

Investigation of heavy metals pollution in water, sediment and fish tissues at Upper Egypt

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Abstract: The present study was aimed to investigate heavy metals pollution in water, sediment and fish tissues at different sites of water (Elhawaweesh, Elahaywa, Dar-Elsalam, Belsofora and Elnemsawy) at two seasons autumn and spring. Heavy metal residues (zinc, copper, lead, manganese and iron) were determined in water, sediment and fish. The study revealed that concentration of Fe, Pb and Mn in water was higher than the permissible limit of WHO, EPA, EC and USEPA except Cu and Zn. It is the same for fish tissue. The levels of all the metals in the sediment were found to be higher than the values in water and fish. This affirmation with most of the research findings of other workers that sediments usually serve as sink for heavy metals. However the average heavy metal concentrations in sediment samples were below the permissible limits (except Mn) compared to the permissible limit. This study discovers seasonal variation in metal accumulations.

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1. Introduction:

Aquatic ecosystem is the ultimate recipient of almost everything including heavy metals. This has long been recognized as a serious pollution problem (Farombi *et al.*, 2007). There are various sources of heavy metals in this ecosystem such as anthropogenic activities like draining of sewage, dumping of domestic wastes and recreational activities. It may also occur in small amounts naturally through the leaching of rocks, airborne dust, forest fires and vegetation (Özmen *et al.*, 2004).

The pollution of aquatic ecosystems by heavy metals is an important environmental problem, as heavy metals constitute some of the most hazardous substances that can bioaccumulate in various biotic systems. Bioaccumulation is a process in which a chemical pollutant enters into the body of an organism and is not excreted, but accumulated in the organism's tissues. Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage, while also posing a threat to human health. Cancer and damage of the nervous system have been documented in humans as a result of metal consumption. The U. S. Environmental Protection Agency conducted a national study of accumulated toxins documenting this concern (Van den Broek *et al.*, 2002).

The heavy metal pollution of aquatic ecosystems is often most obvious in sediments, macrophytes and aquatic animals, than in elevated concentrations in water (Linnik and Zubenko, 2000). Therefore aquatic ecosystems are typically monitored for pollution of heavy metals using biological assays (Wong and Dixon, 1995). Many aquatic organisms have been

used as bioindicators, including aquatic insects (Rayms-Keller *et al.*, 1998), plants (Mohan and Hosetti, 1999), protozoans (Fernandez-Leborans and Olalla-Herrero, 2000), crustaceans (Allinson *et al.*, 2000) and fish (Burger *et al.*, 2002).

Fish is considered as one of the most significant indicators of metal pollution in aquatic environment (Rashed, 2001). Fish may absorb dissolved elements and heavy metals from surrounding water and food. When fish are exposed to heavy metals in an aquatic ecosystem, they tend to take these metals up which may accumulate in various tissues in significant amounts and are eliciting toxicological effects at critical targets (Seymore, 1994). Some edible species of fish have been widely investigated for those hazardous effects of heavy metals on human health (Begum *et al.*, 2009).

Sediments are important sinks for heavy metals in aquatic ecosystem. These metals are non-biodegradable and once discharged into water bodies, they can either be adsorbed on sediment particles or accumulated in aquatic organisms. Heavy metal pollution may increase the susceptibility of aquatic animals to various diseases by interfering with the normal functioning of their immune, reproductive and developmental processes (EPA, 2010).

Heavy metals could be found in water at the trace levels. Nonetheless, these constituents are very toxic and tend to accumulate in a long period of time. Heavy metals such as Pb, Cd and Cr are micro-pollutants and of special interest as they have both health and environmental significance due to their persistence, high toxic and bio-accumulation characteristics in water (WHO, 2008). Heavy metals in human body

can affect his health, hence the need to know the concentration of heavy metals in water, sediment and selected fishes in Upper Egypt reservoir because of its daily usage by man and proximity to urban pollution.

The present study is aimed assessment of heavy metals (Iron (Fe), Copper (Cu), Zinc (Zn), Lead (Pb), and Manganese (Mn)) in water, sediment, herbs and fish tissues from different sites, Upper Egypt using atomic absorption spectrometer.

2. Materials and methods:

Collection of fish, water, herbs and sediment samples:

The samples were collected at two different seasons (autumn and spring) at Elhawaweesh, Elahaywa, Dar-Elsalam, Pelsofora and Elnemsawy, Sohag, Upper Egypt. The fish and sediment samples were collected and kept in plastic bags. The water samples collected and kept in 500 ml sterile plastic containers and it were treated with 1 ml of HNO₃ in 500 ml sample to arrest microbial activities.

Determination of heavy metals in water, sediment and fish:

Digestion of the samples:

Water:

Two hundred and fifty ml of well-mixed water samples were transferred to beakers. Five milliliters of HNO₃ were added in each sample. Then, samples were allowed to reach 80-85° C using hot plates to a final volume of about 10-20 ml before metal precipitation. The digestion procedure was repeated twice. The beaker walls were washed with metal free water and then rinse water was filtered. The filtrate was then transferred to 25 ml volumetric flask (with addition of water) for end determination (APHA, 1998).

Sediment:

One gram of well-mixed sediment samples was transferred to the digestion tube. Ten milliliters of (HNO₃-HCL) (1:3v/v) were added in each sample. Then, samples were heated to reach 90-95°C using heating mantle for one hour. The sample was cooled to room temperature. The content of each digestion tube were filtered through separated acid prewashed filter paper. The digestion tube walls were washed with metal free water and then rinse water was filtered. The filtrate was then transferred to 25 ml volumetric flask (with addition of water) for end determination.

Fish:

One gram of tissue samples was transferred to a clean screw capped glass bottle and digested with 10 ml of digestion solution HNO₃-HClO₄ (4:1v/v) (FAO, 1983). Initial digestion was conducted for 4 hours at room temperature, followed by heating at 40-45° C for one hour in water bath, and then raised to 75°C until the end of digestion. After cooling at room

temperature, the digest was diluted to 25 ml with deionized water and filtered through 0.45 μm whatman filter paper in 25 ml volumetric flask for end determination.

Blank solution:

The same volume of acid, aqua regia and digestion solution, which used in the digestion of water, sediment and fish samples were subjected to the same digestion, dilution and filtration procedures as previously described in the preparation of water, sediment, aquatic weeds and fish samples to detect any possible traces of the studies metals in the acids or.

Quantitative determination of heavy metals:

Quantitative determination of lead, manganese, zinc, copper and iron was conducted by using atomic absorption spectrometer. Thermo atomic absorption spectrometer with hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air-acetylene flame. Recoveries were carried out by the addition of the standards of each element at different levels. All data were corrected according to the recovery percentage values. Blanks were included in each batch of analysis.

Calibration standards were regularly performed to evaluate the accuracy of the analytical method. Working calibration standards of zinc (Zn), iron (Fe), copper (Cu), manganese (Mn) and lead (Pb) were prepared by serial dilution of concentrated stock solution (Merck, Germany) of 1mg/ml. The blank solutions were also analyzed in the same way as for the digested samples.

The limit of quantification for each targeted heavy metal is set at 0.05 ppm.

3. Results:

Results of water analysis:

The comparative study of the heavy metals concentrations from different sites at two seasons were illustrated at table (1) and figure (1). The results showed seasonal variations in heavy metal levels in water samples. The concentrations had the descending order: Fe > Zn > Pb > Mn > Cu.

Results of sediment analysis:

The comparative study of the heavy metals concentrations from different sites at two seasons were illustrated at table (2) and figure (2). The results showed seasonal variations in heavy metal levels in sediment samples. The concentrations had the descending order: Fe > Mn > Zn > Cu > Pb.

Results of fish analysis:

The comparative study of the heavy metals concentrations in fish samples from different sites at two seasons were illustrated at table (3) and figure (3). The results showed seasonal variations in heavy metal

levels in sediment samples. The concentrations had the descending order: Fe > Zn > Pb > Mn > Cu.

Table 1: Heavy metals concentrations ppm (mean ± SE) of water samples collected from different sites at autumn and spring. (n= 5).

sites	Elhawaweesh		Elahaywa		Dar-Elsalam		Pelsofora		Elnemsawy		W.H.O. (mg/l) PL
	Aut.	Spr.	Aut.	Spr.	Aut.	Spr.	Aut.	Spr.	Aut.	Spr.	
Fe	24.56±1.9	13.14±2.1**	22.74±2.1	12.4±1.2**	19.58±1.3	10.23±0.9***	8.49±1.1	5.03±0.21**	7.42±0.7	4.65±0.34**	1-3
Zn	1.67±0.14	0.82±0.07***	5.51±0.42	3.7±0.29**	5.41±0.38	3.24±0.34**	4.04±0.41	2.39±0.2**	3.28±0.41	1.37±0.23**	10-75
Pb	0.92±0.1	0.61±0.07*	0.7±0.08	0.48±0.05*	0.29±0.06	0.09±0.01	0.17±0.04	0.068±0.031	0.09±0.02	0.04±0.007	0.1-0.2
Mn	0.27±0.02	0.18±0.01	0.06±0.05	0.02±0.003	0.56±0.047	Nd	0.1±0.01	Nd	Nd	Nd	0.05
Cu	0.18±0.02	0.05±0.01	0.09±0.004	Nd	0.08±0.1	Nd	Nd	Nd	Nd	Nd	1-3

*significance p<0.01 **high significance p<0.05 ***very high significance p<0.001
 Nd (not detected) LOD (0.017)

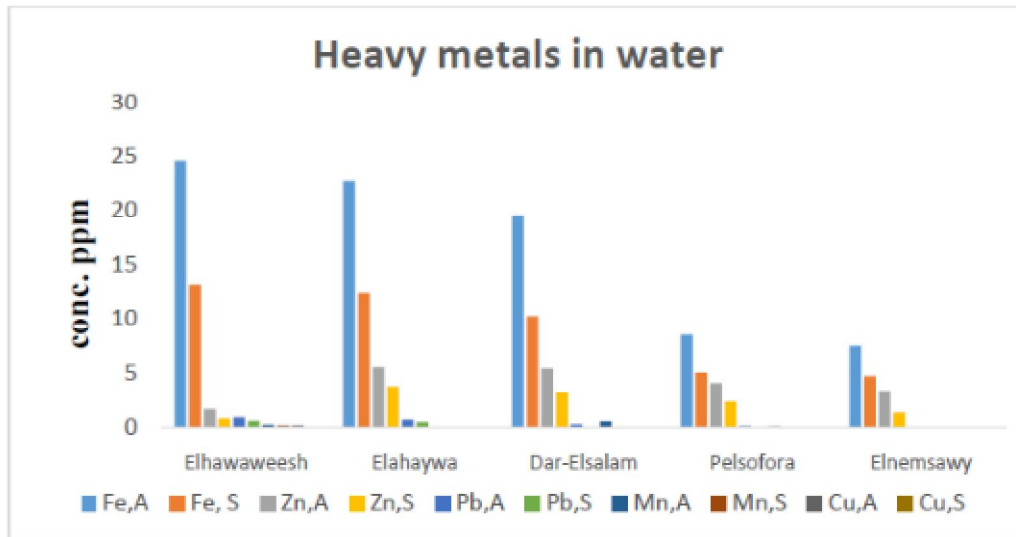


Fig. 1: Heavy metals concentrations (mean ± SE) of water samples (µg/ml) collected from different sites at autumn and spring. (n= 5).

Table 2: Heavy metals concentrations ppm (mean±SE) of sediment samples collected from different sites at autumn and spring (n=5):

sites	Elhawaweesh		Elahaywa		Dar-Elsalam		Pelsofora		Elnemsawy		USEPA allowable limits mg/kg
	Spr.	Aut.	Spr.	Aut.	Spr.	Aut.	Spr.	Aut.	Spr.	Aut.	
Fe	5230.8±126.8	5103.37±107.6	5230.76±117.45	5064.26±118.6	5280.82±78.92	5156.23±104.18	4969.2±97.7	4809.4±86.99	4314.97±112.6	4025.6±120.05	
Zn	49.21±3.23	42.11±2.83	39.2±2.37	37.4±2.62	42.73±3.28	40.18±2.38	39.14±1.57	36.52±2.28	41.15±2.68	33.44±1.91*	7500
Pb	1.66±0.09	0.344±0.03***	8.51±0.82	5.7±0.49**	2.41±0.18	0.324±0.14***	5.04±0.62	3.19±0.14**	3.28±0.41	2.37±0.23*	420
Mn	638.81±32.1	552.21±21.12*	598.42±23.4	485.74±17.4**	538.9±21.71	433.18±10.84**	334.21±32.42	238.24±16.22*	331.6±21.61	213.66±15.25***	230
Cu	32.9±2.06	28.1±1.17*	26.37±1.72	24.53±1.06	33.46±2.11	30.17±2.55	25.31±2.12	20.62±0.84*	23.14±1.81	17.78±0.91*	4300

*significance p<0.01 **high significance p<0.05

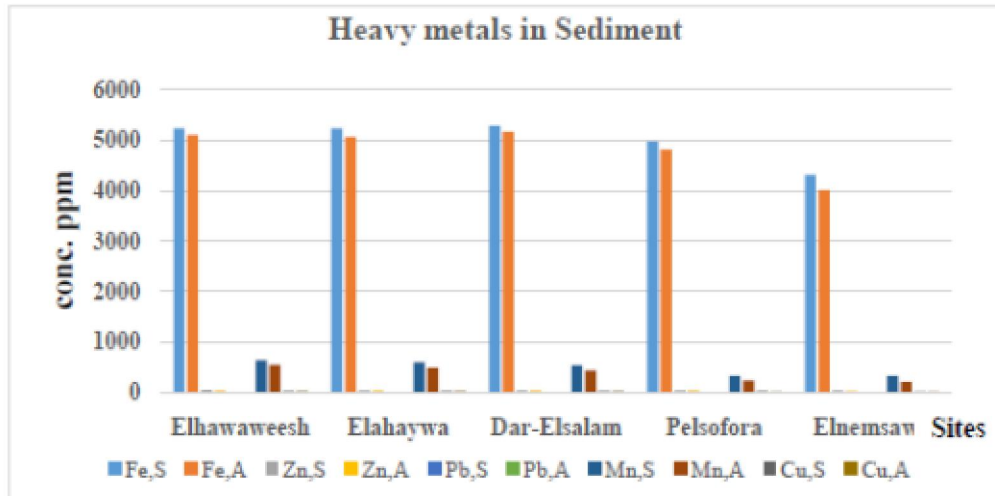


Fig. 2: Heavy metals concentrations of sediments samples collected from different sites at autumn and spring (n=5)

Table 3: Heavy metals concentrations ppm (mean±SE) of fish samples collected from different sites at autumn and spring (n=5):

sites	Elhawaweesh		Elahaywa		Dar-Elsalam		Belfofoora		Elnemsaw		W.H.O mg/kg PL
	Aut.	Spr.	Aut.	Spr.	Aut.	Spr.	Aut.	Spr.	Aut.	Spr.	
Fe	104.95±9.3	73.58±6.21*	57.08±4.8	50.19±2.8	52.51±4.23	48.59±3.21	41.8±2.71	35.55±2.1	40.28±3.21	35.4±2.4	1-3
Zn	39.62±2.1	30.4±1.5**	23.07±1.7	22.91±2.3	22.87±2.1	20.7±1.7	21.6±1.7	20.46±1.5	20.08±1.12	19.52±0.63	10-75
Pb	3.88±0.26	2.73±0.15**	3.75±0.26	2.55±0.14**	3.54±0.31	2.32±0.11*	2.48±0.14	1.78±0.1***	1.31±0.11	1.12±0.03	0.1-0.2
Mn	2.95±0.13	0.878±0.03***	1.77±0.02	1.36±0.01***	1.58±0.078	1.456±0.03	1.4±0.11	Nd	1.34±0.089	Nd	0.05
Cu	0.704±0.06	0.38±0.026***	0.67±0.05	0.24±0.01***	0.56±0.047	Nd	0.116±0.01	Nd	Nd	Nd	1-3

*significance p<0.01 **high significance p<0.05 ***very high significance p<0.001
Nd (not detected) LOD (0.02)

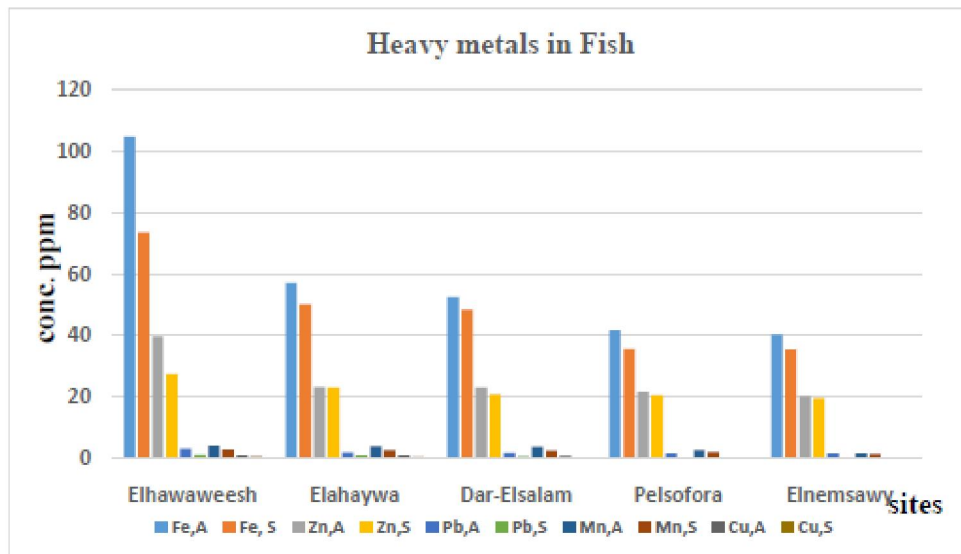


Fig. 3: Heavy metals concentrations of fish samples collected from different sites at autumn and spring (n=5)

4. Discussion:

Heavy metals in water:

For heavy elements measured in water; the statistical analysis showed significant seasonal variation ($p < 0.05$) among Fe, Zn and Pb. However, the concentration of Mn and Cu showed no significant seasonal variation ($p > 0.05$). High levels were detected in autumn, greater than those detected in spring. These results comply with those recorded by **Saeed, 2000** who found that heavy metals concentration showed seasonal variations, being greater in winter and lowest in summer. This may be attributed to the growth of phytoplankton which was higher in autumn seasons that can absorb large quantities of heavy metals from water. The obtained results agree with **Maurya et al., 2018** who studied the seasonal distribution of some heavy metals (Chromium (Cr), Lead (Pb) and Zinc (Zn)) in water and sediment samples collected from Bhagwanpur fish pond, they found that the concentrations of heavy metals in autumn higher than those detected in spring. This may be attributed to the phytoplankton growth which was higher in spring season that can absorb large quantities of heavy metals from water.

Moreover, the highest concentrations of all heavy metals were detected in water samples collected from Elhawaweesh, Elahaywa and Dar-Elsalam, which may be attributed to wastes of industrial activities, drainage water of agriculture and wastewater **Authman, 2008** and **Authman et al., 2008**.

The heavy metals concentrations detected in water had the descending order: Fe > Zn > Pb > Mn > Cu. These findings agree with **ElSayed et al., 2011** and **Maurya et al., 2018**.

Data collected for Fe, Pb and Mn in water was higher than the permissible limit of World Health Organization (**WHO, 2008**) and United States Environmental Protection Agency (**USEPA, 2010**).

Heavy metals in sediment:

With respect to average heavy metal concentrations in sediment samples, the levels were below the permissible limits (except Mn) reported by (**USEPA, 2010**). The heavy metal levels had the descending order: Fe > Mn > Zn > Cu > Pb. These findings agree with **ElSayed et al., 2011** and disagree with **Maurya et al., 2018**; they found that the highest concentration of Pb in sediment followed by Zn and Cu.

An opposite manner of the seasonal distribution pattern of heavy metal in sediment and water was obtained high levels were detected in spring, greater than those detected in autumn, Similar findings were reported by **Mzimela et al., 2003**, **Ali and Abdel-Satar, 2005** and **Maurya et al., 2018**.

The levels of all the metals in the sediment were found to be higher than the values in water and fish.

This affirmation with most of the research findings of other workers that sediments usually serve as sink for heavy metals.

All detected metals (except Fe and Zn) showed a statistically significant seasonal variation (ANOVA, $p < 0.05$). When compared to water, sediment contained a high concentration of metals, since the sediment act as a reservoir for all contaminants and dead organic matter descending from the ecosystem above. Similar findings were reported by **Bazzi, 2014**, **Olawale et al., 2016** and **Maurya et al., 2018**.

Heavy metals in fish:

The concentrations had the descending order: Fe > Zn > Pb > Mn > Cu. These results agree with **ElSayed et al., 2011**.

The results show that the metal concentrations in fish Fe, Pb and Mn were at the toxicity threshold in the muscle of the fish in line with W.H.O standards in food. This can be attributed to the plenty of these minerals in the ecosystem and the equatorial status of fish, **USEPA, 2010**. A remarkable relationship between heavy metals concentrations in water and fish were observed by **Begum et al., 2005**, **Fernandes et al., 2008**, **ElSayed et al., 2011** and **maurya et al., 2018**.

Conclusion and recommendation:

The study revealed that concentration of Fe, Pb and Mn in water was higher than the permissible limit of WHO, EPA, EC and USEPA except Cu and Zn. It is the same for fish tissue. The levels of all the metals in the sediment were found to be higher than the values in water and fish. This affirmation with most of the research findings of other workers that sediments usually serve as sink for heavy metals. However the average heavy metal concentrations in sediment samples were below the permissible limits (except Mn) compared to the permissible limit (**USEPA, 2010**). This study discovers seasonal variation in metal accumulations may be due to the fluctuation of the amount of agricultural drainage water, sewage effluents and industrial waste discharged into the pond water. This pollution level has its bad effect on both of fauna and flora at the area and it can explain the poor quality of the pond fish species, so it is strongly recommended that strict vigilance and constant monitoring are needed to maintain the water quality of the pond.

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