

Bioindicator Mercury of Aquatic Ecosystems in Iraqi Marshland by Using GIS

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Abstract:

This study was conducted to indicate Mercury of the Iraqi marshes by a software program using Geographic Information Systems (GIS) to implement the comparing these elements with the environmental and biological factors with World Health Organization elements (WHO), and the Food and Agriculture Organization (FAO), this study included access to geographical data in six main stations of the Missan governorate (Al- Auda Marsh, Al- Battat Marsh) during October 2016 period. And the selection of environmental factors (Water) and Biological Mollusk (*Melanopsis nodosa*). The results of water in all stations under study showed low concentrations of Mercury concentration and varied mostly similarly limiting factors with natural boundaries of water bodies, A little increase come from of some pollutants that are discharged from the water drainage or waste populated. As well as were examined the elemental mercury in Mollusk, this case with water constitutes of the ecological balance of the pollution, which represent an important indicator of the balance of pollutants with the water and the ability to uptake and accumulation of elemental mercury. The correlation showed significantly between these variables in the aquatic environment, It would be transmitted an ecological balance between organism and water. This bioindicator considered as a very important database for environmental risks and health in aquatic environmental of marsh which can be updated through a unified future other periodic data.

Keywords: Iraqi marsh, Bioindicator, Mercury, Water, Mollusk.

1 INTRODUCTION

Marshes are transitional districts between aquatic systems and terrestrial where water table close or above the land surface have more of the important functions to benefit a wildlife, human, and plants (Mitsch and Gosselink, 2000). The marshes source water were multi origins of groundwater, precipitations. The marshlands make up the largest ecosystem of wetland in the Middle East. These wetlands are situated at the convergence of Euphrates and Tigris rivers in southern of Iraq. This region supported marsh Arab inhabitants of 500,000 as well as numerous common species of invertebrates, birds, fish, mammals, amphibians and reptiles . Aquatic ecosystems pollution by elements is worldwide environmental trouble (2). Metal contamination can contain negative effects on aquatic organisms just after metal uptake and accumulation. Iraqi marshes considered as a filter and store water on ecosystems, collected flood waters beside places of beauty and many recreational activities also Plants found in wetlands to help control water erosion once covered an area (20,000 Km²), and it

extends between the three Iraqi Cities of Amarah in the north, Basra in the south, Naseriyah in the west. AL-Huweizah marshlands are located in southeastern Iraq but also extend across the border into Iran .It lies to the east of the Tigris River, straddling the Iran-Iraq border (Ramsar,2011). Most of the water that supply the marshlands coming from the Tigris and Euphrates Rivers with some input from Al-Huweizah Marsh (USEPA, 2002).

Water levels in marshes respond a hydrological system feature common to both the Tigris and Euphrates prior to the dam contraction which is the heavy concentration of suspended sediment carried at flood-time: they may have transported as much as three million tons of eroded soil from the highlands in a single day these sediments load were deposited within the interior environment (Ajmi, 2012.; Jones, *et al.*, 1991). Many studies have been conducted especially for water from Iraqi Al-Huweizah Marshes most recent concentration of radioactive elements and heavy metals in water and soil samples have been high which revealed the expected pollution in the area could be raised from natural and anthropogenic (UNEP ,2012.

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Ajmi ,etal 2015). Water levels in marshes respond a hydrological system feature common to both the Tigris and Euphrates prior to the dam contraction which is the heavy concentration of suspended sediment carried at flood-time: they may have transported as much as three million tons of eroded soil from the highlands in a single day these sediments load were deposited within the interior environment (Jones, et al., 1991). Many studies have been conducted especially for water from Iraqi Al-Huweizah Marshes most recent concentration of radioactive elements and heavy metals in water and soil samples have been high which revealed the expected pollution in the area could be raised from natural and anthropogenic (UNEP ,2012. Ajmi ,etal 2015).

Bioindicators are actually defined as the systematic use of living organisms and changes in the environment on their responses to determine the status and can be considered as a method of observing impact of internal and external factors can be used to monitor health condition of the environment in which they live their behaviors, changes in the population status , physiology such as organisms to predict the occurrence of an environmental problem in ecosystem (Oertel,etal.2003, Ajmi , 2015).

In 2004 Dating back first used Bioindicator pollution when it was to indicate factory workers for exposure to lead of Physical and measurements of elements commonly form the basis of monitoring due to they provide the complete spectrum of information for pollution (David, 2005). It has been proven to be necessary supplementary for traditional monitoring techniques in Aquatic organisms such as Macroinvertebrates can form as bioindicators to merge their total environment and their responses to complex groups of

environmental conditions such as fish and mollusks (Stevenson and Pan,2001).

Bioindicators are determined when their abundant of organism clearly in any response environmental change in a particular habitat and can be categorized into an early warning, compliance and diagnostic by reveal first signs of disturbance in the environment. Indicators diagnostic used to investigate observed disturbances environmentally, Indicators compliance used to restoration goals and verify maintenance have been achieved (Mouillot et al., 2002). That's mean Bioindicators are habitat specific reacted immediately in response to changes environmental (Celli and Maccagnani, 2003). The extent of reliability in bioindicators with their habitat and assessed by sampling from different weather seasons or conditions by the assemblage of organisms and their environment as a preferable bioindicators such as biochemical contamination (McGeoch et al., 2002, Celli and Maccagnani, 2003).

Mollusks are good indicators of habitats aquatic organism, it used to detect increasing pollution in downstream from industrial pollution and various anthropogenic activities, physical and chemical characteristics and aquatic food webs. In a study (Saaed,etal.,2013) suggests that some types of Mollusks as a regulator balance of pollution having the ability absorption of elements from the water directly.

Metals such as Mercury enter the aquatic environment of southern Iraq from both natural and anthropogenic sources. Natural sources include dust storms, erosion or crustal weathering and decomposition of the biota in the water (FAO, 1994, Ajmi 2010), accumulation and distribution of heavy metals in shell mollusks depend on many factors concentrations of metals, exposure time, temperature and salinity, food habits, physical conditions, growth, age, sex

and pollutants interactions (Abdullah and Abdul-Hassan, Sensitive (Measuring mercury system with a unique 1994). Mercury considered as a nonessential element, highly visual path spectrophotometer provide low detection toxic heavy metal and it has been a global contaminated due limits), Flexible (Easily from the basic "dual-cell__tri- to ability to access long distance from the source of pollution cell" with available for gas analysis. Cost-Effective by the atmospheric transport (Wang et al., 2004). Mercury (less more than traditional mercury analysis exist in the environment as three main chemical form techniques) add of accuracy and performance.

Elemental Mercury (Hg₀) ,Inorganic mercury(Hg⁺) and mercury salts (Hg²⁺) . Mercury and compounds are hazardous material and rated in the high level of environmental pollutants (Lipfert,etal.1995).Studies on assessment of mercury levels in water, Fish, sediment , Mollusks and aquatic plants have been carried out in different region of Iraqi marshland (Al-Imarah,etal.2003;Awad and Abdulsahib,2007 and Hashim,2010.; Ajmi , 2012). Mercury bioavailable decline steadily after weathering processes that made mercury available from origin material, deposition of mercury an important way for sediments, plants and soils (Obrist, et al.2009). According to official data emission, In Europe total Hg anthropogenic emissions was 195 t./year in 2003 and 413 t./year in 1990 (WHO,2007). In natural waters the total concentrations of Mercury very low (1.0 ng/L) . In drinking water value (1.0 ng/L) (WHO 2007) , dissolved total (Hg) values in an open ocean(0.5–3.0 ng/L) in coastal seawater(2.0–15 ng/L) in freshwater lakes and rivers(1.0–3.0 ng/L) . About Soil Hg concentrations range from (10 to 160 ng/kg) reaching a median value of (40 ng/kg) (WHO 2007).

1-2 Principle of Milestone's (DMA-80) Direct Mercury Analyzer:

New technical analysis of Mercury directly analysis to any sample solid and liquid at the same time without need to preparation of samples. Automatically process range 40 samples at (4 hours) start to finish, qualities it safety, productivity (need five minutes to one sample, no need acid digestion),

DMA-80 permits in Nature such as " Hard (Sediment, Plants , Soil, Sludge, Food/Feed , Animal tissues, Oil, Coal, Fish, Wood , Cement, Plastic and Paints) ."Soft (Beverages, Liquids, biological fluids and Wastewater). Environmental(Resources Laboratories, Agriculture, Power Plant, Petrochemical and mines)(USEPA,2006).

1-2-1 : Mechanical working of DMA-80:

Weighed a liquid or solid sample into metal boat or quartz and then transfer sample from the analytical balance to the DMA-80,. Loaded sample boats on to instrument auto sampler, first dried and then thermally decomposed in furnace oxygen,. Released Mercury and combustion products from the sample and carried to the catalyst section furnace, where sulfur oxides and nitrogen and Mercury (Hg) flown by the carrier gas into path of the spectrophotometer where it is quantitatively measured.

All information's system are kept on Windows-based computer and software, providing simple and intuitive, Sample parameters including method profiles , furnace temperatures, , absorbance signals . The results and calibrations are saved, easily transferred information by using a USB memory to Laptop Laboratory (USEPA,2006).

1-2-2: Improve Safety and quality in Bioindicator :

Maintaining the health and reduce the risk exposure in indicator Mercury by Quality Assurance (QA) Focused on providing confidence of quality requirements (ISO

9000:2005) Also Establish a good quality management system and the assessment of its adequacy& conformance audit of the operation system & the review of the system itself (Gurus Quality,2011). Quality Control (QC) Focused on fulfilling requirements quality (ISO 9000:2005). Used (SRM-1974b, SRM-2976) for Water . (TORT-2, TORT-2) for Mollusk. The activities and operational techniques requirements of the product conforms to these planned by activities or techniques used to achieve and maintain the product quality, process and service. An important preventative approach that may be applied at all stages in the food chain involves indicator system (FAO & WHO, 2004). Ability to continue of quality global standards has benefits to ensure high quality and safety (EPC global, 2009). A geographic information system (GIS) is a computer-based tool for mapping and analyzing things that exist and events that happen on earth and integrates common database operations such as query and statistical analysis with the unique visualization and geographic analysis benefits offered by maps. Data-bound or written representation of the formulas for the spatial information core components called simple components such as spatial raster data that represent the points such as the locations of measurement stations and written statements which represent the lines, such as streets or rivers. The data represent the polygonal or areas that can be identified closed line such as lakes and administrative areas, residential neighborhoods (Aronoff, 1991). A spatial data are on a network or matrix of dimensions of small cells called (Pixel) or a sham (Picture Element), and each pixel value reflecting the type of the corresponding teacher. That each pixel is the average illumination or reflectivity measured electronically to the same location on a scale grayscale (Gray Scale) expressed as a number called a digital number (Digital Number DN).These values are positive integers. The grayscale is a measure of light intensity represents the color black (a reflection of lower and higher absorption of electromagnetic radiation), and the highest value representing the color white the highest reflection and less absorption of electromagnetic radiation. The pixel size is the

basis of image resolution, as the smaller pixel size increased the accuracy and clarity of an image (Jensen, 2000).

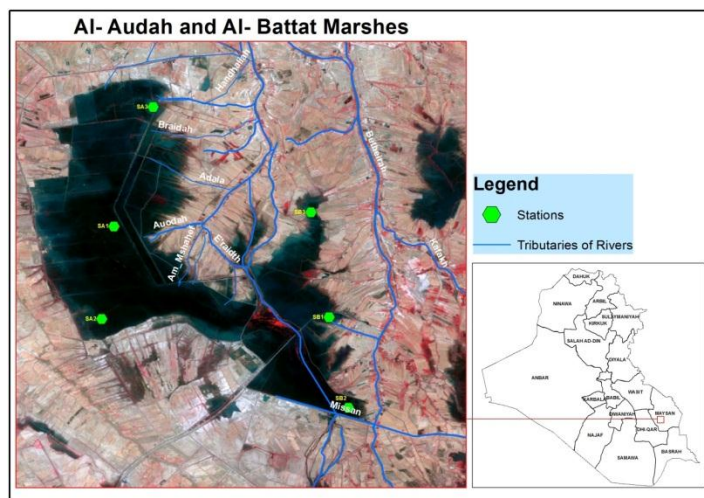
Environment in Aquatic ecosystem is a source of concern resources to indicate this warning need to be more environmentally solutions to reduce environmental impacts therefore, this study aimed to detect water pollution and mollusk in the marsh to reduce risk in the aquatic environment and to identify the etiology of Mercury

2 MATERIALS AND METHODS

2.1 STUDY AREA AND SAMPLE COLLECTION

Six basic stations were chosen in this study in the Maysan Governorate marshes(Al- Auda Marsh, Al-Battat Marsh) , It was chosen three main sites of the (center, middle and end) of each region for the purpose of study and labeled it depending coordinates.

This study was conducted The samples were collected from the study sites in October 2016 , The water samples were collected from the surface water (about 30 cm below the surface) in each community, using 20 litter containers. Water samples (sub-surface) were collected by means of a Van Dorn water sampler. The water samples were immediately filtered through 0.45 μ Millipore filters. The filtrates were placed in glass and/or plastic containers and frozen till time of analysis. Standard methods by (Pearson and Havill, 1988) and Soil Samples were collected by using cleaned polyethylene bags from 30 cm in depth. Have been followed the methods of internationally adopted for the collection of models and by focusing on the parts in Southeastern Iraq Pic (1) Boundaries of the six marshes where samples were collected.



Picture (1): Arc10 Map GIS development Six station under study area.

2-2 EXPERIMENTAL SETUP OF DETECTOR

1- Water samples were collected from the surface water (about 30 cm below the surface) in each community, using 10 replicate to each one station. Water samples (sub-surface) were collected by means of a Van Dorn water sampler. The water samples were immediately filtered through 0.45µ Millipore filters. The filtrates were placed in glass and/or plastic containers and frozen till time of analysis. Standard methods by (Pearson and Havill, 1988).

2. Mollusk sample (Shell *Melanopsis nodosa*) species (Family: Melanopsidae, Class: Gastropoda) (Férussac, 1823) of mollusk were chosen from each station composites sample consisted of uniform sizes were dried by oven and ground to be ready for analysis.

2-3 PREPARING EXPERIMENTAL AND ANALYSES

DMA 80 has been examined in the Ministry of Commerce /General Company for Foodstuff Trading / quality control division was determined with Direct Mercury Analyzer (DMA-80). The instrumental operating parameters were listed in Table(1). Parameters such as flow rates, power, and integration times were recommended by the manufacturer. Before analysis of each sample, flush time was determined to ensure that the signal reached a steady state. This principle was used for all sample analyses. This typically contains an automatic sampler, quartz furnace, cobalt-manganese oxide catalyst, gold-coated

sand amalgamator and an atomic absorption detection cell with three different path lengths (120,165 and 4mm) according Ataro;*etal.*,2008; (Nascimento;*etal.*;2008).

Method for solid sample analysis consists of placing a known amount of milled sample in a nickel or quartz boat (Sample holder). The sample is introduced in the quartz furnace, where it is heated up to 200 °C (drying temperature) for 600 C-1000 C, Maximum temperature allowed by the software of equipment about 105 which set a limit Hg volatilization and reduction of O² Oxygen (99.99%) can be used as combustion and carrier gas. Mercury and combustion gases are flushed through the catalyst, where interferes like halogen compounds, nitrogen oxide and sulfur. Digestion of samples during method development was carried out under power control conditions by two microwave-assisted reaction systems Top wave Analytic Jena AG : MARS 5 (CEM Corporation, Matthews, NC, USA and MARS with Xpress Technology (CEM Corporation, Matthews, NC, USA). Sonication was performed with a Branson Ultrasonic Cleaner (Shelton, CT, USA).

Wavelength	Step	Time	CRM and SRM	Type
Plasma 15	170	16 min	TORT-2	Mollusk
Auxiliary 0.2	100	15 min	SRM-1974b	Mollusk
Nebulizer 0.8	100	10 min	0	Blank
Read delay 5	200	25 min	TORT-2	Water
Replicates 5	175-200	One time to each one	SRM-1974b	Water
Probe in sample (n)	100	10	0	Blank

Table (1): Parameter operating for the determination of Hg By DMA-80

2-4 STATISTICAL METHOD

The statistical analysis was performed according to the AOAC Protocol (Thompson, 2006) was assessed using different measures of statistical sigma plot and coefficient of determination, interclass correlation coefficient and concordance correlation coefficient, mean prediction error the concentration was the concentration of component standard method. The coefficient of determination, r^2 , was calculated where N is the total number of paired observations. A value of $r^2 = 1$ indicates 100% precision between the methods.

3- RESULTS AND DISCUSSION

3-1 GEOGRAPHIC INFORMATION SYSTEM (GIS) ARC 10 GIS ANALYSES

Depending on the latitude and longitude that have been taken by GPS/ Geko 201, It has been identified a graphical Map of the spatial analysis to all the variables of the study areas on the basis natural environmental and biological factors affected by the pollution of the aquatic system in the marshes.

Graphic images that were obtained considered the entrance of the variables as an indicate small spots distributed in the data, so it can be seen that the environmental indicators for the first level of pollution Water and then followed by biological levels of Mollusk, which have been Identified in a variety of influence factor, such as topography area and human activities. Through the process of spatial analysis and interpretation based on the ecological characteristics of mercury, most frequently used methods of GIS interpolation (Einax et al., 1997. Guney et al., 2010 . ESRI, 2012 , Ruimin Liu, 2016) . After checking authenticity sites and conformity with all input data it have been applied to obtain the highest level

of prediction in the food chain (Environmental and Biological) in study areas, the resulting contour general map in study areas are illustrated below Picture (1) .

3-2: MERCURY ANALYSES (Hg):

Mercury was detected in all analyzed samples. Results were discussed and compared with the data from their label and proposed guidelines published by (UNEP, 2003). Through the results that have been obtained there is a relationship between objects as an indicator environmental for mercury as follows

3-2-1: MERCURY IN WATER AND MOLLUSK

Related to change that occur in the environment from other organisms. Mollusks considered as a monitoring of aquatic ecosystems to determine pollution (Rocque, 2004). Mollusk is evidence bioindicator to assess the environmental characteristics most of its requirement of nutrients and the relationship between environmental factors (Alcamo, 1998, Favero, et al., 2003, Ajmi 2015, Ammann, 2002; Gaillardet et al., 2003; Wang and Liu, 2003; Zhang et al., 2008) .

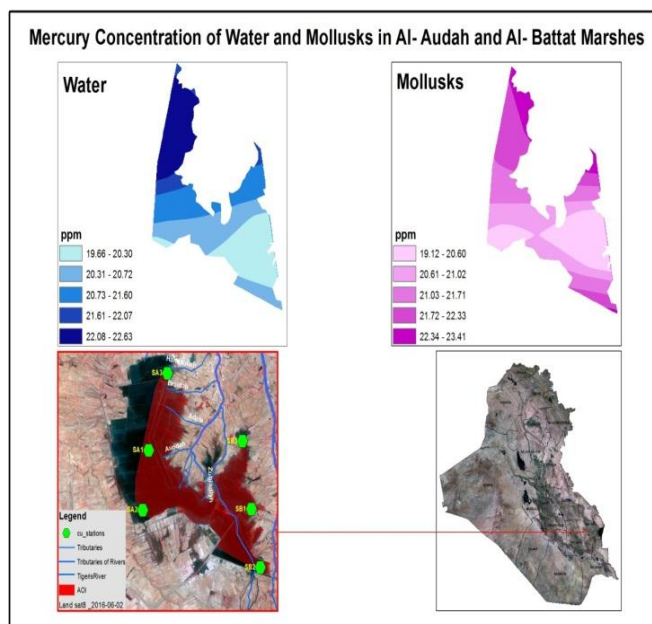
Results mercury in water and Mollusk (*Melanopsis nodosa*) it observed approximate or similarity to the extent of mercury concentration in water and organism as a monitoring of aquatic ecosystems to determine conformity with pollution (Rocque, 2004). Table (2) Showed concentration of mercury in Water and Mollusk under study area. There are no significant difference P-value (0.637, 0.568) in this element this agree with previous studies (Kannan & Falandysz 66) suggested a ratio of

Mercury concentration in mollusk could be used as an important case describing the pollution in water marshes. These conclusions were strongly agreed with same results from (Everaarts, et al., 1993, Ajmi 2015). The Mollusk important indicator for the water balance and the ability to adsorption the Mercury and accumulation this result applies with other researchers (Rama Krishnan, 2003).

Table (2) Approach1 , the concentration of mercury in Water and Mollusk under study area.

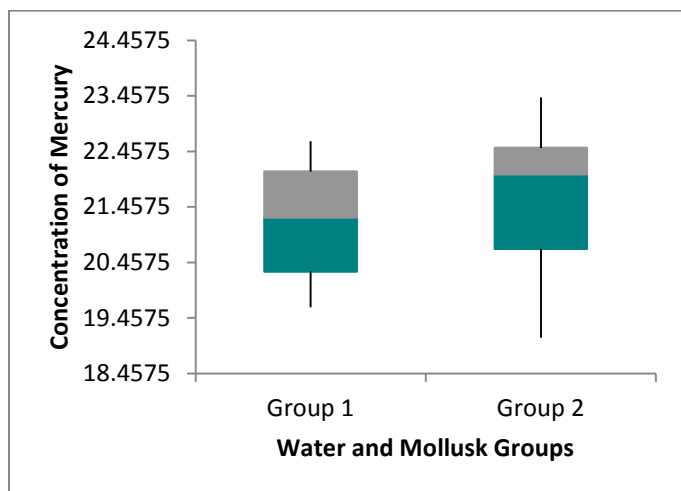
Study Areas	Samples ppm	
	Water	<i>Melanopsis nodosa</i>
1	22.64	21.64
2	20.21	20.39
3	22.00	22.45
4	19.65	19.1
5	20.54	22.54
6	22.12	23.43
Average	21.193	21.592
SD	1.21	1.59
P-Value	0.637	0.568

Spatial analysis and distributions Mercury by geographic information system (GIS) to verify mercury in two groups were selected for this study , Pic (2) following describes equal mercury concentration in two variables as complementary one to the other , Therefore , Water as a good indicator of Mercury contamination its content in bottom sediments, which can store large amounts of this metal as interactions with mollusk, an important factor for cleaner environment and be a site of its many conversions [25].



Picture (2) Approach 2 Spatial Analysis of mercury concentration in Water and Mollusk under study area.

Relatively similar results in respect to their concentration and accumulation between Water and Mollusk type in all station Fig (1) . These conclusions were strongly agreed with same findings (Everaarts, et al., 1993, Ajmi 2015). Mercury content of the mollusk may differ during the breeding seasons and at the periods of the year particularly during the winter dormancy. According to present experimental results, this concentration was positive regarding in the biogenic metals. This means that their ability as favorable biomonitors for levels Mercury. Seasonal variations of the metal concentration at a given site may often be due to seasonal changes of the organisms rather than to any variability of the absolute metal content of the organisms (Phillips and Russo,1978). The Mollusk important indicator for the water balance and the ability to adsorption the Mercury and accumulation this result applies with other researchers (Rama Krishnan, 2003).



Group1: Water , Group2: Mollusk *Melanopsis nodosa*

Figure (1) Approach 3 Showed demonstrates relationship for Water and Mollusk under study area

From analyses the significant relationship, it passes bioaccumulation of Mercury in the effective transfer bioaccumulation (Favero et al 2003, Ajmi, 2009). Obviously that through results of Mollusk to protect itself from high concentrations and toxicity of Mercury and reduce the rate of entry through the permeable surfaces of absorbents and the increase in the output of these metals ions mechanics of the most common (Roberson and Perkins, 1986., Masters and Gilbert, 1991) Depends engender elements in the conch shell on the age and life cycle (Favero et al 2003, Zauke, et al., 1998). There are many external factors that effect of mollusk and water such as organelle complex molecules and inorganic as well as chemiophysiological factors that control metabolism, such as heat, light, Oxygen and Nutrients (Scott, 1989 . Favero et al 2003). reflecting their high filter capacity, enhancing exposure to dissolved metals present in the water column (Mouneyrac et al., 1999; Ettajani et al., 2001; Tran et al., 2001).

3-2-1: BIOINDICATOR MERCURY IN FOOD CHAIN

Through the results of the Mercury concentration that have been obtained from analyzed samples were reached of the bioindication environmental and how to transition in ecosystem of the marshes. The mercury accumulation in aquatic food chains Increasing gradually in Water that means the accumulated element through weathering and shelf of the river practical source through the seasons of the year , because most of them on Mollusk, water, small hydro and benthic invertebrates feed on algae and debris. Thus, it accumulated through many trophic levels and transfers of mercury. Mercury accumulates in the organism when increase the absorption rate. Bioindicator of Mercury in water is decrease compared with the organic contents. This is consistent with (Wang et al. 2007) . Average Mercury in water of the surrounding environment would enhance the metabolism of the Mollusks would be more rapidly eliminated from balance biota. However, the aquatic Mercury could be transferred to food webs by type emergent in aquatic ecosystems according to (Cristol et al., 2008). Mercury ratio in Water and Mollusk ranged between (2% to 16%)(0% to 20%) , Respectively , this result consistent with previous studied (Jin et al., 2006; Houserová et al., 2007 ; Ecosystem Health, 2002) approach was based on climate the region , geology, Tigris and Euphrates rivers and downstream in addition to marshes geomorphology. A variety total of all types 1%, which is a very small percentage to take the plant this element and in aquatic ecosystem is adapted to the environment that's mean have tolerant species and distributed around region. From the results of this

study, we could conclude that Hg contamination in aquatic ecosystem environmental and biota factor as indicator in marshes under the study was not very significant.

3-DISSION AND RECOMMENDATION

Water and Mollusk considered a good environmental indicator used to boundaries with any changes of Iraqi marsh by periodically time to assess and determine the nature reserved of marshes Used spatial analysis by GIS system to combine multiple datasets to get standardized information have been integrated of quantitative computing and qualitative analysis has enhanced the easy and credibility of the elements bioindicator models to describe the general environmental properties and has been applied in the management of Iraqi aquatic systems. The values for the mercury equivalent activity in water sample found to be within the world average allowed the maximum value of average and significant P-value <0.05 . From data obtained standards, there was an affected that depends on the type of radiation produced by representing half-life of radioactive radiation due the disintegration of the alpha radiation resulting from wars, explosives or weapons ashes and this is an internal source , especially for most aquatic ecosystems components organisms and transmission to humans by aquatic food chain and Used spatial analysis by GIS system to combine multiple datasets to get standardized information have been integrated of quantitative computing and qualitative analysis has enhanced the easy and credibility of the elements bioindicator models to describe the general

environmental properties and has been applied in the management of Iraqi aquatic systems. Identified by using standard analytical methods DMA 80a as a newly, easy and fast technique to find Mercury Hg (ppm) concentrations , It was within the allowable standard limits in all Samples. *Melanopsis nodosa* has a mechanism to safety from the high effects of mercury concentrations with water this processes as a balanced indicates of ecological in the aquatic ecosystem thus , we strongly support the more intensive sampling to represent the spatial distribution the risks of mercury in all Iraqi marshes areas to get a whole integrated database and focus on working spatial information about the idea of the relative risk between variables in environmental and biological factors in the food chain by other new technologies such as Telescope and Remote Sensing thats give us Government oversight to control external and internal pollution source and abilities indicator and monitor pollution to prevent potential health risks.

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