ENVIRONMENTAL RISK ASSESSMENT OF ORGANOPHOSPHORUS PESTICIDES IN THE SOUTHERN COASTAL OF CASPIAN SEA

ID 073

Davood BABAEI[1], Zohre BASHAR DOOST[2], R. BASHAR DOOST[3]

[1] ISOICO, Procurement Division, Shahrak Ghods, Tehran, IRAN
[2] Ronass Paint & Protective Coatings, Tehran, IRAN
[3] Amir Kabir University, Polytechnic of Tehran, Tehran, IRAN
ppm2.proc@isoico.com, ronass@ronass.com

ABSTRACT

Environmental risk assessment is an estimate of the likelihood or probability of an adverse impact on the environment resulting from human activities. In reality using this method, effects and risks involved with the presence of hazardous chemicals in environment are identified, their effects are assessed and if possible, different approaches are recommended for risk communication and risk management. In doing so, first the geographical conditions, agricultural lands and various types of soil in southern coasts of Caspian Sea were investigated. At the same time different varieties of living organisms at Caspian Sea which consists of various mammals, birds, fish and marine invertebrates were identified and also results of investigations on the levels of organophosphorus pesticides in the water of various rivers flowing into Caspian sea were used. These determinations were performed using GC/NPD. Malathion, Diazinon, Fenitrothion and phosalone were investigated in different stations along the rivers.

The results indicate that if considering only the stability of these pesticides, due to being unstable at the pH of these river waters, they have a low risk in this area on the living organisms. However, Diazinon was seen in these rivers in spring and summer at higher levels than the recommended values. These pesticides are not stable in the soil of this region and after entering the soil, due to evaporation, chemical and microbial activities are degraded. On the other hand, mobility of these pesticides in sand is higher.

The probability of risk (high, medium and low) in three provinces of cospian Sea, namely, Gilan, Mazandaran and Golestan were evaluated. Using the collected data and information, Mazandaran province has more varieties and number of living organisms, it has a sandy and soft sedimented soil in which the pesticide has higher mobility, and the probability of reaching different sources of water is higher. Also this region has higher levels and varieties of agricultural land and crops. Therefore, Mazandaran province has been identified as a region with a high risk for organophosphorus pesticides, mainly Diazinon.

Gilan and Golestan Provinces with lower varieties of living organisms, higher varieties of soil type and lower levels of agriculture compared with Mazandaran, are regions with

medium and low risk levels respectively. Therefore, it is recommended that we reevaluate the use of Diazinon in Mazandaran province and have a stronger control on it.

Key words: Environmental risk assessment, Toxicity of organophosphorus, Rest of toxicity, pesticide, rivers, definition of toxin.

INTRODUCTION

These were effects on the accumulative growth population, lack of dietary material, undesirable economic requirement, etc. that the statesman's countries should be consideration to agricultural production and dietary material. The fight to blights due to much of production and the necessity for raise level economic society .Therefore this purpose should used to variety ways for fight to blights. Because the chemical struggle of working facility and rapid effects addition to eradicate blights nature enemy, also the most current had way for struggle against to blights. Although this way to use for insects control but there are very problem among pollution environment. One of the major efforts for this was struggle problem world united Nations in recent years .This approach were tried wide organ to name for Food and Agriculture Organization of the united nations world within the mostly mankind had rescued from hot seat which efforts was following on the 3 basis :

1- development cultivation,
2- rise to product on unit of level,
3- Reduction of wastage in product and after stages of product during to use.

An increase surface arable land in regional and geographical circumstance country and it work isn't easy for great expenses. The most basics and level unit was working to up product doing raise to agricultural products. Anyhow we were action to product agricultural material. Observable this product died for blights and different problems that this struggle of blights had mass production. One of ways the struggle to blights chemical combat that should be use of chemical and medicinal material. It material was called pesticide which was categorized to 3: mineral, vegetable and organic. Composition of organic pesticide was by chemist. It compositions was including in 3 group: 1- organocolore .2-organophosphorE 3- Karabmats. An anomalous use from pesticides in healthful and agricultural affairs for control diseases transmitters and the struggle of blights and organic diseases and oversight to environmental problems that enter to new material to return to ambient. It material is possible therefore speared by water, soil and air and there are effects on agricultural ecosystems, sources of nether waters, products of garden and arable.

In addition to above it material through contact to position, supply and making warehouse and too various dietary material unwanted enter to flesh and organisms other that it is possible to making for risks and irrecoverable harms.

The water this life fountainhead was polluted through containment applies to indirect and direct. The rivers, lakes and seas was may by scum of factories and the actual center and citified garbage through the making warehouse had polluted toxic garbage's cisterns factories. The waters polluted may by entry to manures and pesticides which use be in

healthful and agricultural affairs. it material apply to by rain of agricultural lands, sewers and backwaters consequent on industry of pesticides products from indirect resources and blights for control of pests among to use equisetic vermin that they had rate to direct resource water containments and through aquatic ecosystem and polluted their, in addition to ill on aquatics and other creation, pollutant swimming pools hereby the agents supply to pullets of peoples. Some of pesticides even the less density was caused to poisons for aquatic invertebrate and fishes.

MATERIAL AND METHODS

Sampling of rivers

After considering to region case of study had selected sampling (by conjunction place vital subdivisions to rivers, the dispersal of lands cultivation, pests and use of phosphors poisons in mentioned regions). Thereupon, concerning to above cases had selecting for 6 station Sampling on the rivers in order to below and the sampling had done to Nansen bottle. In each station had be modeling 3 of points depth and level of river and the result sample had involved to all quality river and the product sample had mixing to each other and all this samples is take to mixture 1 liter and had spilled in the especial bottles samples. Forthwith they had spilled 5g halite (NaCl) and 50cc organic solvent Di-colormetan for fixation within any test stage was keeping samples with temperature in within temperature of refrigerator was calculated within $4^{\circ}C$ for modeling, pH water by pH meter portable, temperature water and weather. After transfer of samples to laboratory, operation of extraction and condensation on samples was working and analyze by set of gas chromatography with detector NPD.

Stages of extraction and condensation on samples

After the place sampling to sample had additive to amount 5 gram halite sodium and 50 ml of solvent di colormetan and this temperature had adjusted within $4^{o}C$.

Samples had transferred to laborites and in order to under over they fared stages of extraction. A first sample was additive to 1 liter water and 30 g colored sodium and they mixed to time of 5 minutes. before the samples fallen separable funnel and had separated two phase organic and aquatics.The aquatic phase excess to 50^{CC}decolorometan and again the operation had shake for 5 minute. Next in two phases had mixed organic phases each other and for water they used to 20g dioxide sodium sulfate and as well as had mixed . After an admixture flatted by bokhner funnel because it ready to injection GC and decrease to mass that in the research apply to condenser in void or Rotary Evaporator to evaporate in temperature 35-40°C. Samples keeping to injection time of GC system on freezer.

3-7- Equipment and material for extraction, condensation and analysis:

- Di colormetan (solvent),
- Halite (NaCl),

- Sodium sulfat,
- Experiment supplies, Orlon, beaker, ball-peen balloon, dekantor, bokhner, pipette…
- Continues system of evaporation and side effects (condenser in void or Rotary Evaporator),
- Shaker,
- Micro syringe to 1 micro liter for injection to system GC,
- Standard solutions,
- Keromatoporghapy Gas system GC (4400-PU) within specification,
- Capillary column with fixed phase DBI,
- Nitragen selected Detector NSD.

In the research for keromatography gas system were active situation:

- Column temperature 117-250°C (3 minutes in117oc before received to rapid 3^{o}C in minute to temperature 350^{o}C)
- Temperature of Detector 320^{o}C
- Temperature of injection: 180^{o}C
- Rate sample injection: 1 micro litter
- Solvent: methanol
- About sensitive 0.1ppb
- Time of analysis: 40-45minute

System calibration

First kermatograph gas system had calibrated to densities of standard 15 phosphors toxin in according to below table: then for quality and quantity toxics in water samples, shall be increase to any dry sample l ml methanol and under had injection of system.

Table 1-4-8.: Standard density third mixed for system calibration according to ppb.

Standard	Fozalon– colr pirfos	Di-metovat	Other toxins	Malathion	Finton
1	30	12	4	30	0.5
2	15	6	2	15	0.25
3	7.5	3	1	7.5	0.125
4	3.75	1.5	0.5	3.75	0.063

A region has measurement in them including as:
1- Caspian sea river 2- Baboolrod river 3- Tonekabon river 4-Namakabrod river 5- Shirrod river 6-Tajan river 7- Neka river 8-Anzali wetland.

In this region was according to different seasons (autumn, winter, spring and summer) to measure toxins (Malathion, Fenitrotiyon, Fozalen, Azin – phos – methyl l, Diazinon).

RESULT

Table 16-2-8.: Influence of assessment phosphore toxins (Malathion) in coasts southern Caspian sea (provinces of Gilan, Mazandarn, Golestan)

Name toxin	Malathion	Kind of soil	Effect on soil	Water	Organism	Mostly amount in season	Use	Risk	Conclusion
Name provinces	Gilan	Sediments to coast sandy	Not see	Not see	Very small toxins	Not see	Most north region & gardens	-	Safe pesticide and it isn't risk in 3 provinces Mazandaran , Gilan Golestan
	Mazandaran	Soil sediment	Not see	Not see	Very small toxins	Not see	Most north region & gardens	-	Safe pesticide and it isn't risk in 3 provinces Mazandaran, Gilan, Golestan
	Golestan	Nitrate soil and marshy	Not see	Not see	Very small toxins	Not see	Most north region & gardens	-	Safe pesticide and it isn't risk in 3 provinces Mazandaran, Gilan, Golestan

Table 17-2-8.: Influences of assessment phosphore toxins (Diazinon) in Southern Coasts Caspian sea (provinces of Gilan, Mazandarn, Golestan).

Name toxin	Diazinon	Kind of soil	Effect on soil	Water	Organism	Mostly amount in season	Use	Risk	Conclusion
Name provinces	***Gilan***	Sediments to coast sandy	The soil have effect with level medium risk	exist	toxicity	summer	Paddies and composites	-	There are moderate safe in region
	Mazandaran	Soil sediment	The soil have effect with level high risk	There are very high	toxicity	Spring – summer-autumn - winter	Paddies and composites	-	There are high safe in region
	Golestan	Nitrate soil and marshy	The soil have low effect with level low risk	There are very high	toxicity	summer	Paddies and composites	-	There are small safe in region

Table 18-2-8.: Influences of assessment phosphore toxins (Fozalen) in Southern Coasts Caspian Sea (provinces of Gilan, Mazandarn, Golestan).

Name toxin	Fozalen	Kind of soil	Effect on soil	Water	Organism	Mostly amount in season	Use	Risk	Conclusion
Name provinces	**Gilan**	Sediments to coast sandy	Not see	Not see	low toxicity	Not see	North Region & fruit gardens	-	Fozalen was very speed analysis and it is not safe in southern coast Caspian sea
	Mazandaran	Soil sediment	Not see	Not see	low toxicity	Not see	North Region & fruit gardens	-	
	Golestan	Nitrate soil and marshy	Not see	Not see	low toxicity	Not see	Region working soy been	-	

Table 19-2-8.: Influences of assessment phosphore toxins (Fenitortion) in Southern Coasts Caspian sea (provinces of Gilan, Mazandarn, Golestan).

Name toxin	Fenitortion	Kind of soil	Effect on soil	Water	Organism	Mostly amount in season	Use	Risk	Conclusion
Name provinces	Gilan	Sediments to coast sandy	Not study	Not see	low toxicity	Not see	paddies	-	There are very high water in seasons spring and summer .the province Mazandaran were rather than two province other
	Mazandaran	Soil sediment	Not study	Not see	low toxicity	Not see	paddies	-	
	Golestan	Nitrate soil and marshy	Not study	Not see	low toxicity	Not see	paddies	-	

Table 20-2-8.: Influences of assessment phosphore toxins (Azinphos metil) in Southern Coasts Caspian Sea (provinces of Gilan, Mazandarn, Golestan).

Name toxin	*Azinphos Methyl*	*Kind of soil*	*Effect on soil*	*Water*	*Organism*	*Mostly amount in season*	*Use*	*Risk*	*Conclusion*
Name provinces	***Gilan***	**Sediments to coast sandy**	**Not see**	**Not see**	**Very toxic**	**Not see**	**Region olive**	**-**	**Concerning to high toxicity analyzed and evacuated. neither it isn't see in 3 province**
	Mzandaran	**Soil sediment**	**Not see**	**Not see**	**Very toxic**	**Not see**	**Most fruit gardens**	**-**	
	Golestan	**Nitrate soil and marshy**	**Not see**	**Not see**	**Very toxic**	**Not see**	**Most fruit gardens, cotton farms**	**-**	

Cosideration Malathion in Southern Coasts Caspian Sea

Malathion is toxin organophosphore that wide used to pesticide in agricultural farms and gardens. An effect on ecologic Malathion toxins had showed that mammals have weak to amount toxin and birds and fishes. a pesticide is safe because they wasn't identified in resources aquatics resources rivers is not identify to 3 provinces as Gilan , Mazandaran , Golestan which haven't risk and they have seldom between phosphore pesticide .

Table 1-1-18.: Malathion toxicity in mammals, birds and fishes.

Risk toxicity	Level toxicity	Density Malathion
mammals	less	LD50=1400mg/kg
birds	very small	LD50=3500-4320mg/kg
fishes	very very small	LD50=0.1-0.28mg/lit

Two important factors for fixation and decrease analysis toxins phosphore in water.

1- temperature	1 - Low temperature was under speed chemical Hydrolyze - low activity microbe. 2 - High temperature was increase speed chemical Hydrolyze-raise activity microbe.
2-pH	1- variable alkali pH. 2- stable acidic pH.

Consideration Diazinon in Southern Coasts Caspian sea

Diazinon was a toxins organophosopher which have used to in paddies and garden. An amount to it was very small in mammals and influenced over growth vermin and youth and chiggers. It is pesticide and nonsystematic for pesticide and fungicide wide spectrum and they have low property killing chigger. Two compound have high used Diaznion in agricultural 4E, AG500 which haven't influence in oneself formula Etil benzene, metal benzene, gezilen.

Diazinon have uninfluenced on many birds, fishes, positive arthropod and germs.

Table 1-2-8.: Table of toxicity Diazinon in mammals, birds and fishes.

Risk toxicity	***Level toxicity***	***Density Malathion***
mammals	much	300-400mg/kg
birds	much	LD50=3.5-4.5mg/kg
fishes	much	LC50=2.6-23.4mg/lit
Rainbow trout	much	LC50=2.6-3.2mg/lit
Fish bivgillsum	much	LC50=3.15mg/lit

Table of toxicity Fozalen in mammals, birds and fishes

Fozalen is a pesticide and killing chigger organophosophere that use to apply in composites gardens and farms against had analyzed alkali and acidic material that is half life in soil 7 day. It durability is in plant of 14 time and then due to phosporeh tioat compost that later compost was analayize speed.

Table 1-1-4-8.: Table of toxicity Fozalen in mammals, birds and fishes.

Risk toxicity	***Level toxicity***	***Density Azinofus metil***
Mammals (mouse)	medium	LD50=170-135mg/kg
birds	medium to much	LC50=290-2552mg/kg
fishes	small	0.11-2mg/lit

Consideration Azinofus metal in Southern Coasts Caspian Sea

One of toxicity is oreganophosphor which has effect to contact and digestion as pesticide have application in composites gardens and cotton farms and it is commercial name of Gozatiyon –M.

For alimentary channel, from healthy skin and while had spread sniff particles and absorption toxicity. Aziynofus to active absorption and metabolism in mammals. Mainly metabolites this toxicity as like metal phosphore Tyoehk Acid, Di metal phosphoreic Acid, des metal Aziynofus metal Acson . Quickly part Benzotei Azin without evacuate analyzes Aziynofus metal hare in group five toxicity material and infinitely toxic .Probably it toxicity was killing for people by eating way for body weight between 5 of 50 mg/kg nearly 7 drop or 1 teaspoon . toxicity of skin was 21 day in rabbit get to body weight loss in doe (40-70%) loss of blood- red cells in male rabbit (10%), rise liver and milt in male rabbit and many rating to change inflammatory in all male rabbit in doze for body weigh 20mg/kg .

Table 1-1-3-8.: Toxins Azinofus metil in mammals, birds and fishes.

Risk toxicity	***Level toxicity***	***Density Azinofus metil***
mammals	much	LD50forat=16mg/kg
birds	much	LD50=32mg/kg
fishes	much	LC50=0.02-0.12

Consideration Fenitrition in Southern Coasts Caspian Sea

The pesticide was very high organophpspohere that it is commercial name of Somitionon. For struggle to injurious pests grain, worm rice pedicel – field and aboriginal grasshopper in farms used to wheat and barely and meadows and too grain aped .but it pesticide isn't very high toxicity and it pesticide have resistance in pH=4 with time 109 day.

Table 1-1-5-8.: Density of toxicity Fenintorn in mammals, birds and fishes.

Risk toxicity	***Level toxicity***	***Density Fenintoron***
mammals	low	LC50=800mr/kg
birds	low	LC50=23.6-1190mg/kg
fishes	low	LC50=1.7-4.1mg/lit

Deletions Dyazion of soil Southern Coasts Caspian Sea

In according to there exist in data bank EPA Dayzinon in both surface water and nether water. Among them toxicities phosphere Dayzinon is over stability (movement ability in fair soil was upward). Diazinon stable is in soil 10 of 12 week. Whatsoever, typical station can extant out 20 weeks in soil. Possibly, Diazinon had entered by surface water (through influence in soil) which definite trace Diazinon according mg/kg.

Only Diazinon is a pesticide that had be stable in alkali pH thus region soil sediment Mazandarn was soft texture which Diazinon pesticide in kind of soil was absorption fast Homos and possibility have risk there are prosperity pH acidy or neuter soil region Gilan and Golestan this region have to rating second risk to orange color . in region rainfall were washing pesticide used of surface soil and absorption to soil depth that it deep was definite for over time trace 30cm also a relict pesticide in soil depend on moisture of soil to pH land, temperature, acidic and chemical properties, use to order pesticide and formulation. A pesticide was as Geanvol and enduring totally the best pesticide phosphoere was rest to soil for within 3 month.

Delation Diazinon of rivers water Southern Coast Caspian Sea

According to done experiment in rivers of Tajen, Neka, Babolrod, Namkabrod, Tonkabon, Shirrod and Anazali Talab in seasons of summer, spring, winter and autumn although toxicity Dazinon had be higher than two region other and the risk is very high in the river Shirood.

These cases could to solve problems. Therefore which were suggestion they had need to education for farmers, users, sellers of pesticides used to in agriculture. Texts of needful education could be to track UNEP, FAO and other references.

CONCLUSION

The concerning to result in seasons of spring, summer and autumn and winter had compared to rivers to Neka, Tajen, Babolrod, Tonekabon, Shirood, Talabe Azali that in two regions Mazandarn higher two provinces other and whereof following with 1- texture region soil including to coast tape in province of Mazandaran 75% of total coast and line

soil was kind of alluvial sediments the Diazinon pesticide was to rapid absorption Homos in it soil and also it pesticide is resistance in soil for 3 month. But the region soil have alkali pH that it have stable toxicity Diazinon. 2- Similarly the deep well is in low region and very wells that glaze toxics enter to nether water region. People of water be used for drink and health hence it water is enter to environment and people and organism is dangerous. 3-In fish blveglish /sum have effect toxicity and dead. 4-in regions Namakabord, Tonekabon, Babelrod, shirod cause to of rice cultivation be very region that used to many toxic. 5-a status climate have impressible. Because an orientation wind of side northwest to northeast in here the wind is caused to had diffuseness toxicity in superior region and the weather region was polluted. 6- again the pesticides is Geranoevel as later these was free influence material but have very durability. 7- rating to Diazinon toxicity be to change seasons variable. For example, rating to many Diazinon in winter and it toxicity have high risk. but they are quantity more high than in spring in province Mazandaran that it region have risk and was seen to rate Diazinon and Fnitortiyon which have exceeding in summer a region Mazandaran as Namakabrod, Shirod, Babolrod an Tajen regions.

The region of Gilan has risk in second level:

1- Line of soil region was to kind of sediment to coast sandy. Diazinon toxicity in region soil stays to between" 10 to 12" week whereas rice cultivation has superiority as composites but in level first used to Diazinon.
2- A organisms of this toxicity was affected including as an immigrant birds which seen in Anzali region. Some of this bird's toxin Geranols take mistake to eating spore and used them by the toxin was entering in body. Therefore half of propriety is Geranol that gradually had affected in oneself track at birds body and whole dead birds.
3- Affected this toxicity on Sime fish was in Gilan province situated at Talabe Anzali region recently the kind of fish is very low in region it .
4- Region Golestan have third level thus there are low risk as two province because: 1- kind of soil in Gorgan plain of nitrate and easy to toxicity of washing surface soil and power absorption in soil and also these haven't fixity on surface soil. 2- for organism, various and some of aquatics animals is small province. Therefore emigrant birds, this region seen to as small as Talabe Anzali. 3- In this region extremely level of subculture due to cotton in region composites was small culture consequently no apply to Diazinon. Because this region has small risk and which have level third.

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