Surface water quality in a water run-off canal system: A case study in Jubail Industrial City, Kingdom of Saudi Arabia

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Abstract

Water quality in a run-off canal system in an industrial area was evaluated for a range of physical and chemical properties comprising trace metals (including mercury (Hg), chromium (Cr), iron (Fe), manganese (Mn), salinity, pH, turbidity, total dissolved solids, total suspended solids, chemical oxygen demand (COD), and dissolved oxygen). High concentrations of potassium (K) (1.260–2.345 mg/l) and calcium (Ca) (19.170–35510 mg/l) demonstrated that the salinity in the water was high, which indicates that industrial effluents from fertilizer manufacturing and Chlor-alkali units are being discharged into the canal system. Almost all the metal concentrations in water and sediment were within the thresholds established by the local regulatory body. Concentrations of Cr (0.0154–0.0184 mg/l), Mn (0.0608–0.199 mg/l), Fe (0.023–0.035 mg/l), COD (807–916 mg/l), and turbidity (633 ± 15–783 ± 22 NTU) were high where the canal discharges into the Persian Gulf; these discharges may compromise the health of the aquatic ecosystem. There is concern about the levels of Hg in water (0.00135–0.0084 mg/l), suspended sediment (0.00308–0.0096 mg/l), and bed sediment (0.00172–0.00442 mg/l) because of the bio-accumulative nature of Hg. We also compared the total Hg concentrations in fish from Jubail, and two nearby cities. Hg contents were highest in fish tissues from Jubail. This is the first time that heavy metal pollution has been assessed in this water run-off canal system; information about Hg is of particular
interest and will form the basis of an Hg database for the area that will be useful for future investigations.

Keywords: Analytical chemistry, Environmental science

1. Introduction

Jubail Industrial City in the Kingdom of Saudi Arabia (KSA) is being developed under the umbrella of the Saudi Basic Industries Corporation to accommodate industrial organizations mainly related to petrochemicals. The products manufactured by these industries include methanol, organic intermediates, petroleum products, industrial gases, plastics, fertilizers, aluminum, and steel. The city has a water run-off canal system that mainly transports water from occasional rainfall and flooding, and overflow water from the Persian Gulf; it also functions as a channel for treated water that is discharged from different industries and destined for industrial re-use. Flow in this canal system varies from being stagnant, slow-flowing, or fast-flowing, depending on the volume of water. Although there are strict regulations in place surrounding the quality of treated water, monitoring information about the quality of the surface water in the canal system is never reported. Water quality is defined by the physical, chemical, and biological requirements (Khalil et al., 2011). Heavy metals has become a major concern over recent years because of their toxicity, and associated threats to human health (Ma and Rao, 1997). As a result of enhanced human industrial-activities, the levels of heavy metals have increased dramatically in the aquatic environment in recent decades (Merian, 1991; O’Neil, 1993). Several studies of heavy metals in rivers, soils, and industrial discharges have been reported, due to its implications on human and ecosystem (Grosheva et al., 2000; Klavins et al., 2000). Many heavy metals, including Fe, Mn, and Cr, are essential elements for growth, but almost all become phytotoxic at higher concentrations thus cause considerable environmental degradation and ecological damage in water, air, and soil (Nesa and Azad, 2008).

Mercury (Hg), a heavy metal, is a dangerous neurotoxin. It damages the brain and the nervous system either through inhalation, ingestion, or contact with the skin. It is particularly dangerous to pregnant women and children. It is known to affect the development of the in-vitro brain (Siddiqi and Lu, 2015). Mercury level is reported to exceeded 5.8 μg/L (the safety limit of the United States Environment Protection Agency (USEPA) in blood and follicular fluid (Al-Saleh et al., 2016)). In low doses, mercury may affect a child’s development, by delaying walking and talking, and causing learning disabilities. Furthermore, high prenatal doses and infant exposure to mercury can cause mental retardation, deafness, and blindness. Mercury poisoning in adults can adversely affect fertility, blood-pressure, memory, and vision. A worldwide ban on the manufacture, export, and import of products that contain mercury will be in place by 2020 (Editor, 2013). Table 1
Table 1. Mercury emission by industrial sectors (Pirrone et al., 2001; Pirrone and Mason, 2009).

| Industries                              | Amount of Hg emission | Year reported | Major emitter                                                                 |
|-----------------------------------------|-----------------------|---------------|------------------------------------------------------------------------------|
| Iron steel manufacturing                | 43 Mg/year            | 1990-2000     | Asia (14.4 Mg yr⁻¹), Europe and North America (12.5 Mg/year each)            |
| Primary & secondary non-ferrous metal Smelters | 310 Mg/year          | 2008          | Developing countries including China                                           |
| Caustic Soda production (Chlor-alkali plants) | 162.9 Mg/year        | 2008          | Global production including China and India                                  |
| Cement production                       | 232 Mg/year           | 2005          | Global                                                                       |
| Waste derived from industrial processes | 183 Mg/year           | 2000          | Global                                                                       |
| Landfill process                        | 0.29–0.83 Mg/landfill | -             | Finland                                                                      |
| Wastewater treatment process            | 0.6–3 mg/Kg of sewage sludge | 1995/1998  | 7 EU countries                                                               |
(Pirrone et al., 2001; Pirrone and Mason, 2009) shows mercury emissions from different industrial sectors; because some of these sectors operate in Jubail Industrial City, there is concern that the area may be polluted by mercury.

Mercury in water, sediments, and fish has been the subject of many studies worldwide (Agha et al., 2007; Ali et al., 2011; Al-Nabalshi et al., 2009; Al-Sulami et al., 2002; Lai et al., 2007; Rahimi et al., 2010; Rahimi and Behzadnia, 2011; Sadiq, 1994; Sadiq, 2002). Fish living in polluted waters tend to accumulate heavy metals in their tissues depending on the metal concentrations; duration of exposure; method of metal uptake; environmental conditions, including water temperature, pH, hardness, salinity, and intrinsic factors, such as fish age and feeding habits. Various metals show different affinities to fish tissues. Most of them mainly accumulate in the liver, kidney, and gills, and, compared with other tissues, concentrations are lowest in fish muscles. Metal distribution in various organs is time-dependent (Jezierska and Witeska, 2006). Out of 38 species studied in the Gulf of Mexico, tilefish (0.65–3.73 ppm, mean value of 1.45) and king mackerel (0.30–1.67 ppm, mean value of 0.73) had the highest levels of total Hg, while swordfish (0.10–3.22 ppm, mean value of 1.00) and shark (0.05–4.54 ppm, mean value of 0.96) had the highest levels of methyl Hg (FDA, 2010). A technical report suggested that the Hg level in canned tuna fish was between 0.18 and 0.86 μg g\(^{-1}\) (USEPA limit 0.5 μg g\(^{-1}\)). The Hg levels in the tuna samples are not very high compared with internationally reported values that range from 0.8 to 1.2 ppm (Ashraf et al., 2006). Within the last 20 years, there has been an average increase of 30% in Hg levels in the Pacific Ocean, with significant increases observed in the coastal regions of Mexico, Japan, and Singapore (Davidson et al., 2013). The Hg contents in shrimp and fish species from the Persian Gulf coasts have been reported previously (Al-Saleh and Al-Daush, 2002). Also fish species, locally known as bassi (Nemipterus tolu), badah (Gerres argyreus), and shieri (Lethrinus nebulosus), and shrimp species (Penaeus semisulcatus), were analyzed for Hg, arsenic (As), lead (Pb), copper (Cu), and zinc (Zn) (Al-Sulami et al., 2002). An editorial article on the topic of Hg in the marine environment suggested that Hg contamination of marine systems has important implications for human health (Chen et al., 2012). A recent study in the Gulf of Oman reported that Hg levels in fish samples were higher than the legal limits of the World Health Organisation (WHO, 1993), Food and Drug Administration (FDA) and the USEPA (Behrooz et al., 2013). It is worth considering that the Persian Gulf is an important source of seafood for the area (Sadiq, 1994; Saeed et al., 1995; Samhan et al., 1989). However, a recent study undertaken in Jubail concluded that the high levels of Zn and Cu off the city coast are mostly the result of uncontrolled discharges of industrial waste into the coastal zone (Alkhalifa et al., 2012). Thus regular monitoring of the aquatic ecosystems in the Kingdom is suggested (Mahboob et al., 2014).
The aims of the present study were (1) to determine the quality of the water in the run-off water canal system; and (2) to determine the concentrations of metals and heavy metals, especially Hg, in the water. In the event that Hg is detected in water, a further aim is to investigate the distribution of Hg in suspended and bed sediment, and to compare the distribution of Hg in fish tissues in Jubail and other nearby cities.

2. Materials and methods

2.1. Study area and sampling sites

Jubail Industrial City is situated in the Kingdom of Saudi Arabia (KSA) between 27.0000° N and 49.6667° E. Three sampling sites were chosen as follows: Site 1 (26.99° N, 49.57° E), Site 2 (27.01° N, 49.52° E), and Site 3 (27.12° N, 49.57° E). The three sites were located in different parts of the run-off canal system and had different flow characteristics: one was stagnant, one was slow flowing, and the other was fast flowing (Fig. 1). Water and sediment samples were collected from the three sites on 3 September, 2014. Fish samples were collected by fishermen in the Riyadh, Al-Hassa, and Jubail districts of KSA on 2 November, 2015.

Fig. 1. Sampling sites (A) Map of Saudi Arabia showing Riyadh, Al-Hassa and Jubail (B) Map of Jubail Industrial City (C) Site #3, where water from water run-off canal system meets Persian Gulf (D) Site #1 and site #2, surrounded by a number of industries.
2.2. Chemicals used

Chemicals for inductively coupled plasma mass spectrometry (ICP-MS) analysis were ultra-high purity (Anal R grades). Anal R grade chemicals were also used for other analyses.

2.3. Instruments used

Trace metals were determined by ICP-MS (Agilent ICP-MS 7500C) with a method detection limit of 10 ppb. Hg was determined by cold vapor atomic fluorescence (CVAF) spectroscopy using a Hydra II $AF$ Hg Analyzer. Water color was detected with a colorimeter (LaMotte SMART 3 Colorimeter). pH was determined using a benchtop pH meter (Hanna Bench top HI-207/UK). Turbidity was determined by a Thermo-Scientific/ORION AQ 3010 turbidity meter; conductivity was measured with a HACH/51800-10 meter; dissolved oxygen (DO) was measured with an in situ analyzer (EUTECH Instruments DO 6 Plus), and chemical oxygen demand (COD) was determined using a digestion block heater (HACH DRB 200) and a spectrophotometer (HACH DR 2800).

2.4. Sample collection and preparation:

2.4.1. Water samples

A total of 30 water samples, 10 from each of the three sites, were collected following standard procedures (APHA, AWWA, and WEF, 2005). Water samples were collected in stopper-fitted polyethylene bottles from the surface of the water, holding the bottle away from the flow direction. Nitric acid was added to reduce the pH of the samples to below 2 to minimize precipitation and adsorption on the container walls. After collection, samples were transferred immediately to the laboratory in iceboxes. Strictly sterilized conditions were maintained throughout the sample collection and transportation. Analysis for DO and COD was started within 2 hours of sample collection. Samples for other analyses were refrigerated at 4 °C.

2.4.2. Solid/sediment and suspended sediment samples

Five sets of bed sediment samples were collected at the three sites from immediately below the water surface with a plastic spade, and were immediately transferred into polythene bags. The sediment samples were air-dried at room temperature in the laboratory and pulverized by hand (Sadiq, 2002). Triplicate 2 g portions of each well-mixed sediment sample were placed in 125 ml digestion tubes, and 20 ml of concentrated nitric acid was added slowly. The sediment-acid mixtures were left overnight then digested at 120 °C for 3 h in a block digester. The
tubes were cooled, and the contents were filtered through Whatman 44 filter paper, and the volume of each filtrate was increased to 50 ml using distilled water.

Five sets of suspended sediments were also collected at the three sites using wide mouth plastic bottles. Before analyzing the suspended particles in water samples, 1 L of water was filtered through Whatman 44 paper, and the sediment and filter paper were treated with 10 ml concentrated HNO₃. To obtain a clear solution, the mixture was heated as above, filtered, and diluted up to 50 ml with distilled water.

2.4.3. Fish samples

In total, 28 different fishes were collected in duplicate, nine types from each of three districts, namely Jubail, Al-Hassa, and Riyadh. These fishes were netted by professional fishermen and were dead at the time of collection from the local fish markets of three districts. No ethical animal guidelines were followed as the fish samples thus collected were not alive. The fish samples were wrapped in a polythene bag and stored in refrigerated conditions.

2.5. Sample analysis

2.5.1. Physical parameters

Water samples were analyzed for turbidity, total suspended solids (TSS), total dissolved solids (TDS), and total solids (TS) without diluting or concentrating the samples. TDS, TSS and TS were measured by gravimetric method of analysis for solids. Results of the analysis are reported in Fig. 2.

2.5.2. Chemical parameters

Parameters such as pH, DO, and COD, were determined using different instruments, as mentioned earlier. The closed reflex titrimetric method was used for COD. For conductivity measurements no pretreatment was done. The instruments were calibrated before measurements were made. Results of the analysis are reported in Fig. 2.

2.5.3. Trace metals

Twenty-one trace metals, potassium (K), calcium (Ca), barium (Ba), manganese (Mn), iron (Fe), chromium (Cr), lithium (Li), beryllium (Be), aluminum (Al), vanadium (V), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), strontium (Sr), gold (Ag), cadmium (Cd), lead (Pb), bismuth (Bi), excluding Hg, were determined by ICP-MS. The instrument was calibrated as outlined in the manufacturer’s instructions. Water samples were acidified with HNO₃ (2–3 drops of concentrated acid) before analysis Table 2.
Fig. 2. Co-relations between different physical and chemical properties in water at three sites.

Table 2. Trace metal analysis for surface water samples from water run-off canal system.

| Metal/heavy metal | ML† (ppb) | Site 1 (ppb) | Site 2 (ppb) | Site 3 (ppb) |
|-------------------|-----------|--------------|--------------|--------------|
| K                 | -         | 1260± 2.0    | 2345± 2.6    | 1438± 2.2    |
| Ca                | -         | 19170 ± 2.0  | 35510 ± 3.2  | 19740± 2.4   |
| Ba                | 2000      | 37± 0.2      | 16.8± 0.2    | ND           |
| Mn                | 1000      | 199± 0.6     | 60.8 ± 0.5   | ND           |
| Fe                | 10000     | 23± 0.4      | 49± 0.6      | 23.9 ± 0.5   |
| Cr Total          | 500       | ND           | 15.4± 0.3    | 18.4 ± 0.4   |
| Li, Be, Al, V, Co, Ni, Cu, Zn, As, Se, Sr, Ag, Cd, Pb, Bi | -        | ND*          | ND           | ND           |

*ND = Non detectable.
†ML = Maximum limit for direct discharge to the coastal waters local standard (RC, 2010).
2.5.4. Total Hg in water, suspension and sediment

Samples were analyzed for Hg using CVAF spectroscopy. The calibration curve was derived from Hg solutions of 0.00, 2.00, 5.00, and 10.0 ppb ($r^2 = 0.9998$). Water samples were analyzed after filtration through Whatman 44 paper. The concentrations of the digested and diluted samples of suspended and bed sediments were also derived from the calibration curve mentioned earlier. Fig. 3 shows the level of mercury in water, suspension and sediment from water run-off canal system at three sites.

2.5.5. Total Hg in fish tissues

The Hg concentrations in fish samples were determined by CVAF spectroscopy. The samples were digested as per the modified version of US EPA Method 1631. The experimental procedures were followed as given in the manual of Hg Analyzer (Hydra HAF) manufactured by Teledyne Leeman Labs (Application notes number 1067, 2016). Dorsal tissues of all fish samples (different amounts ranging from 0.1004 g to 0.1290 g, see Table 3 and Fig. 4) except Veneridae (Venus clams) and Portunus sp. (for which 0.1042 g and 0.1021 g respectively, of soft tissues) were transferred to 50 mL polypropylene test tubes, and then 5.0 ml of mixture of H$_2$SO$_4$ and HNO$_3$ in the ratio of 3:1 (w/w) was added. The resulting mixture was allowed to settle at 25 ± 1 °C for 2 hours, after which the samples were heated to 80 °C for 40 min, resulting in liquefied samples. Thereafter 15.0 ml of 6 N HCl, 3.0 ml of 0.1 N BrCl solution, and 4.0 ml of de-ionized water were added. After mixing and heating the samples to 60°C for 60 min, a clear yellow solution was found. Then each sample was diluted to a ratio of 1:10 with 2% (w/v) HCl.

![Figure 3](http://dx.doi.org/10.1016/j.heliyon.2016.e00128)

Fig. 3. Level of mercury in water, suspension and sediment from water-runoff canal system at three sites.
Table 3. Analysis of fish tissues for total Hg from Riyadh, Al-Hassa and Jubail (for pictures of fishes refer to Fig. 4).

| SN | Bio-name/Local name | Mass of Tissue (g) | Hg (ppb) ± | SN | Bio-name/Local name | Mass of Tissue (g) | Hg (ppb) ± | SN | Bio-name/Local name | Mass of Tissue (g) | Hg (ppb) ± |
|----|---------------------|--------------------|------------|----|---------------------|--------------------|------------|----|---------------------|--------------------|------------|
| R-1 | Lethrinus nebulosus/ Sal/gahash | 0.1015 | 57.74 ±1.15 | A-1 | Katsuwonus pelamis/ Shiriwa | 0.1290 | 42.08 ±0.84 | J-1 | Epinephelus coioides/ Hammour | 0.1050 | 173.05 ±2.94 |
| R-2 | Acanthopagrus bifasciatus/ Faskar | 0.1153 | 217.05 ±3.41 | A-2 | Trachinotus carolinus/AnThallah | 0.1010 | 172.19 ±2.9 | J-2 | Mullolichthys vanicolensis/ Tamrah/Biah | 0.1100 | 224.16 ±3.66 |
| R-3 | Trachinotus blochii/ Thallah | 0.1007 | 115.13 ±2.34 | A-3 | Trachinotus blochii/ Thallah | 0.1055 | 175.37 ±2.8 | & | J-7 | Acanthopagrus bifasciatus/ Faskar | 0.1075 | 179.35 ±2.85 |
| R-4 | Sardinella gibbosa/ Sardines | 0.1004 | 30.41 ±0.62 | A-4 | Acanthopagrus bifasciatus/Faskar | 0.1060 | 110.04 ±2.44 | J-4 | Kyphosus sp. /AlSibin/AlShaba | 0.1160 | 189.52 ±3.32 |
| R-5 | Sardinella longiceps/ Ooma/alfa | 0.1066 | 10.89 ±0.22 | A-5 | Latidaecalcarifer/Sarrah/Naisarah | 0.1030 | 18.21 ±0.38 | J-5 | Carangoides ferdau/ Hammam | 0.1050 | 184.00 ±3.72 |
| R-6 | Amblygaster leio gaster/ Kumal/chimkhen | 0.1102 | 91.46 ±1.82 | A-6 | Liza subviridis/ Boori/Bolty | 0.1016 | 42.54 ±0.78 | J-6 | Parapeneus multifasciatus/ Sultan Ibrahim | 0.1065 | 168.11 ±3.73 |
| R-7 | Veneridae (venus)/Clams | 0.1042 | 27.77 ±0.54 | A-7 | Mullolichthys vanicolensis/Tamrah/Biah | 0.1060 | 205.74 ±4.23 | J-8 | Trachinotus carolinus/ AnThallah | 0.1103 | 253.24 ±5.06 |
| R-8 | Portunus sp/ Gabgoob | 0.1021 | 54.59 ±1.30 | A-8 | Parapeneus multifasciatus/ Sultan Ibrahim | 0.1093 | 129.93 ±2.58 | J-9 | Gnathanodon speciosus/ Rabeeb | 0.1160 | 479.41 ±6.83 |
| R-9 | Engraulidae sp/ Barriya | 0.1090 | 30.81 ±0.64 | A-9 | Lethrinus lentjan/ Shaour | 0.1066 | 107.68 ±2.45 | J-10 | Lethrinus olivaceus/ Shiriwa | 0.1108 | 237.02 ±4.91 |

SN = Sample number; R-1 to R-9 Samples from Riyadh; A-1 to A-9 Samples from Al-Hassa; J-1 to J-10: Samples from Jubail.
followed by addition of 0.1 ml of hydroxylamine hydrochloride to remove any free bromine. The calibration curve described earlier was used to determine the concentrations of Hg in the digested sample solutions. The Hg concentrations were obtained by multiplying the original sample results by 4.0 (the volume of standard added) and dividing by the sample weight. The certified reference material was further diluted (1:2) with 2% HCl so that it was within the calibration range (Application notes number 1067, 2016).

3. Results and discussion

Various industrial production units emit Hg into the environment (Table 1), meaning that industrial cities such as Jubail are vulnerable to mercury pollution. Physical (TS, TSS, TDS, turbidity and conductivity) and chemical properties (pH, COD and OD) of all samples from three sites and correlations within physical (Fig. 2A–C) and chemical properties (Fig. 2D–F), are presented in Fig. 2. Trace metal concentrations in water samples are presented in Table 2, and, to facilitate comparison, Saudi Arabian standards for wastewater discharge and reuse are provided in Table 4.

3.1. Physical properties

The turbidity of water samples at all three sites was much higher (633–783 NTU) than the environmental thresholds designated by the Royal Commission (RC) (75 NTU), the Ministry of Agriculture, Jubail & Yambu, Saudi Arabia (MA), Riyadh, Saudi Arabia and the Presidency of Meteorology and Environment (PME), Riyadh, Saudi Arabia (see Table 4); values of TSS, TS, and TDS were also high (Fig. 2).
Turbidity (783 ± 9 NTU), TDS (422 ± 2 ppm) and TSS (591 ± 2 ppm) were highest at site 1. There was a positive correlation between TDS and TS ($r^2 = 0.985$; Fig. 2A), a weak positive correlation between TSS and turbidity ($r^2 = 0.81$; Fig. 2B), and a very weak positive correlation between TDS and conductivity ($r^2 = 0.303$; Fig. 2C). The high value for TDS indicates the nature of surface water, and is in agreement with values reported in earlier studies in the eastern region of the Kingdom (Ahmed et al., 2005). TDS values tend to be higher in arid or desert areas than in tropical areas that receive abundant rainfall (Uhl et al., 2009). Thus, the water at site 3, which converges with water from the Persian Gulf, must be cleaned and treated before discharge.

### 3.2. Chemical properties

The pH values of the water samples at all sites were below the maximum limit (pH 6–9). The DO level was below the threshold limit at site 1 (1.38 ppm), but was above the limit at the other sites. pH and COD were positively correlated ($r^2 = 0.99$; Fig. 2D), and pH and DO ($r^2 = 0.97$; Fig. 2E) and DO and COD ($r^2 = 0.98$; Fig. 2F) were negatively correlated. COD values were 916 ppm at site 1, 842 ppm at site 2, and 807 ppm at site 3, all of which are much higher than the threshold limit for either direct discharge to coastal waters (200 ppm, RC regulation) or restricted irrigation (150 ppm, PME standard). The higher COD concentrations suggest elevated concentrations of organics such as branched alkanes, branched alkenes, aliphatic ketones, substituted thiophenes, substituted phenols, aromatics, and aromatic alcohols (Ahmad et al., 2008) at all three sites. The COD values in this study are much higher than those reported by Mohorjy and Khan (2006) for a sampling site near a fish market on the Red Sea Coast (352 mg/l). The high color

| Parameters* | Unrestricted Irrigation | Restricted Irrigation |
|-------------|-------------------------|-----------------------|
| DO          | 2.0                     | -                     |
| COD         | -                       | - 150                 |
| TSS, monthly average | 10.0        | 20.0 15               |
| Hg          | 0.001                   | 0.001 0.001           |
| Zn          | 4.0                     | 4.0 1.0               |
| Cr          | 0.01                    | 0.01 0.1              |
| Al          | 5.0                     | 5.0                   |
| pH          | 6.0–8.4                 | 6.0–8.4 6–9           |
| Turbidity   | 1.0                     | 1.0 75                |

*All units are in ppm, except pH, and turbidity (NTU).
content at site 1 indicates that the water composition is complex; water at this site is close to many different types of industries that produce both organic and inorganic materials.

3.3. Trace metals

Higher concentrations of K and Ca (Table 2) suggest that water is very salty at all three sites; the concentrations were highest at site 2 (K = 2.345 ppm; Ca = 35.510 ppm), and were sufficiently high to ensure that the water was unfit for discharge into any water bodies, including the Persian Gulf. High salinity in irrigation water has negative impacts on the environment. For example, Hussain and Alshammary (2008) reported that the survival period of trees decreased significantly with increases in soil salinity because of high salinity levels in irrigation water. The poor water quality may reflect discharges from fertilizer manufacturing and chlor-alkali units. However, the higher Cr (0.0154–0.0184 ppm), Fe (0.023–0.049 ppm), and Mn (0.0608–0.199 ppm) concentrations suggest that the source is industrial discharge from metal or steel production units. There are many petroleum-based industries, a fertilizer plant, and at least one steel industry near site 1 and site 2 (Fig. 1). Similar to the results of this study, low levels of Cr, Fe, and Mn were also reported in a study of water quality along the eastern coast of the Persian Gulf because of industrial discharge (Al-Sulami et al., 2002). Heavy metals in water bodies can transfer to fishes like salmon, sardine, and tuna fish that are later processed and canned for human consumption (Ashraf et al., 2006), or to fish such as A.d. dispar (a type of Arabian toothcarp) and Poecilia latipinna that are available in Riyadh, KSA (Mahboob et al., 2014). Therefore, when estimating heavy metals in water, it is important to know how they transfer into the food chain. We found that the concentrations of other trace metals, including Ni, Cu, Zn, Ag, Cd, Pb, Bi, Al, Co, Li, V, As, Se, Sr, Be, and Ba, were either lower than the permissible limits or non-delectable (below 10 ppb) in water samples collected from the three sites. These data may be used as the basis for further studies of the water run-off canal system in Jubail.

3.4. Mercury analysis

Total Hg (THg) concentrations in water, suspended and bed sediments were below the permissible limits, 5.0 ppb and 0.001 ppm for water set by RC regulations (RC, 2010) and MA (Draft, 1989), respectively (Fig. 3). The concentrations of Hg (4.42 ppb) in sediment, suspension (3.08 ppb), and water (1.35 ppb) at site 3 were higher than those at the other two sites, suggesting that site 3 should be monitored further because of the accumulation of Hg (total in water, suspended sediment, and bed sediment) and the environmental setting (at the point where the canal water meets with gulf water). The highest concentrations of Hg (5.61 ppb) in sediment samples were almost 10 times higher than the lowest concentrations (0.52 ppb), which
somewhat supports the observation that effluent from the desalination plant has an influence on sediment quality (Sadiq, 2002). We might assume therefore that effluent from a water desalination plant downstream of site 3 has an influence on the water quality at site 3, as water from the gulf overflows into the canal system during high tide in the Persian Gulf. In general, sediment Hg concentrations are higher than Hg concentrations in water, which suggests that Hg accumulates in sediment over time; for this study, Hg accumulation was highest at site 3 (4.42 ppb). We may assume that the source of the Hg in water and bed sediment in the water run-off canal system is industrial effluent, as there are no other point sources in the area. It has been reported that more metals were transferred to fish from water than from sediments (Abdel-Baki et al., 2011). As water from the canal system discharges into the Persian Gulf water at site 3, there is a real danger of Hg bio-accumulation in fishes in the Persian Gulf water.

3.5. Total Hg (THg) in fish tissues

In a previous study, heavy metals were lowest in the muscle compared with other organ tissues (Fahmy and Fathi, 2011). Therefore, the amount of Hg in fish tissue (Table 3) was suggested to be lowest compared with other parts of the fish. The Hg concentrations in all fish samples collected from Jubail, Al-Hassa, and Riyadh were well below the maximum allowable limit (MAL) of 1.0 ppm suggested by the Saudi Arabian Standards Organization (SASO, 1997) and the 0.5 ppm value established by the WHO. The results from this study are similar to the conclusions of another study in which fish species known locally as bassi (Nemipterus tolu), badah (Gerres argyreus), and shieri (Lethrinus nebulosus), and shrimp species (Penaeus semisulcatus) were analyzed for Hg and other heavy metals (Al-Sulami et al., 2002). Similarly, another previous study reported Hg concentrations that were below the allowable limit in the Persian Gulf and the Caspian Sea (Agha et al., 2007). Moreover, results from our study (Table 3) suggest that, in general, the THg content in fish tissues was higher in fish from Jubail (up to 479.41 ppb) than in fish from Riyadh (up to 217.05 ppb) and Al-Hassa (up to 205.74 ppb). This observation is evidence that the elevated Hg concentrations in fish collected from Jubail are caused by the large scale industrial activities.

4. Conclusion

The elevated values for TSS, TDS and COD at site 1, the heavy metal concentrations that were lower than the threshold values at site 2, and the accumulation of Hg, while still below the threshold limits, at site 3 demonstrate that the water quality in the study area had been influenced by discharges from the industrial units in the vicinity of the sampling sites. Also, the concentrations of Hg in water, sediment, and fish tissues were not too high in Jubail Industrial City; however, the Hg contents were higher in fish tissues from Jubail than in fish tissues
from two neighboring cities. Notably, the potential sources of pollution could have come from some or all of the following: the production units for fertilizer, chlor-alkali industries, a steel plant, a desalination plant, non-ferrous metal smelters, and many other petrochemical-based manufacturing units in the vicinity. Therefore we recommend further monitoring of the Hg concentrations in water and sediment and in fish from the Persian Gulf.

Declarations

Author contribution statement

Zia M. Siddiqi: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mohammad Saleem, Chanbasha Basheer: Performed the experiments; Contributed reagents, materials, analysis tools or data.

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Additional information

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References

Abdel-Baki, A.S., Dkhil, M.A., Al-Quraishy, S., 2011. Bioaccumulation of some heavy metals in tilapia fish relevant to their concentration in water and sediment of Wadi Hanifah, Saudi Arabia. Afr. J. Biotechnol. 10 (13), 2541–2547.
Ahmad, M., Bajahlan, A.S., Hammad, W.S., 2008. Industrial effluent quality, pollution monitoring and environmental management. Environ. Monit. Assess. 147, 297–306.

Ahmed, S.M., Hussain, M., Abderrahman, W., 2005. Using multivariate factor analysis to assess surface/logged water quality and source of contamination at a large irrigation project at Al-Fadhli, Eastern Province, Saudi Arabia. Bull. Eng. Geol. Environ. 64, 319–327.

Agha, A., Leermakers, M., Elskens, M., Fatemi, S.M.R., Baeyens, W., 2007. Total mercury and methyl mercury concentrations in fish from the Persian Gulf and the Caspian Sea. Water Air Soil Poll. 181, 95–105.

Ali, A.A., Elazein, E.M., Alian, M.A., 2011. Determination of heavy metals in four common fish, water and sediment collected from Red Sea at Jeddah Islamic Port Coast. J. Appl. Environ. Biol. Sci. 1 (10), 453–459.

Alkhalifa, A.H., Al-Homaidan, A.A., Shehata, A.I., Al-Khamis, H.H., Al-Ghanayem, A.A., Ibrahim, S.S., 2012. Brown macroalgae as bio-indicators for heavy metals pollution of Al-Jubail coastal area of Saudi Arabia. Afr. J. Biotechnol. 11 (92), 15888–15895.

Al-Nabalshi, H.A.R., Bu-Olayan, A., Thomas, B.V., 2009. Mercury pollution and its synergism with season, nutrient and hydrological variables in Kuwait coastal waters. J. Appl. Sci. 4 (2), 115–124.

Al-Saleh, I., Al-Daush, I., 2002. Mercury content in shrimp and fish species from Gulf Coast of Saudi Arabia. Bull. Environ. Contam. Toxicol. 68, 576–583.

Al-Saleh, I., Coskun, S., Mashhour, A., Shinwari, N., El-Dousha, I., Billedoa, G., Jaroudi, K., Al-Shahrani, A., Al-Kabra, M., El Din Mohamed, G., 2016. Exposure to heavy metals (lead, cadmium and mercury) and its effect on the outcome of in-vitro fertilization treatment. Int. J. Hyg. Environ. Health.

Al-Sulami, S., Al-Hassan, A.M., Daili, D., Mohd, M.M.K., Fita, N.A., Ibrahim, M.M., Hassan, M.A., 2002. Study on the distribution of toxic heavy metals in the fishes, sediments & water of Arabian Gulf along the eastern coast of Saudi Arabia. SWCC, Issued as Technical Report No. APP 3803/96011.

APHA, AWWA, and WEF, 2005. Standard methods for the examination of water and wastewater, 21st edition Standard Methods, Washington, D.C.

Application notes number, 2016. Application notes number 1067 of the Hydra Hg Analyzer. Teledyne Leeman Labs.
Ashraf, W., Seddigi, Z., Abukibash, A., Khalidi, K., 2006. Level of selected metals in canned fish consumed in Kingdom of Saudi Arabia. Environ. Monit. Assess. 117, 271–279.

Behrooz, R.D., Sahebib, S., Majnonib, F., Ahmadpourc, M., Hoseinic, S.H., 2013. Mercury contamination in commercial fresh and salt water fish of the Zabol Chahnimeh reservoirs and the Gulf of Oman (Iran). Food Addit. Contam. 6 (3), 175–180.

Chen, C.Y., Driscoll, C.T., Lambert, K.F., Mason, R.P., 2012. Marine mercury fate: From sources to seafood consumers. Environ. Res. 119, 1–2.

Davidson, B.C., Philpot, S., Onyeokoro, U., Jones, W., Amelingmeier, L., Kamel, J., Madhavan, R., 2013. Assessment of the degree of mercury contamination of marine fish around Bonaire. Toxicol. Environ. Chem. 95 (10), 1675–1679.

Draft, 1989. MA Draft Standards. Ministry of Agriculture, Riyadh, Saudi Arabia.

Editor, 2013. Governments strike first global mercury control treaty Environment News Service. Accessed 20 June 2015 http://ens-newswire.com/2013/01/26/governments-agree-first-global-mercury-control-treaty/.

Fahmy, G.H., Fathi, A.A., 2011. Limnological Studies on the Wetland Lake, Al-Asfar, with Special References to Heavy Metal Accumulation by Fish. Am. J. Environ. Sci. 7 (6), 515–524.

FDA, 2010. National Marine Fisheries Service Survey of Trace Elements in the Fishery Resource Report 1978 The Occurrence of Mercury in the Fishery Resources of the Gulf of Mexico Report 2000.

Grosheva, E.J., Voronskaya, G.N., Pastukhove, M.V., 2000. Trace element bioavailability in Lake Baikal. Aquat. Ecosyst. Health Manag. 3, 229–234.

Hussain, G., Alshammary, S.F., 2008. Effect of Water Salinity on Survival and Growth of Landscape Trees in Saudi Arabia. Arid Land Res. Manag. 22, 320–333.

Jezierska, B., Witeska, M., et al., 2006. The metal uptake and accumulation in fish living in polluted waters. In: Twardowska, I. (Ed.), Soil and Water Pollution Monitoring, Protection and Remediation. Springer, 3–23.

Khalil, B., Ouarda, T., St-Hilaire, A., 2011. Estimation of water characteristics at unguarded sites using artificial neutral networks and canonical co-relation analysis. J. Hydrol. 405, 277–287.

Klavins, M., Briede, A., Parele, E., Kokorite, I., Rodnov, V., Klavina, I., 2000. Heavy metals in rivers of Latvia. Sci. Total Environ. 262, 175–184.
Lai, S., Holsen, T.M., Han, Y., Hopke, P.P., Yi, S., Blanchard, P., Pagano, J.J., Milligan, M., 2007. Estimation of mercury loadings to Lake Ontario: results from the Lake Ontario atmospheric deposition study (LOADS). Atmos. Environ. 41, 8205–8218.

Ma, L.Q., Rao, G.N., 1997. Chemical fractionation of Cadmium, Nickel, and Zinc in contaminated soils. J. Environ. Qual. 26, 259–264.

Mahboob, S., Al-Balawi, H.F.A., Al-Misned, F., Al-Quraishy, S., Ahmad, Z., 2014. Tissue Metal Distribution and Risk Assessment for Important Fish Species from Saudi Arabia. Bull. Environ. Contam. Toxicol. 92, 61–66.

Metals and their compounds in the environment: occurrence, analysis and biological relevance. In: Merian, E. (Ed.), UCH, Weiheim-New-York-Basel-Cambridge.

Mohorjy, A.M., Khan, A.M., 2006. Preliminary assessment of water quality along the Red Sea coast near Jeddah, Saudi Arabia. Water Int. 31 (1), 109–115.

Nesa, N., Azad, P., 2008. Studies on trace metal levels in soil and water of Tipong, Tirap and Tikak Collieries of Makum coal, Tinsukia, Assam. Poll Res. 27 (2), 237–239.

O’Neil, P., 1993. Environmental chemistry. Chapman and Hall, London, pp. 193.

Pirrone, N., Costa, P., Pacyna, J.M., Ferrara, R., 2001. Mercury Emissions to the Atmosphere from natural and anthropogenic sources in the Mediterranean Region. Atmos. Environ 35, 2997–3006.

Mercury Fate and Transport in the Global Atmosphere. In: Pirrone, N., Mason, R. (Eds.), Springer Science + Business Media, LLC doi:http://dx.doi.org/10.1007/978-0-387-93958-2-1.

Rahimi, E., Hajisalehi, M., Kazemeini, H.R., Chakeri, A., Khodabakhsh, A., Derakhshesh, M., Mirdamadi, M., Ebadi Seyed, A.G., Rezvani, A., Kashkahi, M. F., 2010. Analysis and determination of mercury, cadmium and lead in canned tuna fish marketed in Iran. Afr. J. Biotechnol. 9 (31), 4938–4941.

Rahimi, E., Behzadnia, A., 2011. Determination of mercury in fish (Otolithes ruber) and canned Tuna fish in Khuzestan and Shiraz, Iran. World Appl. Sci. J. 15 (11), 1553–1556.

RC, 2010. Regulations and Standards, Royal Commission Environmental Regulations, RCER-2010, Volume 1.

Sadiq, M., 1994. Gulf shrimp quality: some problems and probable solutions. Proceedings of The Technical Consultation on Shrimp Management in the Gulf, 1–12.
Sadiq, M., 2002. Metal contamination in sediments from a desalination plant effluent outfall area. Sci. Total Environ. 287, 37–44.

Saeed, T., Al-Yakoob, S., Al-Hashash, H., Al-Bahloul, M., 1995. Preliminary exposure assessment for Kuwaiti consumers to polycyclic aromatic hydrocarbons in seafood. Environ Int. 21, 255–263.

Samhan, O., Morel, G., Zorba, M., Hashash, H., Al-Bloushi, A., Al-Matrouk, K., Jacob, P.G., 1989. Preliminary screening of petroleum and organic mercury in some Kuwaiti fish. Kuwait: Kuwait Institute for Scientific Research, KISR, pp. 3047.

SASO, 1997. Maximum limits of contaminating metallic elements in foods. Saudi Arabian Standards Organization, Riyadh, Saudi Arabia.

Siddiqi, Z.M., Lu, J., 2015. Measurements of mercury associated with airborne particulate matter: use of two sampling devices. Fresen. Environ. Bull. 24 (4), 1326–1332.

Standard, 2001. PME Performance Standards for Direct Discharge Presidency of Meteorology and Environment Riyadh, Saudi Arabia. Accessed 30 September 2009 http://www.pme.gov.sa/en/env_law.asp.

Uhl, V.W., Baron, J.A., Davis, W.W., Warner, D.B., Seremet, C.C., 2009. Groundwater development: basic concepts for expanding CRS water programs. Catholic Relief Services, United States Conference of Catholic Bishops, 73.

WHO, 1993. World Health Organization, Evaluation of Certain Food Additives and Contaminants, Forty-first Report of the Joint FAO/WHO Expert Committee on Food Additives, WHO Technical Report Series No. 837. World Health Organization, Geneva.