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## Evaluation of Residual Amounts of Persistent Organic Pollutants and Traces of Heavy Metals in King Talal Dam.

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**ABSTRACT**

In this study, concentrations of different persistent organic pollutants(POP's) and heavy metals in samples from King Talal Dam (KTD) were investigated. The levels of PAH's were in the range from below the detection limit of 1 ng/l to 120 ng/L for water samples and from below the detection limit of <1 mg/kg to 23 mg/kg(dry weight) for sediment samples. From the 15 chlorinated pesticides studied in this work, Alpha and Gamma hexachlorocyclohexanes (α-, γ- HCH) were frequently detected in water samples with an average concentrations of 3.2 and 8.1 ng/L, respectively. However, in fish and sediment, DDT and its metabolites were the most frequently detected pesticides. DDT was found in livers of the catfish samples in the range of 0.1 to 2.4 mg/kg with a mean value of 0.53 mg/kg . In sediment samples DDT, DDD and linadne (γ-HCH) pesticides were found at an average concentrations of 37.8, 6.3 and 45 ng/g , respectively. In the acidic fraction of water, the parent compound (phenol) was the most frequently detected species, and it has the highest concentration with an average of 17 μg/L and a range of 4 to 28 μg/L. The levels of 10 metals analyzed in surface water of KTD were below the accepted levels of irrigation water standards. However, elevated concentrations of toxic lead (Pb) with mean values of 9.6 and 3.2 mg/kg were found in livers and muscles of catfish, respectively.
**Keywords:** King Talal Dam, Heavy metals, POP's, Water pollution

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# INTRODUCTION

The levels and numbers of potentially hazardous chemical pollutants that can reach the aquatic environment are continuously increasing because of the rapid development of industry and high population growth along with the lack of appropriate wastewater treatments. New chemical substances (pollutants) are also regularly being synthesized and released into environment. Water pollution is one of the main consequences and one of the most important environmental concerns. Contaminants can have different chemical characteristics and can be classified into organic, inorganic and metal contaminants. Organic pollutants in the environment are released into various environmental compartments mainly from anthropogenic sources due to various human activities [1], both domestic originating from households, such as sterols, endocrine disrupting chemicals (EDCs), pharmaceuticals and personal care products and industrial such as polychlorobiphenyls (PCB's), pesticides, poly aromatic hydrocarbons(PAH) and combustion by-products including dioxins.

The presence of some pollutants such as sterols ,caffeine , L-menthol, bisphenol A and nonylphenol at elevated concentrations in the aquatic environments refers to the pollution by domestic wastewater[2]. On the other hand, the persistent organic pollutants (POP's) are widespread contaminants throughout the environment, they have good ability for long-distance transfer. Therefore, POP's could be accumulated in regions far away from their original sources [3]. POPs encompass many different and varied groups of man-made chemicals such as poly aromatic hydrocarbons(PAH's ), organochlorine pesticides(OCP's), dioxins and polychlorobiphenyls( PCB's).

Polycyclic aromatic hydrocarbons (PAHs) are mainly produced by processes involving incomplete combustion of fossil fuel and other organic materials, they enter the aquatic environment via wet and dry atmospheric deposition, urban runoff, municipal and industrial effluents and oil spillage [4]. Carcinogenic character of several compounds of these PAHs place them on the list of priority contaminants that must be environmentally monitored [5]. Polychlorobiphenyls( PCB's) are produced as industrial chemicals that are mainly used for insulation in electrical equipments ( dielectric fluid in capacitors and transformers)[6]. They are also produced as by-products of combustion of chlorine containing substances. Organo-chlorine pesticides (OCP's) such as DDT, HCH , aldrin and dieldrin are used mainly in agricultural activities. Because of their toxicity and persistence, PAHs , PCBs and OCP's are hazardous to ecosystems. Though their use in industry is prohibited, they still occur in the environment.

Other than organic pollutants, some heavy metals such as mercury(Hg), cadmium( Cd ) and lead(Pb) are of great concern because they have some toxic properties. For instance, mercury and lead have adverse and harmful effects on health; cadmium accumulation may cause damages to bones and reproductive system, lung disease and kidney dysfunction [7]. Mercury compounds may cause the damage to developing fetuses [8]. Lead exposure is linked to renal failure, liver damage and premature births in humans; it is also associated with the reduced cognitive development in children [9]. The individual exposure to very low levels of toxic metals through drinking water is not likely to cause acute harm effect. However, the chronic and prolonged exposure and the buildup of toxic metals in human body may increase the risk of serious health problems. For this reason several studies have been conducted on the evaluation of levels of toxic elements in various food stuff [10-12].

The King Talal Dam (KTD) is the largest surface reservoir in Jordan, it has a gross capacity of 86 million cubic meter($m^3$).The main purpose of this reservoir is to supply agricultural irrigation water to the Jordan Valley. KTD receives water mainly from Zarqa river which is heavily polluted by the discharging of industrial and domestic wastewater. .In this work both organic contaminants and metal contents of various environmental samples from King Talal Dam (KTD) were analyzed and compared with the international standards.

## MATERIALS AND METHODS

### Sampling

Water, fish and sediment samples were collected during the period of April to August 2013, from different sites along the King Talal Dam(KTD) .Water samples for metal analysis were collected from surface water (0-0.5 m) in previously acid-washed 2L-Teflon bottles, samples were filtered through 0.45 µm membrane filter, and the filtrates were acidified with 1% nitric acid. For organic analysis, Water samples were collected from surface water (0-0.5 m) in dark-brown glass bottles( amber) and preserved with 10 ml of dichloromethane(DCM).

Fish samples were captured and brought to the laboratory on ice-box, the weight and sizes were measured before the edible muscle and some liver samples were obtained from the fish, about 10-15 g were obtained from muscle tissues. Samples were stored in freezer at -18 °C before used for analysis.

Surface sediment samples were collected by SCUBA divers from the upper layer of the sediment (0–5 cm) using cylindrical plastic tubes, after drying; samples were sieved through 63um sieve and preserved in freezer until analysis.

### Analytical method for Metal Analysis

The pH values of the water filtrate samples were adjusted to ~6 by adding 30-50 ml of ammonium acetate buffer. Various elements were pre-concentrated by passing the filtrate through a column of Chelex-100 at a flow rate of approx 1ml/min, after column washing, metals were eluted with a minimum amount of $HNO_3$ so that the concentration factor was more than 100 times. For analysis of metals in fish, the homogenized tissue samples (1 g to 3 g wet sample) were digested in 200 ml glass beakers with 20 ml of a mixture of freshly prepared solution of (1:1) (v/v) $HNO_3$ (65%) – $H_2O_2$ (30%). Each beaker was covered with a watch glass and stored at room temperature for 24 hours. The samples were then heated on hot plate at 150-165°C, aliquots of nitric acid were added until the solutions were clear. Solutions were contentiously boiled until the volume for each sample reduced to about 5 ml. The solutions were then allowed to cool, filtered (glass wool), and diluted up to 50 ml with acidified ($HNO_3$) deionised water, and then placed in acid washed 60mL polyethylene bottles. A blank digest was carried out in the same way.

All digested samples ( water and fish) were analyzed, in triplicate, for Zn, Mn, Pb, Cu, Co, Cr, Fe, Ni and Cd contents using Inductively Coupled Plasma Optical atomic Emission Spectrometry (ICP-OES)(VISTA–MPX instrument[®]). The simultaneous ICP-OES was equipped with axial vision, a radio frequency (RF) source of 30 MHz, a CCD (Charge Coupled Device), a peristaltic pump, and a Glass concentric nebulizer. Multielement standard calibration of mixed elements at concentration of 1000 mg $L^{-1}$ was used. The multielement standard solution was appropriately diluted and used to calibrate the ICP-OES before metal determination.

For mercury determinations, the mercury analyzer Hydra C[®] was used. Samples were analyzed based on the principle of thermal decomposition, amalgamation and atomic absorption spectrophotometry detection.

### Analytical Method for Organic Analysis

Water samples collected for organic analysis were divided for the screening of organic pollutants and for the analysis of acid and base-neutral organics. In the screening method the water sample was directly extracted 3-times with dichloromethane( DCM) , and the extracts were combined and reduced to about 1ml.

For the analysis of semi-volatile organic acids and bases, the method EPA -625 was adopted [13]. A flow chart showing the summary of the method is presented in Figure 1.

For the analysis of residual organics in fish and sediments samples, a known weight of the sample was taken exactly( about 1 g sediment or fish muscle), the sample was mixed with anhydrous sodium sulfate ( $Na_2SO_4$) to make a dry paste. The paste was then extracted 3-times with acetone. The combined extracts were reduced to about 1-3 ml and cleaned up by passing through a small column of activated silica gel. Organics

were eluted from the column with dichloromethane and hexane solvents. The eluted portions were evaporated to 3-5 ml and under a stream of pure nitrogen the samples were reduced to 1ml. The samples caped in a vials and kept in freezer for the GC-injection. The GC-MS instrumentation consisted of Shimadzu QP-2010 series, the quadruple mass spectrometer operated in electron ionization mode and the separation was performed using a fused silica column HP-5MS( 30 m × 0.25mm × 0.25 µm). A single ion monitoring mode(SIM) was used for quantitative analysis, injections of 1µl sample volumes were carried out using split-splittles mode. Individual standards of a mixture of polyaromatic hydrocarbons(PAH's), organochlorine pesticides(OCP's), phenols and deuteriated compounds were obtained from Supelco and used for the calibration of GC-MS.
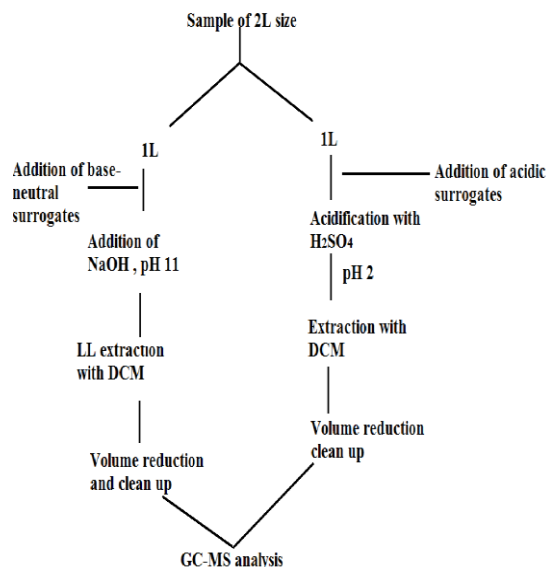
Figure 1: A flow chart for the analysis of acidic and basic organics from water

**Methods validation**

The accuracy of the analytical method for metal analysis in water was verified by the analysis of spiked deionized water(DI) samples; exactly 1L of DI water sample was spiked with known concentrations of multi-element standard and analyzed through the whole procedure. On average, the percentage recovery was above 97%. The results are shown in Table 1. In addition, the standard reference material (DORM-2, Dogfish muscle) obtained from National Research Council (NRC) Canada was used for the verification of selected metal analysis in fish muscle. The results are shown in Table 2.

The analytical method for the analysis of semi-volatile organic acids and bases was verified by the analysis of spiked samples with 2-flurophenol for the acidic part and deuteriated "benzo(a)anthracene"-$_{d12}$ for the base-neutrals fraction. The mean percentage recovery was above 91%. The results are shown in Table 3.

Table 1: Percentage recovery of spiked trace elements concentrations in water samples

| Element | Added amount µg/L | Found µg/L | % Recovery |
|---------|-------------------|------------|------------|
| Zn | 0.1 | 0.105 | 105 |
| Mn | 0.05 | 0.043 | 86 |
| Pb | 0.05 | 0.051 | 102 |
| Cu | 0.05 | 0.05 | 100 |
| Co | 0.05 | 0.046 | 92 |
| Cr | 0.05 | 0.045 | 90 |
| Fe | 0.1 | 0.093 | 93 |
| Ni | 0.1 | 0.102 | 102 |
| Cd | 0.1 | 0.089 | 89 |

**Table 2: Trace elements concentrations in certified reference material (DORM-2, Dogfish muscle)**

| Element | Certified values(ug/g) | Measured values(ug/g) | Recovery (%) |
|---------|------------------------|------------------------|--------------|
| Cd | 0.043 | 0.040 | 93 |
| Pb | 0.065 | 0.061 | 94 |
| Zn | 25.6 | 26.1 | 102 |
| Ni | 19.4 | 18.8 | 97 |
| Mn | 3.66 | 3.4 | 93 |
| Cu | 2.34 | 2.17 | 93 |
| Co | 0.18 | 0.17 | 94 |
| Cr | 34.7 | 35.62 | 103 |
| Fe | 142 | 148 | 104 |
| Hg* | 4.64 | 4.60 | 99 |

\* analyzed by Hydra-C mercury analyzer

**Table 3:The range of percentage recovery of spiked flourophenol and deuteriated "benzo(a)anthracene"-$_{d12}$ in the analysis of organic pollutants.**

| Spiked compound | Spiking level µg/L | Determined level µg/L | Range of % recovery |
|-----------------|--------------------|-----------------------|---------------------|
| 2-Fluoro-phenol | 3 | 2.55-2.89 | 85- 96 |
| Benzo(a)anthracene-$_{d12}$ | 5 | 4-4.7 | 80-94 |

## RESULTS AND DISCUSSION

The range of pH values for the KTD surface water samples was between 7.70 and 8.20 with an overall mean value of 7.88 while the mean temperature of the surface water samples ranged between 16.50 and 24.90 °C with an overall mean value of 21.80 °C.

The total content of selected compounds of PAHs in water and sediment samples from the KTD are presented in Table 4. The levels of PAH's were in the range from below the detection limit of 1 ng/l to 120 ng/L for water samples and from below the detection limit of <1 mg/kg to 23 mg/kg(dry weight) for sediment samples. The highest level was found for naphthalene followed by Phenanthrene and pyrene. In other related works, the total PAH concentration level of 1.5 ug/L in the wastewaters from the Montreal urban community (Canada) was determined[14]. The mean of total content of PAH compounds in surface water and sediment from the Odra river( China) were 393.3 ng/L and 18.5 mg/kg, respectively[15]. In a recent study, 6 compounds of PAH were detected in KTD in the range of 3-35ng/L[16]. The previously mentioned results were in good agreements with the results of this work. However, higher levels of PAH were detected in other studies. For instance, concentration of PAHs varies from 944.03 to 6654.6 ng/l with a mean of 4123.8 ng/l in the Macao water column of the Pearl River ( China)[17] . Fluoranthene was also determined in the raw wastewaters at an average concentration of 77.4 ng/l with a range of 0.2 to 400 ng/L[18]. Indeed, the concentrations of PAHs in sediment samples in this work were much higher than that of water samples , this is because of the high adsorption affinity of PAHS to particulate materials. By inspection of the concentration levels of all the PAHs in the KTD water samples, it is clear that all the samples contents were below the recommendation or the accepted levels of the international standards for the irrigation water.

The concentrations of chlorinated pesticides in water , fish and sediment of KTD are presented in Table 5. In water samples, Alpha and Gamma hexachlorocyclohexanes (α-, γ- HCH) were frequently detected with an average concentrations of 3.2 and 8.1 ng/L, respectively. The concentration range of α-HCH was 1- 9 ng/L, and that of γ-HCH was 1-24 ng/L. Endosulfan was found at very low concentrations in the range of below detection limit(<0.01) to 0.05 ng/L with a mean value of 0.02 ng/L. All other chlorinated pesticides examined were below the detection limits. In fish and sediment samples, DDT and its metabolites were the most frequently detected pesticides. DDT was found in livers of the catfish samples in the range of 0.1 to 2.4 mg/kg with a mean value of 0.53 mg/kg. In sediment samples DDT, DDD and linadne (γ-HCH) pesticides were found at an average concentrations of 37.8, 6.3 and 45 ng/g , respectively. This result indicates a biomagnifications of DDT in fish which is in good agreements with previous results[19, 20]. Few studies on residues of chlorinated pesticides in agricultural soil from different locations in Jordan reveals the use of these pesticides in agricultural activities[21,22]. The Agricultural runoff is a major source of DDT input into aquatic systems.

Eleven compounds of phenol and chlorinated phenols were analyzed in surface water of KTD. The results of analysis expressed in µg/L are presented in Table 6. The parent compound (phenol) was the most frequently detected species , and it has the highest concentration with an average of 17 µg/L and a range of 4 to 28 µg/L. Mono- and dichloro-phenols were determined at levels of 3 and 11 µg/L, repsecively. However , other poly chlorinated phenols such as trichloro- and pentachloro- phenols were not detected. Similar results has been established by a recent study [16]. Phenolic compounds may be discharged from various industrial activities involved and located in the catchment area of the KTD.

The chromatographic screening of various organic pollutants in surface water of KTD is shown in Figure 2. The analysis showed that more than 50 organic compounds were detected, these compounds belong to different classes. The most frequently detected compounds were alkylphenol ethoxylate (nonionic surfactant), cholesterol, alkyl benzene sulfonates, phtalate esters(diethyl phthalate, diethylhexyl phthalate) , bisphenol A, caffeine, benzophenone, chlorpyrifos( insecticide),2 -methylnaphthalenediphenylamine, alkyl benzene, nonylphenol, various alkanes and cyclo alkanes. Most of these pollutants were previously detected in various types of surface water especially the untreated wastewater [23- 25].

**Table 4: The mean concentrations of polyaromatic hydrocarbons in water and sediments of KTD .**

| Compound | Water ng/L | Sediment mg/kg |
|---|---|---|
| Naphthalene | 120 | 23 |
| Acenaphthylene | 11 | 4 |
| Fluorene | nd | nd |
| Phenanthrene | 19 | 11.8 |
| Anthracene | 6 | 8.6 |
| Fluoranthene | 11.9 | 4.68 |
| Pyrene | 16 | 5.81 |
| Benzo(a)anthracene | 3 | 2.6 |
| Chrysene | nd | nd |
| Benzo(b)fluoranthene | nd | nd |
| Benzo(k)fluoranthene | nd | nd |
| Benzo(a)pyrene | 0.8 | 1.0 |
| Indeno(1,2,3)pyrene | nd | nd |
| Dibenzo(a,h) anthracene | nd | nd |
| Benzo(g,h,i) perylene | 1.3 | 1.9 |

**Table 5:The mean concentrations of chlorinated pesticides in KTD samples.**

| Pesticide | Water ng/L | Fish liver mg/kg | Sediment ng/g (dry) |
|---|---|---|---|
| α-HCH | 3.2 | nd | nd |
| β-HCH | nd | nd | nd |
| γ-HCH | 8.1 | nd | 45 |
| δ-HCH | nd | nd | nd |
| ΣDDE | nd | nd | nd |
| ΣDDD | nd | nd | 6.3 |
| ΣDDT | nd | 0.59 | 37.8 |
| Heptachlor | nd | nd | nd |
| Aldrin | nd | nd | nd |
| Dieldrin | nd | 0.063 | nd |
| Endrin | nd | nd | nd |
| Endosulfan I | 0.02 | nd | nd |
| Endosulfan sulfate | nd | nd | nd |
| Endrin aldehyde | nd | nd | nd |
| Heptachlor epoxide | nd | nd | nd |

nd: not detected

**Table 6: The mean concentrations of phenolic compounds in KTD surface water.**

| Compound | Concentration in water ug/L |
|---|---|
| Phenol | 17 |
| 2-chlorophenol | 3 |
| 2-nitrophenol | nd |
| **2**,4-dimethyl phenol | nd |
| 2-mthyl-4,6-dinitrophenol | nd |
| 2,4-dinitrol phenol | nd |
| 4-chloro-3-methyl phenol | nd |
| 4-nitrophenol | 8 |
| 2,4-dichloro phenol | 11 |
| 2,4,6-trichloro phenol | nd |
| Pentachloro phenol | nd |

nd: Not detected

**Table 7: Metal contents of water and fish samples from KTD**

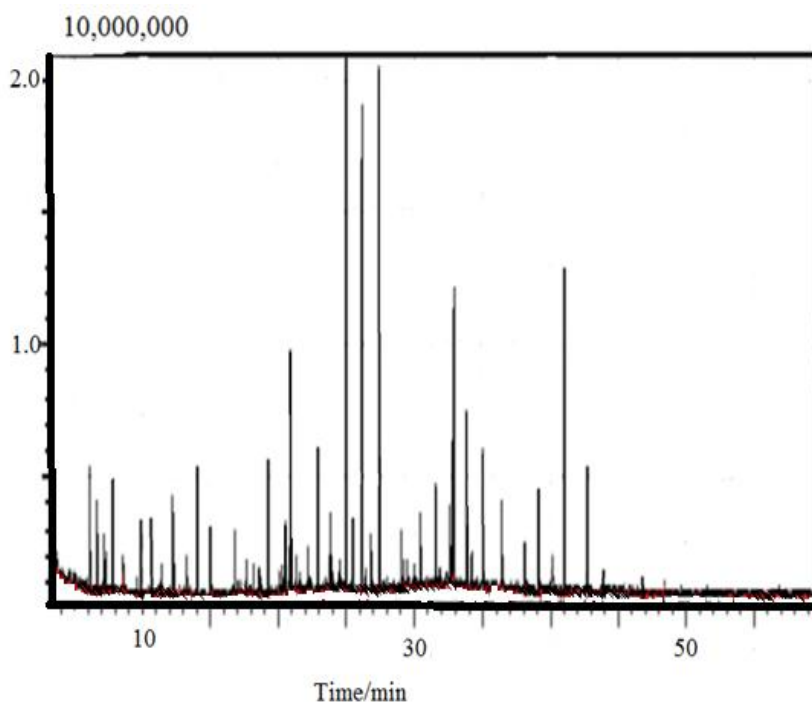| Sample | Zn | Mn | Pb | Cu | Co | Cr | Fe | Ni | Cd | Hg |
|---|---|---|---|---|---|---|---|---|---|---|
| Water, µg/L | 0.028 | 0.008 | 0.043 | 0.003 | 0.007 | nd | 0.063 | 0.007 | 0.003 | 0.004 |
| Catfish liver, mg/kg | 28.6 | 0.61 | 3.1 | 36.2 | 0.17 | 0.04 | 334.6 | 0.19 | 0.23 | 0.48 |
| Catfish muscle, mg/kg | 6.28 | 0.084 | 9.6 | 0.03 | 0.01 | 0.67 | 12.3 | 0.24 | 0.11 | 0.51 |

nd: not detected(below 0.001)



**Figure 2:  Scanning chromatogram by (GC/MS) for water sample collected from KTD.**

Metals are naturally present in the aquatic environmental. However,  a number of anthropogenic activities contribute to increase their levels. Metals are environmentally persistent, non-biodegradable and can bio-accumulate in plants and animals [26]. The levels of 10 metals in surface water and fish of KTD are presented in Table 7. The levels of these elements in surface water were below the accepted levels of irrigated water standards. However, elevated concentrations of toxic lead with mean values of 9.6 and 3.2 mg/kg were found in livers and muscles of catfish, respectively. Mercury in fish was found at concentrations closed to the maximum allowable levels of 0.5mg/kg set by WHO. The levels of various metals in KTD samples were similar to other related studies [25, 27, 28].

## CONCLUSION

The data obtained from the analysis of water samples show that the water pollution of KTD with chlorinated pesticides, polyaromatic hydrocarbons and heavy metals is insignificant. However, the presence of various components of phenols refers to contamination with industrial wastewater. Indeed, the presence of trace amounts of pesticides refers to agricultural activities located in the catchment area of the KTD. The pollution of KTD with untreated domestic wastewater is confirmed by detection of some species such as cholesterols, nonyl-phenol and caffeine.

The overall results indicate that the KTD is not heavily contaminated. However, various environmental samples of KTD must be monitored frequently for their contents of POP's and toxic metals especially Pb, Hg and Cd.

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