on Human

OCPs are known to interrupt the hormone in the endocrine system and promote the development of cancer diseases in a variety of vital organisms such as brain, lung, gonads, liver and the urinary region. Although, the causes for the cancers can be ascribed to a variety of factors, pesticides pose a significant risk human health (Davies and Barlow, 1995; Patlak, 1996). The Environmental Protection Agency (US-EPA) has published its current human cancer risk assessment for different groups of OCPs that related to human carcinogens and are shown in Table 2.1.

Table 2.1 Cancer classification of pesticides in human carcinogen stated by US-EPA

Chemicals	Cancer Classification1*	Report Date2*
Aldrin	GroupB2-Probable Human Carcinogen	CRAVE (3/22/87)
DDD	Group B2--Probable Human Carcinogen	CRAVE (6/24/87)
DDE	Group B2--Probable Human Carcinogen	CRAVE (6/24/87)
DDT	Group B2--Probable Human Carcinogen	CRAVE (6/24/87)
Dicofol	Group C--Possible Human Carcinogen	OPP (4/15/92)
Dieldrin	Group B2--Probable Human Carcinogen	CRAVE (3/5/87)
Endrin	Group D--Not Classifiable as to Human Carcinogenicity	CRAVE (10/19/88)
Heptachlor	Group B2–Probable Human Carcinogen	CRAVE (4/1/87)
Heptachlor epoxide	Group B2–Probable Human Carcinogen	CRAVE (4/1/87)
HCB	Group B2–Probable Human Carcinogen	CRAVE (3/1/89)
HCH	Group B2–Probable Human Carcinogen	CRAVE(12/17/86)
Lindane	Suggestive Evidence of Carcinogenicity, but Not Sufficient to Assess Human Carcinogenic Potential	OPP (11/29/01)
Endosulfan	Not Likely to be Carcinogenic to Humans	OPP (1/31/2000)

Source: EPA, 2004

Group B2: This classification is used for agents in which there is "sufficient" evidence from animal studies but for which there is" inadequate evidence" or "no data" from epidemiologic studies.

Group C: This classification is used for agents with limited evidence of carcinogenicity in animals in the absence of human data.

Group D: This classification is generally used for agents with inadequate human and animal evidence of carcinogenicity or for which no data is available.

1*- Cancer Classification: Unless otherwise indicated, chemicals were evaluated and classified either by the Office of Pesticide Programs (OPP), Cancer Assessment Review Committee (CARC) or Hazard Identification Assessment Review Committee (HIARC).

2*- CRAVE/CAG: Chemicals were evaluated and classified by other Peer Review Committees within the US EPA: the Carcinogen Risk Assessment Validation Effort (CRAVE); or the Cancer Assessment Group (CAG).

2.2 The OCPs Effects on Human Breast Milk

Zhao *et al.* (2007) measured the levels of six OCPs in human milk and three types of food were collected from Luqiao and Pingqiao in Zhejiang Province, China. The researchers found that the OCPs levels in food and human milk of the two localities were comparable and suggesting that the pesticides were a major source of contamination via their intensive use in agriculture. Further, from 77 papers that have been published during 1965 to 1996 in different regions of the world (America, Europe, oceanic countries and Asia), 46 papers concluded that the high concentration of OCPs residues were detected in breast milk, bird raptors and marine mammals as reported by Harris *et al.* (2001).

Chao (2006) determined the residues of OCPs in 36 samples of human milk collected from healthy women aged between 20 and 36 years in central Taiwan between

December 2000 and November 2001. The OCPs were analyzed by GC/MS and the concentrations of *p,p′*-DDE, *p,p′*-DDT, α-HCH, heptachlor epoxide, heptachlor, β-HCH, and γ-HCH, were 228, 19, 7.4, 4.0, 2.3, 1.2, and 0.8 ng/g lipid, respectively.

Stuetz (2001) detected DDT in all the samples analyzed with a median and maximum level of 209 and 2012ng/mL milk of total DDT isomers, respectively. In 15 samples heptachlor was detected in its metabolized form of heptachlor-epoxide with a median value of 4.4ng/mL. The estimated daily intakes of DDT, heptachlor and heptachlor-epoxide by infants exceeded up to 20 times the acceptable daily intakes as recommended by the FAO and WHO. In fact, the mean sum-DDT residues of 14.96 mg/kg milk fat, as well as the estimated daily intake by infants were one of the highest reported in the 1990s.

2.3 The OCPs and Lipophilicity

OCPs and polychlorinated biphenyls are ubiquitous anthropogenic environmental contaminants and their application poses a serious health problem. Due to their lipophilic nature, lipophilicity and persistence, they bio-accumulate in the food chain and these substances penetrate into cell membranes relatively easily and have several toxic effects (Smith and Gangoli, 2002; Turgut, 2003).

Generally, OCPs have been restricted or even banned because of their long residence and half life. In fact, they are one of the most persistent organic micro pollutants present in water. Consequently their presence in water is regulated by legislation (Meijer *et al*., 2001). The worldwide application of organochlorines pesticides is a major health problem. For instance, DDT is a fat soluble OCPs disseminated by air and water in terrestrial and aquatic ecosystems. When DDT enters a water environment, it is ingested by aquatic animals and becomes part of the food chain, accumulating and concentrating in the fat of predatory species. DDT also remains residual in upper soil layers and accumulates in many terrestrial animal species. OCP have low water solubility, they are lipophilic with high octanol/water partition coefficients. Most of OCPs have octanol-water partition coefficients (K_{OW}) whose log value varies between 3.5 and 6 and, thus, are very soluble in lipids. Moreover, these chemicals are fat soluble, resist metabolic degradation and have a propensity to bio-accumulate in the food chain (Harris *et al*., 2001 and Carvalho *et al.*, 1999).

2.4 The Worldwide Usage of Pesticides

The use of pesticides has grown worldwide gradually since the late 1940s and at present about 2.5 million tons of pesticides are used annually costing to approximately US $20 billion. Despite the application of these amounts of pesticide plus the use of various biological and other non-chemical controls, about 35% of all agricultural crop production is lost to pests (Pimentel, 1991), while the overall estimation of pesticides compounds use in worldwide during the 1948-1997 period were amounted to 10Mt (Li, 1999). In a report by WHO (1992), it was mentioned that during 1990 the world market in pesticides was valued at US $26,400 million. Herbicides accounted for more than 40 percents of total usage while insecticides accounted for approximately 30 percents and fungicides encompassed less than 30 percents of overall pesticides use.

In Bangaladesh, the amount of applied chemicals within the 12 last years have increased by three times Rahman *et al.* (1995). About 8,000 tons of the formulated products were used during 1994 in the agricultural sector compared to 2,510 tons in 1982-1983 and 5,150 tons in 1988-1989. Matin (1995) pointed out that within three decades the use of fertilizers and pesticides compounds to improve crops yields has increased the production of food grains rapidly from 9.7 Mt in 1961 to about 20 Mt in 1993.

In Greece, the three major categories of pesticides compounds used for agricultural and non-agricultural purposes in the whole country included insecticides, herbicides and fungicides and their quantities amounted to 3520, 3440 and 2800 tons/year, respectively. Organochlorine insecticides such as DDT, endrin, dieldrin, aldrin, heptachlor, heptachlor epoxide and technical grade benzenehexachloride (BHC) were extensively used in Greece before 1972 (Albanis *et al*., 1998). While, the amount of fungicides (3,600 tons) used in Greece was almost identical to the amount of herbicides (3000 tons) used (Readman *et al*., 1997).

Quyen *et al*., (1998) was reported that the total consumption of pesticides in Vietnam in 1992 was 21,400 tons whereas in 1997, the consumption of chemicals components was increased almost to double (40,973 tons). In fact, estimated annual expenditure was US $30 per hectare in Vietnam (Quyen *et al.,* 1995). These pesticides were applied not only in the agriculture sector but also in the health sector. For instance, about 24,042 tons of DDT was used against malaria/ mosquito from 1957 to 1994 (Tu and Bien, 1998; Hien, 1999).

Table 2.2 shows that about 80 percents of total pesticides world consumption used in developed countries while only 20 percents of the total amounts of pesticides used in developing countries (Pimentel, 1996). The total usage of pesticides in N. America, developing countries, Europe, Japan, Russian, and Australia were 35, 20, 20, 12, 11 and 2 percents, respectively. Among the developing countries, Brazil, India, Mexico, Korea, Indonesia and other countries were 35, 35, 10, 9, 6, and 5 percents, respectively (WMAS, 1999).

Table 2.2 Estimation of annual usage of pesticides in worldwide

Country / region	Pesticides used (10^6 tones)
USA	0.5
Canada	0.1
Europe	0.8
Other developed countries	0.5
Asia developing countries	0.3
Latin America	0.2
Africa	0.1
World	2.5

Source: Pimentel, 1993a.

In the USA, the usage of insecticides and herbicides has stabilized to about 0.5 $\times 10^9$ kg of active ingredients (ai) annually while 75% of herbicides were used for agricultural purposes based on 1993 estimates (Aspin, 1994). Data collected by the US Environmental Protection Agency in 1988 indicated that 38 US states have at least trace levels of pesticides and nitrates in their groundwater (Williams *et al.* 1988).

China, use more than 100000 tons of DDT over the last decade (Voldner and Li, 1995). N fact, Hexachlorocyclohexane (HCHs) and lindane (γ-HCH) are still being used extensively in China, although there has been increased efforts to control the use of OCPs components in many countries of the region (Li, 1991). Beside of this, almost 6,320 tons of pesticides used over 14700 km^2 areas encompassing the Jiulong River (China) catchment zone in Fujian province (Zulin *et al*., 2002). Huang (1989) estimated that total usage of technical grade of HCH stood at 6 million tons at end of 1980. Finally, Li *et al*. (1998b) cited that the total usage such as China, Japan, India and the US had increased to 6.23 million tons within the 1948-1995 periods.

2.5 Movement Media of Pesticides

In order to determine the environmental impact of pesticides, it is necessary to determine the extent to which they are transported by various types of media. Studies have shown that the extent of movement in each of these media depends on many variables such as the physico-chemical properties of the pesticides, soil application, methods of application, prevailing temperatures, time of rainfall and ambient conditions during and after application. The widespread usage of pesticides in the environment and their appearance in soil, surface water, groundwater and air has led to an understanding of the cyclic behavior of the environment (Plate 2.1). Generally, pesticides may be transported or moved over a considerable distances by soil movement, groundwater, surface run off and wind deposition (Cogger *et al*., 1998; Alegria and Shaw, 1999). Leonard, (1990) mentioned that, there are too many factors related to the amount lost from fields and transported to surface waters such as soil characteristics, topography, weather, agricultural method as well as the chemical and environmental properties of individual pesticides. In fact, the combined effect of these factors on the temporal and spatial magnitude of pesticide contaminations and fluxes in large integrating river systems is largely unknown (Larson *et al.,* 1995). The chemicals that used in agricultural activities were transferred by run off after soils erosion enters the surface water and sea. The presence of pesticide residues in the soil and their movement in the water and soil system are key indicators of their environmental behavior process (Richards and Baker, 1993 and CACAR, 1997).

According to Plate 2.1, chemicals such as synthetic organic compounds can enter the aquatic environment via atmospheric transport, groundwater leaching, soil, sewage inputs and run off. Therefore, during and after spraying of plant protection products, the compounds applied to crops or soil can be partly moved by air to non-target areas (in the wind ways) where they can stress fauna, flora and humans (Van den Berg *et al*., 1999).

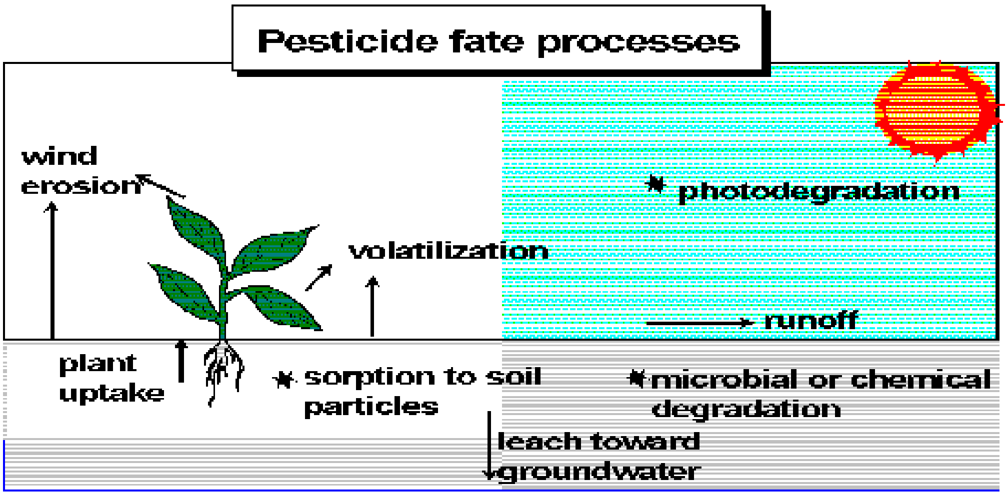

Plate 2.1 The pesticides movement environment cycle (soil, groundwater, surface run off, and air)

Source: Van den Berg *et al*., 1999

2.6 The Leachability of Pesticides

A few studies show that the pesticide leaching was a non-point source of contamination for surface water and groundwater (Boesten and van der Pas, 2000). Therefore, the surface water and groundwater were contaminated by pesticides leaching, industrial and agricultural wastes for a long period (Holden *et al*., 1992). In the United States, 17 pesticides have been detected in the groundwater of 17 states and this has been caused by the leaching of pesticides and their concentration at levels exceeding health advisory levels (Parsons and Witt, 1988). Also, leaching of pesticides from agricultural soils that contaminated surface and groundwater by run off and drainage should be minimized as much as possible. This surface water contamination may have eco-toxicological effects for both aquatic flora and fauna, and human health (Miyamoto *et al.,* 1990). The usage of pesticide in crop production is a major source of non-point-source of pollution in groundwater and surface water by leaching and run off.

2.7 Pesticides Monitoring in Different Countries

Many developed countries banned or restricted OCPs usage in 1970s, and this restriction was followed by many developing countries in 1980s, because of their biological persistence in the environment (Voldner and Li, 1995). However, certain countries in Europe, Asia, Africa and the US are probably using these chemicals in the agriculture and public sectors as explained briefly as follow:

2.7.1 Argentina

In Argentina, a large number of pesticides have been used for agricultural and public health purposes. The application of such chemicals often contaminates the aquatic environment as these pesticides are metabolized in the liver of marine life. In fact, in some cases, chemical such as heptachlor have biotransformation metabolites that are more toxic than that of the original product. Besides this, OCPs are known to resist biodegradation and are bio-accumulates due to their capacity to bind to lipids. Thus they can be redistributed through the food chain (Erichson and Joy, 1982). Reconquista River in Argentina is good receptor of toxic wastes generated on land. More than three million people are settled on its basin and can make more pollution and damage to the water quality of the river. Since 1990 the water pollution in Reconquista River has been studied and more recently additional studies were conducted to identify and quantify its contaminants (Castañé *et al.*, 1998; Topalián *et al*, 1999).