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Evaluation of Heavy Metals (As and Cd) Contamination in the Edible Fish Along Karachi-Makran Coast

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Abstract.- The aim of this paper is to measure the concentration levels of As and Cd in edible fish from the area of Karachi – Makaran coast, Pakistan. These two metals are very toxic with serious health effects. These metals are released directly through the industrial sewage into Malir River and transferred to fish and then to human beings. It was observed that the high concentration of As in fish flesh samples were most probably due to the presence of significant amount of As in the industrial effluents discharged into the Indus river. The fish of sporadic occurrence also exhibits variable Cd concentrations in the flesh, which do not meet the standards of World Health Organizations.

Key words: Heavy metals pollution, industrial waste, arsenic, cadmium.

INTRODCUTION

Accumulation of heavy metals in marine ecosystems is of global importance. Metals generally enter the aquatic environment through erosion of geological matrix, atmospheric deposition, due to anthropogenic activities caused by industrial effluents, domestic sewage and mining wastes (Gumgum *et al*., 1994; Alam *et al*., 2002). The metal contaminants in aquatic systems usually remain either in soluble or suspended form and finally tend to settle down to the bottom or are taken up by the organisms. The progressive and irreversible accumulation of these metals in various organs of marine creatures ultimately lead to metal-related diseases in the long run because of their toxicity, thereby endangering the aquatic biota and other organisms (Watling, 1983; Hart, 1982; Lee, *et al*., 2001; Melville *et al*., 2002). Fishes being one of the main aquatic organisms in the food chain, may often accumulate large amounts of certain metals (Mansour *et al*., 2002; Hadson, 1988). Essentially, fishes assimilate these heavy metals through ingestion of suspended particulates, food materials and/or by constant ion-exchange process of dissolved metals across lipophilic membranes like the gills or adsorption of dissolved metals on tissue and membrane surfaces.

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Arsenic is a metal that occurs at ultratrace levels. It has been suggested that this metal could play an essential role in humans because decreases in serum arsenic concentration have been correlated with injuries of the central nervous system, vascular disease and cancer (Nielsen, 1999). On the other hand, some studies indicate the potential of this trace element to induce skin lesions when individuals are exposed to high arsenic content from water (Smith *et al*., 2000) or nonmelanoma skin carcinoma for individuals exposed to high environmental arsenic levels as consequence of a coal-burning power plant (Pesch *et al*., 2002). Because mechanisms exist for homeostatic regulation of arsenic, its toxicity through oral intake is relatively low. Toxic quantities of inorganic arsenic generally are reported in milligrams (Nielsen, 1999), usually found in contaminated geographical areas mainly in waters where inorganic forms of the trace element are predominant (Smith *et al*., 2000; Del Razo *et al.*, 2002). However, arsenic exposure has been related to the appearance of some types of cancer (Pesch *et al*., 2002). Recently, a report on an assessment of the cancer risk associated with consumption of oysters caused a panic among consumers in Taiwan, producing significant effects on related industries (Guo, 2002).

Cadmium is principally dispersed in natural and agricultural environments through various agricultural, mining and industrial activities as well as resulting from the exhaust gases of automobiles (Das *et al*., 1997). This trace metal is pollutant and potential toxin that has no known function in any

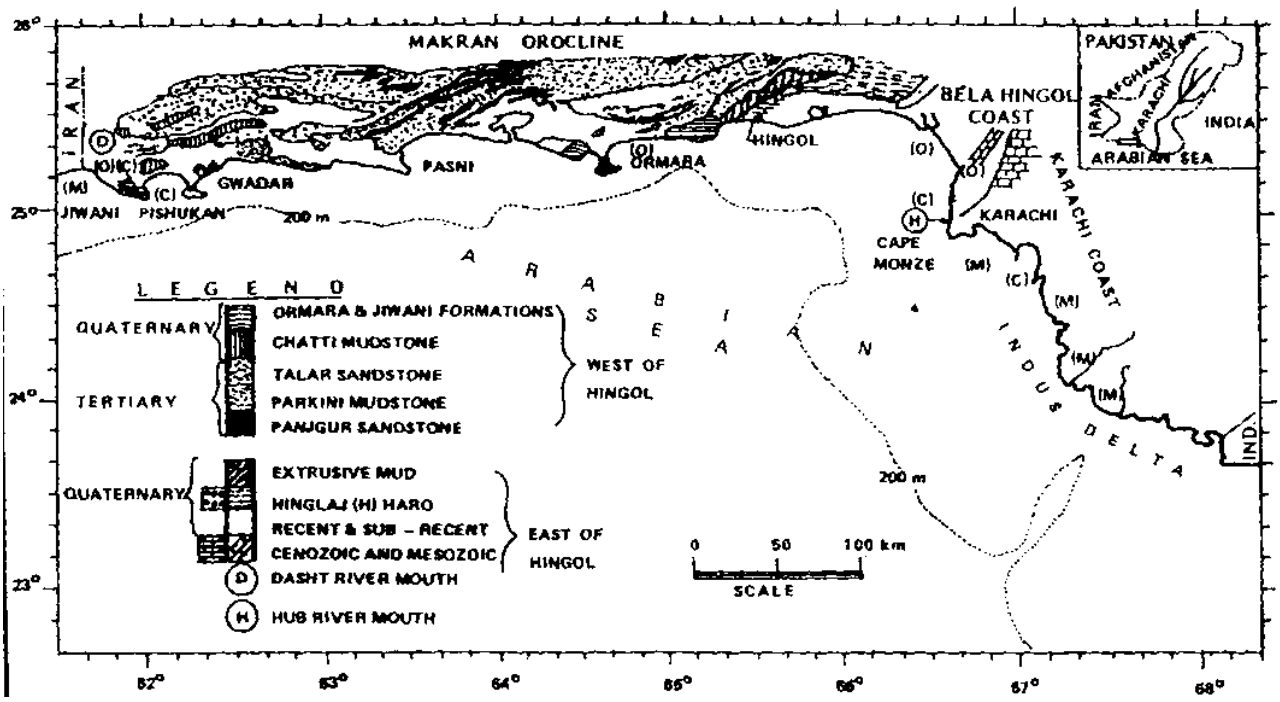

Fig. 1. Karachi –Makran Coastal area.

biological organism, and is one of the most dangerous heavy metals for the environments due its high mobility and low concentration in organisms.

The beaches of Karachi and Makran are located on the coast of Arabian Sea (Fig. 1). The beaches of Karachi are almost bounded by the Hub River in the West and the Indus River basin in the East. It is reported that 18000 tons oil is spilled every year in the vicinity of Karachi Harbor, which has significant effect on the suspended load and metallic cations (Beg, 1994; Crawford *et al*., 1993).

It is expected that the fish collected from the study area will illustrate the interactions between the intensity of heavy metal concentration in beach water sediments and the absorption of heavy metals by the fish. The estimation of heavy metals in fish flesh is also expected to explain the degree of uptake of heavy metals by the fish both in polluted and relatively unpolluted locations under study. Those species, which have localized occurrence but are of commercial importance, are expected to reveal the absorption capacity of metals and the minor differences in the environmental controls. For example the effects of turbidity, in-pouring of varieties of pollutants such as industrial wastes, sewage and by human activities along the coast.

MATERIALS AND METODS

Sampling

The following fishes were collected from the study area. Fish samples from the relatively deeper seawater 10 to 15 meters adjacent to the beaches of Keti Bandar in the East to Gadani in the West (Fig. 2) were collected to investigate the concentration of selected heavy metals in the flesh of the fish. Due consideration was given in the selection of fish to the common occurrence and consumption of these fish within country and also for export purposes: F1, *Arius serratus*; F2, *Opisthopterus tardoore* F3, *Otolithes rubber*; F4, *Pampus argenteus*; F5, *Parastromateus niger*; F6, *Pomadays maculates*; F7, *Sillago sihama*; F8, *Sparus sarba*; F9, *Therapon jarbua*; F10, *Dussumieria acuta*; F11, *Mugil longimanus*; F12, *Mugil speigleri*; F13, *Nematolosa nasus*; F14, *Polydactylus sexfilis*; F15, *Pseudosciaena axillaris.*

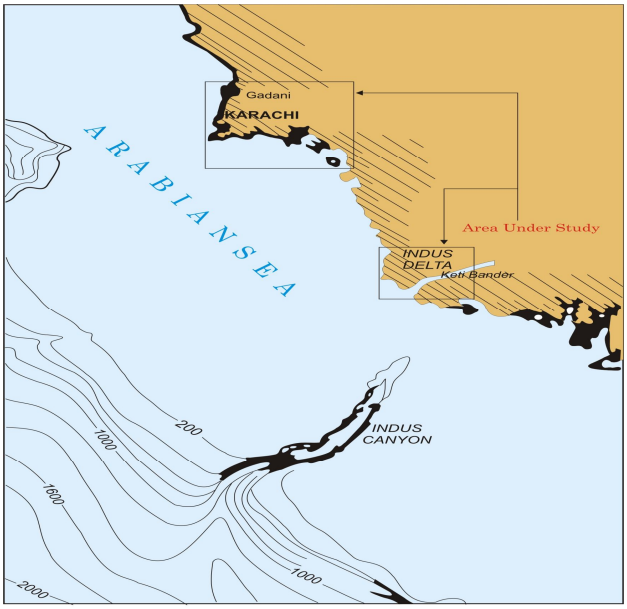

Fig. 2. Bathemetric map showing study area.

Preparation and analysis of samples

Trace metals As and Cd were analyzed by the method described by Ralf *et al*. (2002). Approximately 2 g of frozen (wet), equivalent to 0.5 g freeze dried tissue was wet digested with 10 ml of nitric acid and 5 ml of perchloric acid. The resulting solution was diluted to 20 ml by weight. Acid extracts of tissue were used for estimation of heavy metals.

Quality control

After sample digestion, the appropriate dilution and level of internal standard additions was determined. A calibration standard analyzed every 10 samples to monitor the response stability of the instrument. for as, hydride generation followed by ICP was conducted using 4 ml HCl and 0.5% Sodium borohydride (Goldstein *et al*., 1996).

Data analysis

The data was analyzed through the standard method of the statistical analysis.

RESULTS AND DISCUSSION

Figures 3 and 4 show heavy metal concentrations of As and Cd in the flesh of the fish, respectively, for common species found all along the beaches of Karachi and Makran (F-1 to F-9) and dissimilar species which show irregular and localized occurrence (F-10 to F-15) collected from the locations.

Arsenic (As)

The concentration of As in fish flesh samples of location No.1 is (0.748 ppm) higher than the concentration of As in beach water (0.648), but less than that of the beach sediments (5.060 ppm). The maximum As content was noted in F-11 *(Eleutheronema tetradactylum*) commonly known as Seeri and is being commercially utilized (Fig. 3)**.** This species is not uniformly distributed in the beach water all along the study area but is limited to the beach water of location No.1 and 2 only.

The As content is drastically decreased (0.051 ppm) in the beach water of location No.2 as compared to location No.1. It appears that the industrial pollutants brought by River Indus from the upstream and in-pouring at location No.1 are being diluted by wave action in westward direction and hence the dilution of As concentration in beach water at location No.2 appears logical. In location No.2, industries like Pakistan Steel Mill, Bin Qasim Thermal Power Plant and Port Bin Qasim are situated on the coast and discharge their effluents which appear to contain very little amount of arsenic compared to other industries. This could also be a possible reason of lesser concentration of As in the fish flesh samples. This argument is further strengthened when the concentration of As in the beach water of the two locations are compared. At locations 3 (Ibrahim Hadiri), 4 (Gizri Creek) and 5 (Clifton) described together for concentration of As in fish flesh are situated on the western side of location No.2 and show relatively lower concentration of arsenic due to very little effect of less number of pollutants, while the species F-1 to F-9, show maximum content (0.025 ppm) of As in F-5

However, some degree of variation in As content within the fishes are also evident and can be attributed to the local factors such as the presence of tanneries industries, automobile batteries industries, oil refinery etc. In this location F-10 (*Dussumieria acuta*), not found in locations 1 and 2 shows the highest content of As (0.040 ppm) absorbed in its flesh.

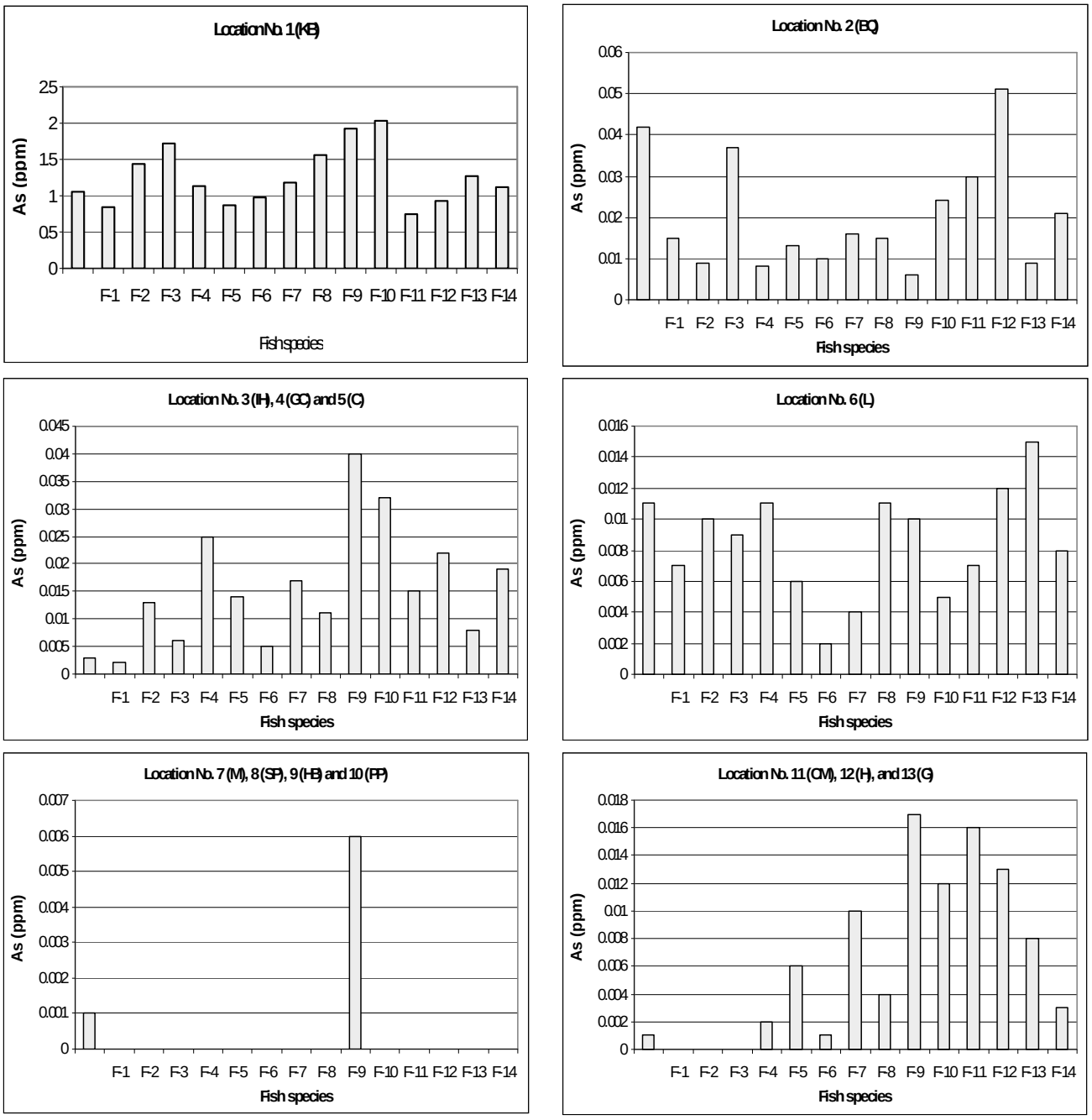

Fig. 3. Concentration of As (ppm) in the selected edible fishes of Arabian Sea along Karachi-Makran Coast. F1, *Arius serratus*; F2, *Opisthopterus tardoore* F3, *Otolithes rubber*; F4, *Pampus argenteus* ; F5, *Parastromateus niger*; F6, *Pomadays maculates*; F7, *Sillago sihama*; F8, *Sparus sarba*; F9, *Therapon jarbua*; F10, *Dussumieria acuta*; F11, *Mugil longimanus* ; F12, *Mugil speigleri* ; F13, *Nematolosa nasus* ; F14, *Polydactylus sexfilis* ; F15, *Pseudosciaena axillaries.*

The comparative study of As concentrations in the fish flesh of locations 1 to 5 very clearly indicates a variation in absorption of As by the species. This variation in As concentration in fish

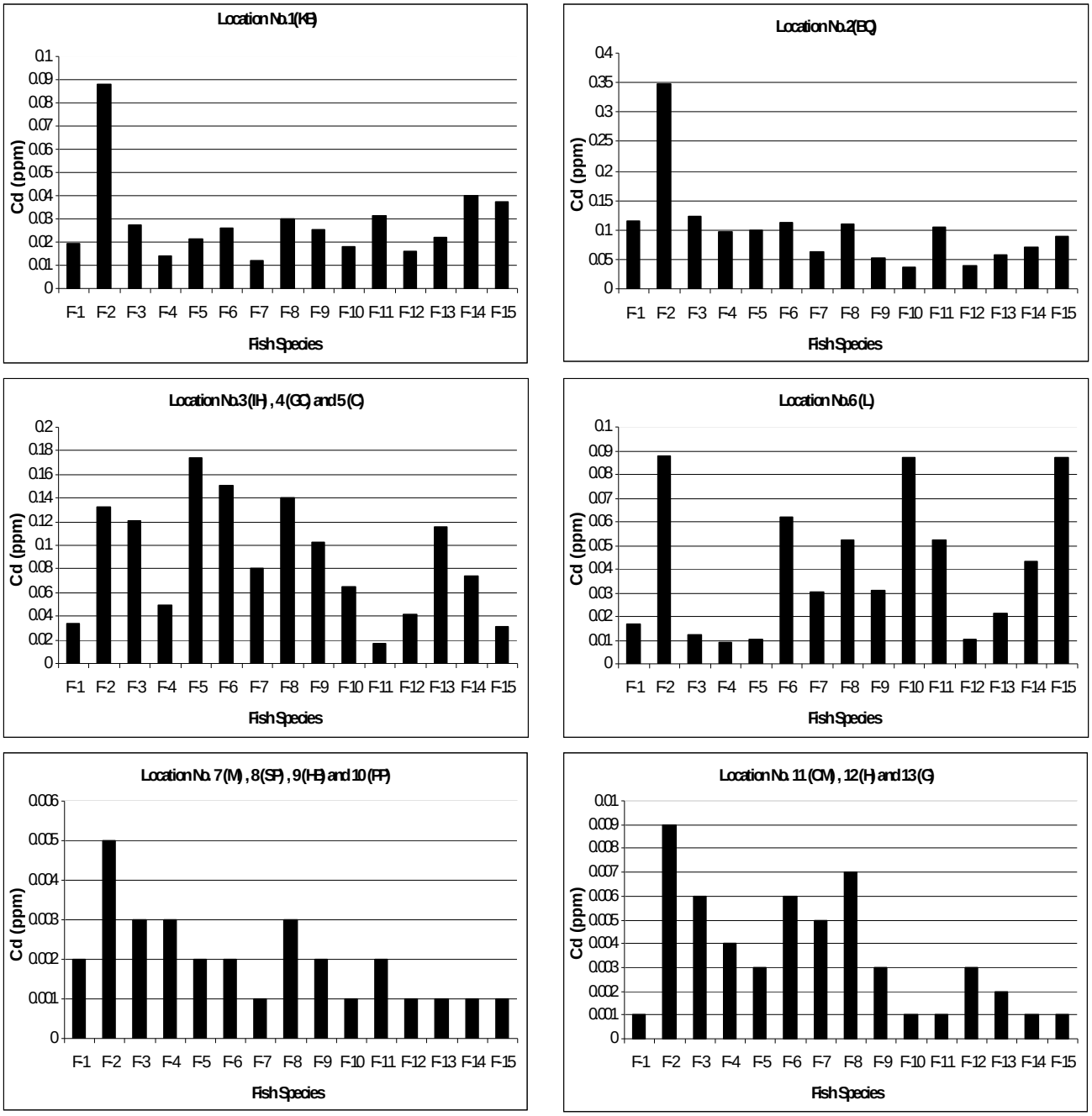

Fig 4. Concentration of Cd (ppm) in the selected edible fishes of Arabian Sea along Karachi-Makran Coast. For abbreviations see Fig. 3.

species, most probably reflects to different absorption capacity for arsenic in relation to the local geochemical and environmental controls.

Further west, location No.6 (Layari) represents the the location of in-pouring industrial and civic effluents through River Layari. This

location shows As content of varying concentration in the fish flesh which are regularly distributed in the beach waters and also in those fishes which are of local occurrences but are of commercial importance. The highest content of As was noted in F-14, *Polydactyllus sexfilis* (0.015 ppm) which is commonly known as Dangi fish and is extensively utilized locally. Further West at locations 7 (Manora), 8 (Sands Pit), 9 (Hawks Bay) and 10 (Paradise Point) which are separated from Eastern beaches by the protruded landmass of Manora appear to act as a barrier so far as the pollutants distribution in beach water is concerned. This appears that the pollutants brought by River Layari poured on the Eastern side of the protruded landmass of Manora are localized. This is also reflected in the concentration of As in beach water samples of the locations 7 to 10, where the As content is either below the detection limit or if present, it is very little except at site PP 2 (0.067 ppm) of location No.10 where Karachi Nuclear Power Plant is situated. This pattern is very well reflected also in fish flesh samples except in F-1 of regular distribution and F-10 of sporadic occurrence which contain 0.001 ppm and 0.006 ppm respectively (Fig. 3).

The samples of locations 11 (Cape Monze), 12 (Hub) and 13 (Gadani) show very little content of As in fish flesh samples of F-1 to F-9 of regular distribution. In some of the samples like F-2 to F-4, arsenic was below detection limit (Fig. 3). Most probably this reflects their more migratory nature from one location to the other, and hence the absorption of As appears changing. The species from F-10 to F-15 which are of sporadic occurrence but of high commercial value are locally known as Bangda, Aal, Gurako, Bukko, Dhar Mahi and Pinn respectively and show the effects of pollutants being contributed in the beach water through River Hub which brings industrial pollutants from Hub Industrial Trading Estate and Hubco Thermal Power Plant situated at the mouth of River. The ship breaking industry on the West near Gadani beach is also a source of pollutants in beach water. The highest content of As was noted in F-10 (0.017 ppm) which most probably reflects to its capacity for absorbing higher arsenic as compared to other species.

Cadmium (Cd)

The concentration of Cd in fish flesh samples in beach waters show appreciable amount of Cd absorption of in beach waters at various locations. This relative increase in content of Cd in fishes as compared to beach water, most probably reflects differential absorption capacity for Cd in the fishes. This is very clearly indicated by the concentration of Cd in fish sample F-2 (*Opisthopterus tardoore*) that is of regular occurrence in study area and contains higher concentration of Cd in most of the locations except in location 3, 4 and 5. The other fishes of regular occurrences show variable concentration of Cd in their flesh.

Location No.1 marked as Keti Bandar (KB), which receives pollutants from the industrial wastes of Hyderabad and Kotri Cities through River Indus does not show higher concentration of Cd compared to adjacent location No.2 in the West. Most probably the effluents of location No.1 do not have higher content of Cd. Moreover, the influx of the effluents into the beach water in the deltaic area is relatively stronger and the interaction of beach water and the pollutant creates an environment to keep Cd in ionized condition for a longer period.

At location No.2 the beach water is relatively turbid, most probably due to industrial pollutants of six Thermal Power Plants, Pakistan Steel Mill and Port Bin Qasim which are the main contributors of Cd. It appears that Cd was partly taken up by the clay particles of turbid water in which the fishes flourish (Fig. 4). The lesser amount of Cd in beach water of location No.2 as compared to location No.1 and higher content of Cd in beach sediments of location No.2 as compared to location No 1 facilitates in describing the possible distribution of the element. It is also significant to note that the flesh of fish samples of location No.2 exhibits the highest content of Cd and reflects the content of Cd in beach sediments (Fig. 4). Variable degree of absorption of cadmium by the fish both of regular and sporadic distribution was observed all along the beach waters. Location No 3 (IH), 4 (GC) and 5 (C) on the western side of location No.2 (Ibrahim Hadiri, Gizri Creek and Clifton), show lower content of Cd in fish flesh samples as compared to location No.2, but higher than location No.1 (Fig.4).

It appears that the Cd content in sediments

and water of location No.2 affect these beaches. It is significant to note that the content of Cd in beach water of location No.2 is similar to a great extent to that of beach waters of locations 3 to 5, most probably due to free movement of beach water on low sloped sandy beaches free from geomorphic hindrances between these locations. The higher content of Cd in fish flesh samples of locations 2 to 5 appears to be related to the in-pouring effluents if industries like automobile batteries, textile, bleaching and painting, oil refinery etc as the main contributors of Cd from the coastal area. At location No.6 marked as Layari, the content of Cd in fish flesh samples is decreased as compared to locations up to 5 in the east, although River Layari pours its effluents into the beach water of this location.

The concentration of Cd in the flesh of the fish of this location goes down drastically (highest content of Cd in fish flesh samples of locations 3 to 5 is 0.174 ppm and at location No.6 it is less than 0.088 ppm (Fig. 4**).** The lower content of Cd in flesh of the fishes of this location as compared to sediment but lower than the beach water reveals the geochemical controls similar to location No.2 as described earlier. The movement of fishing boats, steamers and ships embarking at Karachi Port create agitating water conditions in which the fish population is expected to be disturbed to some extent. The activities in coastal water due to the factors mentioned above and the dilution of in-pouring pollutants of Layari River may be described as the possible causes. The absence of argillites which create turbidity in water and absorbs the heavy metals, the beach water of this location reveals higher content of Cd as compared to location No.2 where turbidity in water was relatively higher.

Minimum concentration of Cd was noted in the flesh of the fish from locations 7 to 10 on the western side of location No.6 (Fig. 4**).** In these locations, apparently no significant industrial pollutants are pouring into the beach water except sewage discharge of the limited population in the coastal area specially at location No.7 where Naval colony is situated and mangroves are present in the muggy area. The other possible source is the effluent of Karachi Nuclear Power Plant situated at location No. 10. The beach water is clear, agitating and full of human activities at the beaches. The beach water contains higher Cd as compared to the fishes both of regular distribution (F-1 to F-9) and of sporadic occurrences (F-10 to F15). The lesser content of Cd in the fishes of these locations may be attributed to the occurrence of gentle slope beaches both of sandy and mixed nature and open turbid free water movement. However, final conclusion needs further work in this regard. The fishes of locations 11 to 13 exhibit the second lowest content of Cd in their flesh (0.001-0.009 ppm (Fig. 4**).**

CONCLUSION

The highest concentration of As in fish flesh samples of location No.1 compared to other locations is certainly due to the presence of significant amount of As in the pollutants coming through River Indus. The locations 2, 6 and 10 also show higher concentration of As but less compared to location No.1. The concentration of As in these locations appear to be related to the in-pouring industrial and sewage effluents of Pakistan Steel Mill, Bin Qasim Thermal power Plants at location No.2, Layari River industrial effluents at location No.6 and the effluents of Karachi Nuclear Power Plant at location No.10. Significant As concentration was also noted at location No.4 due to the impact of industrial effluents brought by River Malir. The Cd level shows a marked variation which can be attributed to the local factors and geochemical control of the area. In most of the locations fish species *Opisthopterus tardoore* (F-2) appear to be more sensitive and absorb Cd to its highest concentration among the regularly distributed species. The fishes of sporadic occurrences also exhibit variable Cd concentration limits in their flesh.

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