Bull. Environ. Contam. Toxicol. (1994) 52:825–832

Environmental Contamination and Toxicology

Lead and Other Metals in Dried Fish from Nigerian Markets

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Received: 21 July 1992/Accepted: 24 October 1993

The Nigerian economy witnessed remarkable industrial growth between 1970 and 1980 due to a large increase in crude oil sales. Since then, industrialization and urbanization have been sustained albeit at a much slower rate. Nevertheless, waste management remains grossly underdeveloped. Environmental concern is only a recent phenomenon in the country, resulting thus far in the launching of a monthly clean-up campaign in 1984 and the establishment of the Federal Environmental Protection Agency (FEPA) in 1988. Even then, the level of public awareness has not been encouraging in spite of enlightenment programs initiated by the FEPA and other non-governmental organizations. The indiscriminate discharge of largely untreated factory and urban effluents has continued. Streets and home surroundings become littered again soon after the monthly clean-up exercises. Inadequate facilities contribute in no small measure to the unwholesome situation. Refuse collecting centers are mostly without any holding containers, and solid wastes, the focus of the monthly clean-up, are left on the bare ground. In addition, heavy automobile traffic and high lead content of the local automobile fuels have not helped matters.

Heavy metals in the human environment have been of global concern due to known hazards caused by many, such as mercury, cadmium and lead (FAO/WHO 1972; Nauen 1983). In many developed countries, limits of concentrations in fish and other foods have been set (Nauen 1983) in order to safeguard public health. Nigeria has yet to set any standards because of the paucity of baseline data. Within the last decade, scientists have been reporting on heavy metal levels in fish from the aquatic environment of Nigeria (Fodeke 1980; Kakulu et al. 1987; Okoye 1991). Okoye (1991) reported the relative enrichment of the Lagos Lagoon fish by nine heavy metals. Among the metals, lead was the most prominent, with a mean value comparable to the set limits in Great Britain and New Zealand (Nauen 1983).

The present study was aimed at further establishing the levels of contamination in fish by lead and other metals in the Nigerian aquatic systems. Smoke-dried fish, being the most consumed by the local population, was chosen for the survey on the levels of cadmium, cobalt, copper, chromium, iron, manganese, lead and zinc. Possible surface contamination arising from observed poor handling practices was also investigated.

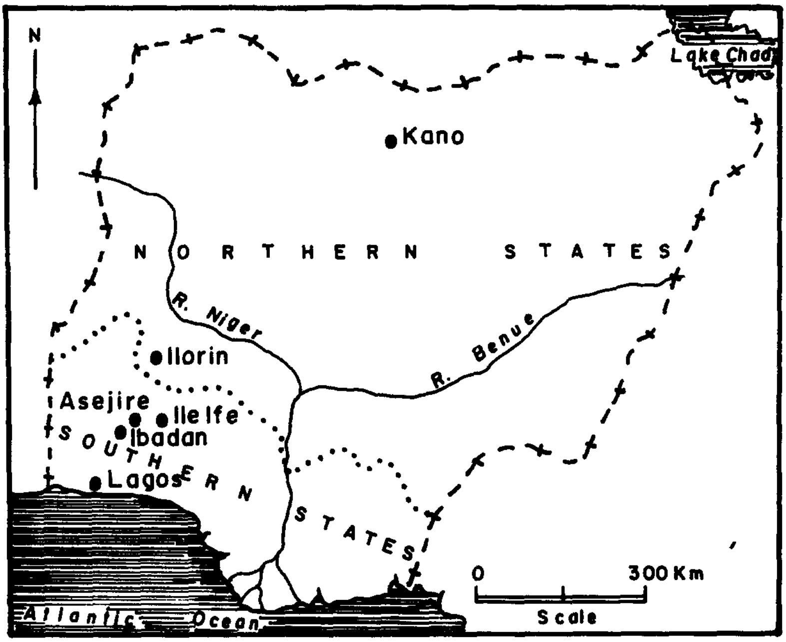

Figure 1: Map of Nigeria showing sampling stations

MATERIALS AND METHODS

A total of fifty-five fish samples was purchased from various markets located in the towns indicated in Figure 1. Smoke-dried Clarias lazera and Tilapia guineensis were purchased from markets in the southern towns of Asejire, Ibadan and Ile-Ife and in kano and Ilorin in the north. These were labelled "smoke-dried and exposed" (SDE) samples. Samples of Sardinella aurita, kiln-dried and packed in polyethylene bag, were purchased from the Lagos State Fisheries Board (LSFB) in Lagos and labelled "kiln-dried and not exposed" (KDN) samples. In addition, samples of fresh T guineensis were purchased from the commercial fish driers at the Asejire River bank and were dried at 80°C in the laboratory. These were packed in polyethylene and labelled "oven-dried and not exposed" (ODN) samples.

All whole fish samples were later dried at 105°C until constant weight. The heads, skin and muscle were separated and each part ground in a porcelain mortar. A 1-g portion of each ground sample was accurately weighed in a porcelain crucible, followed by the addition of 1 ml conc. HNO_3 , which was allowed to predigest the sample overnight, to minimize volatilization of metals such as cadmium and zinc during ashing. After carbonizing on an electric hot plate, the samples were ashed in a muffle furnace at 550°C for 4 hr. The ash was dissolved with 5 ml. HCl, filtered with whatman no.1 filter paper, into 25 ml standard flasks and diluted to the marks with distilled water. A blank solution was prepared by diluting 1 ml conc HNO_3 plus 5 ml HCl to 25 ml, and serially diluted mixed metal aqueous standards containing the same quantities of acids were also prepared. The metal concentrations were determined on a Pye Unicam model Sp 9 atomic absorption spectrophotometer with an air-acetylene flame. Surface contamination was investigated by comparing the ODN head and skin data with those of the SDE T guineensis samples from the same Asejire market; and by comparing both the ODN and the KDN data with those of the SDE.

RESULTS AND DISCUSSION

The results of the metal analyses are summarized in Table 1. A one way analysis of variance showed that metal concentrations in different body compartments (head, muscle and skin) varied significantly as follows: Cd, Co, Cu, Fe and Zn ($p<0.001$), Cr and Mn ($p<0.01$) and Pb ($p<0.05$). Applying the Duncan multiple range test to their mean values in the head, muscle and skin, muscle had relatively low levels ($p<0.05$). The head and skin showed comparable levels allowing for the grand mean values presented in Table 2.

The variations in metal concentrations (Table 2) could not be obviously ascribed to fish species, although C lazera showed generally lower metal levels than T guineensis and S aurita. There was also no evidence that the variations depended reasonably on fish group. Nonetheless, the KDN samples and the Ilorin and kano SDE samples showed high total metal content in comparison to the rest of the samples. The levels of cobalt, copper, chromium and zinc found in the heads and skins of the Asejire ODN and SDE T guineensis samples differed significantly ($p<0.05$), but the lower content of the ODN samples compared favorably with those of the Ibadan and Ile-Ife SDE samples. Lead concentrations did not vary as widely as the others, which might indicate that while point sources may exist for the other metals, lead contamination comes from diffuse non-point sources. Apparently, the metal levels varied with locality. This was confirmed by the results of the muscle analysis presented in Table 3. Jointly, Tables 2 and 3 show that manganese is peculiarly high in Asejire samples, in the same manner as iron in the Ilorin samples. The Lagos samples showed high values of cadmium, cobalt, copper and chromium. Personal observations of the local commercial fish driers at the Asejire River bank showed that they rarely cleaned the fresh fish adequately before smoke-drying. Usually, the dried fish on display in the markets were exposed to atmospheric deposition. These airborne particulates are known to be trace-metal enriched. Wilke et al (1984) reported that lead and cobalt levels of dust during harmattan (a dry dusty N.E. wind from the desert in W.Africa), in the Kano area were very high in comparison to their levels in the soils of the area. The above poor handling practices could possibly explain why ash solutions of the heads and skins of the KDN, the Ilorin and kano SDE samples and the heads of other SDE samples, left residues of sandy matter on filtration. Larger quantities were found in those of the Ilorin and Kano samples. The presence of the extraneous matter in the head and skin of the neatly packaged KDN samples is viewed partly as a manifestation of careless handling, mainly inadequate washing of the fresh fish before drying. This and tiny scales, present on the Lagos fish samples which were not removed before analysis, could account for the relatively high metal content of those samples. However, the occurrence of Cd,Co, Cu and Cr, metals whose main anthropogenic sources are wastes of industrial origin, at the relatively high levels

Table 1. Summary of mean values of heavy metals in dried fish from Nigerian markets.

Metal	Whole fish*	Head	Muscle	Skin
#Cd	0.45 ± 0.28	0.52 ± 0.22^{a}	0.26 ± 0.15^{a}	0.34 ± 0.25
#Co	0.99 ± 0.65	1.55 ± 0.62^{b}	0.70 ± 0.33^{bc}	1.34 ± 0.83^{c}
#Cu	2.59 ± 1.90	3.84 ± 2.37	1.83 ± 1.11^{d}	3.29 ± 2.18^{d}
@Cr	1.48 ± 0.67	1.65 ± 0.74^{e}	1.03 ± 0.37^{ef}	1.79 ± 0.66^{f}
#Fe	77.45 ± 74.32	113.52 ± 60.94^{g}	35.05 ± 30.63^{gk}	131.18 ± 88.83^{k}
@Mn	16.07 ± 15.25	34.69 ± 14.28^{p}	8.70 ± 11.20^{pq}	18.84 ± 12.29^{q}
$Pb	8.99 ± 4.20	10.36 ± 2.50^{r}	6.70 ± 2.30^{rs}	12.20 ± 4.99^{s}
#Zn	35.82 ± 17.20	38.99 ± 9.81	23.81 ± 6.43^{t}	54.87 ± 15.34^{t}

Values ± std deviations are in mg/kg, dry wt. *Overall mean values. Corresponding superscript denotes a significant difference (#$p<0.001$; @$p<0.01$; $\$p<0.05$).

in the fish samples, indicate the existence of point sources. Many water bodies in the Lagos area, including the Lagos Lagoon, are polluted with industrial wastes (FMHE 1981; Okoye et al 1991). It is very likely that the S aurita, a pelagic species common in Lagos and other coastal towns of Nigeria, were caught from one of the polluted waters.

The long dry season (October to May) prevalent in northern Nigeria, with the intensive harmattan between December and March, when dust deposition rate can reach 99 g/m^2 (Wilke et al 1984), is believed to contribute to the larger quantities of sandy matter and high metal content in the Ilorin and Kano samples. On the other hand, the south experiences a short dry season (December to February/march) with mild and brief harmattan. Thus, atmospheric deposition might be an important source of heavy metal contamination in dried fish only in the north. Broadly, the metal levels determined in this study could be classified to be low in the Ibadan and Ile-Ife samples, medium in the Asejire samples and high in the Lagos, Ilorin and Kano samples.

Table 4 compares metal contents obtained in the present study with values obtained from various studies in some African countries as well as some standards. No set standards were found for cobalt, chromium, iron and manganese levels in fish from the available literature. Cobalt and chromium occurred at lower levels than in the Lagos Lagoon fish (Okoye 1991), but much lower chromium level (0.17 mg/kg, dry wt) was reported by Suffern et al (1981) in Tilapia species grown in wastewater oxidation ponds at the Oak Ridge National Laboratory (ORNL) in the United States of America. Cobalt, chromium, manganese, iron and zinc are all essential as micronutrients in humans, but at high concentrations they become toxic. Chromium, for example, is carcinogenic when it occurs at elevated levels in food and water (Suffern et al.1981), and the World Health Organization (WHO) has set 0.05 mg/l as the guideline value for the metal in drinking water (Twort et al.1985). The levels of copper and zinc obtained in this study were far below the WHO standards and the values reported for the Lagos Lagoon fish, but compared well with values reported in other African

Table 2. Mean values of heavy metals from combined data of head and skin analyses in fish of various species, groups and localities.

	Cd	Co	Cu	Cr	Fe	Mn	Pb	Zn.
S aurita (KDN) n = 4								
Lagos	0.58 ± 0.31	2.50 ± 0.12	3.30 ± 2.22	2.63 ± 0.44	60.27 ± 45.10	11.93 ± 4.16	13.45 ± 2.41	49.17 ± 4.34
T guineensis (ODN) n = 4								
Asejire	0.19 ± 0.22	0.63 ± 0.23	1.32 ± 0.28	1.40 ± 0.58	44.91 ± 7.25	35.39 ± 13.83	8.31 ± 2.22	37.04 ± 10.95
T guineensis (SDE) n = 8								
Asejire	0.12 ± 0.15	1.48 ± 0.74	4.15 ± 2.24	2.28 ± 1.14	44.45 ± 10.45	37.71 ± 24.44	9.34 ± 3.41	43.58 ± 9.64
Ilorin	0.65 ± 0.13	0.76 ± 0.88	5.71 ± 2.53	1.58 ± 0.23	253.32 ± 40.36	26.78 ± 8.22	13.48 ± 1.00	65.48 ± 27.15
C lazera (SDE) n = 16								
Ibadan	0.25 ± 0.30	1.24 ± 0.40	4.41 ± 1.85	0.45 ± 0.53	145.64 ± 20.40	21.06 ± 14.00	9.85 ± 1.70	40.73 ± 16.20
Ile-Ife	nd -	0.73 ± 0.84	1.65 ± 0.89	0.68 ± 0.80	143.06 ± 19.13	15.49 ± 10.60	9.83 ± 3.43	48.84 ± 8.18
Ilorin	0.55 ± 0.07	0.67 ± 0.27	3.60 ± 0.70	1.42 ± 0.13	208.17 ± 47.28	28.31 ± 7.22	12.28 ± 1.39	52.22 ± 18.48
Kano	0.25 ± 0.11	1.51 ± 0.37	6.70 ± 1.92	2.25 ± 0.26	155.51 ± 21.64	39.36 ± 17.18	12.73 ± 2.14	56.63 ± 6.16

Values ± std deviations are in mg/kg,dry wt. KDN, ODN and SDE are groups according to handling. nd = not detectable, n = number of composite samples.

countries. The average iron content of 35.05 mg/kg is far below the value obtained for the Lagos Lagoon fish, but comparable to the average value (34.11 mg/kg) in cooked beef (Martin 1971).

Based on the 15% maximum absorption of iron from fish sources, and the estimated daily dietary requirement of about 1 mg absorbed Fe for normal adult man and woman (non-menstruating) having average body weights of 65 kg and 55 kg, respectively (WHO 1970), the fish samples could serve as good sources of dietary iron. The average manganese content of 8.70 mg/kg is low compared

Table 3. Mean values of heavy metals in dried fish muscle samples.

	Cd	Co	Cu	Cr	Fe	Mn	Pb	Zn
S aurita (n=6)								
Lagos	nd	0.75 ± 0.14	3.84 ± 0.49	1.19 ± 0.26	20.25 ± 5.66	2.34 ± 0.31	6.56 ± 0.46	26.65 ± 2.70
C lazera(n=28)								
Asejire	0.16 ± 0.07	1.03 ± 0.14	0.95 ± 0.50	1.20 ± 0.20	38.99 ± 18.77	31.82 ± 22.37	4.46 ± 1.20	24.76 ± 3.39
Ibadan	nd	0.66 ± 0.27	0.82 ± 0.18	nd	21.63 ± 5.52	3.76 ± 2.82	6.87 ± 1.27	20.69 ± 2.90
Ile-ife	0.35 ± 0.05	0.49 ± 0.24	1.74 ± 0.60	1.22 ± 0.41	36.56 ± 7.85	3.76 ± 1.99	7.95 ± 1.15	25.48 ± 0.92
Ilorin	0.45 ± 0.18	0.56 ± 0.35	1.81 ± 1.15	1.13 ± 0.21	86.26 ± 61.61	9.30 ± 7.02	9.83 ± 4.04	32.44 ± 7.38
Kano	0.15 ± 0.06	0.95 ± 0.45	2.28 ± 0.37	1.35 ± 0.50	24.28 ± 3.38	4.41 ± 1.12	6.73 ± 1.01	18.97 ± 1.72
T guineensis (n=21)								
Asejire	0.22 ± 0.19	0.99 ± 0.12	2.42 ± 0.40	0.79 ± 0.17	16.20 ± 9.04	9.54 ± 5.58	4.86 ± 1.09	13.52 ± 2.62
Ibadan	0.23 ± 0.02	0.38 ± 0.25	0.78 ± 0.20	nd	18.37 ± 1.91	6.92 ± 1.39	5.17 ± 0.78	22.83 ± 3.07
Ilorin	0.34 ± 0.04	0.66 ± 0.13	2.70 ± 0.80	0.53 ± 0.22	69.65 ± 6.36	5.56 ± 2.37	9.31 ± 1.16	32.06 ± 3.53

Values ± std. deviations are in mg/kg dry wt., nd = not detectable, n= number of samples.

to the values reported for the Lagos Lagoon fish and in Zimbabwe (Table 4), but comparable to the average concentration (8 mg/kg, dry wt) found in vegetables (McLeod and Robinson 1972). Cadmium and lead are practically non-beneficial elements and toxic to humans at low levels. Cadmium damages liver and kidney while lead causes encephalopathy, anemia and renal problems (FAO/WHO 1972). Cadmium was found at very low levels. The average lead concentration (6.70 mg/kg) is high in comparison to the British standard of 5 mg/kg in dried fish (Nauen 1983) and elevated in comparison to the WHO limit of 8 mg/kg; with the

Table 4: Average heavy metal concentrations (mg/kg, dry wt) in fish muscle from the present study and values[a] obtained from set standards and other studies.

Present study		WHO[b] stds	Niger[b] Delta (Nig)	Lagos[c] Lagoon	Coastal[d] water (Ghana)	Lake[e] (Egypt)	Lake[f] (kenya)	Lake[g] (Zimb)
Cd	0.26	8.0	0.12	nd	0.4-1.2	0.016	0.32	0.08
Co	0.70	-	–	2.62	–	–	–	–
Cu	1.83	120	2.80	28.24	0.8-22.4	7.08	1.36	4.32
Cr	1.03	-	–	3.54	–	–	–	–
Fe	35.05	_	21.60	382.00	–	–	10.40	–
Mn	8.70	–	4.40	37.42	–	_	1.72	21.60
Pb	6.70	8.0	1.92	9.00	0.8-2.6	2.68	2.96	0.68
Zn	23.81	4000	19.20	74.78	2-64	29.60	18.40	38.40

[a]Original values in fresh wt x 4, dry wt, based on 75% moisture content obtained in fresh T guineensis [b]Kakulu et al. (1987); [c]Okoye (1991); [d]Biney (1985); [e] El Nabawi et al. (1987); [f]Wandiga and Onyari (1987); [g] Greichus et al.(1978), nd = not detectable, Zimb = Zimbabwe.

values reported in other African countries (Table 4), it is extreme. This survey corroborates high lead values reported for Lagos Lagoon fish (Okoye 1991), indicating serious lead contamination in Nigeria, the low content of the Niger Delta fish (Kakulu et al. 1987) notwithstanding. This is no surprise in view of the high lead content of local automobile fuels, as confirmed by a recent analysis which gave average values of 0.64 g Pb and 0.45 g Pb per liter of petrol and diesel oil, respectively. The state of affairs is offensive, especially as the world trend has moved toward drastic reduction or total elimination of lead tetraethyl additive in automobile fuels (Arah 1985). The present level of lead in fish may not cause immediate hazard to the consumer, but if the indiscriminate discharge of untreated industrial wastes into aquatic systems is continued and the high lead levels of local automobile fuels are not curtailed, lead pollution may become an increasingly important problem in Nigeria.

Acknowledgment. The author thanks Dr. K.O. Ipinmoroti, of Chemistry Department, F.U.T., Akure, for lead values of local automobile fuels.

REFERENCES

Arah RO (1985) Lead-free gasoline in Nigeria by year 2000. Proc 4th Int Seminar on Petroleum Industry and the Nigerian Environment, Fed Min Works Housing/Nig Nat Pet Corp Kaduna, Nigeria, 339-346

Biney CA (1985) Analysis of heavy metals in fish from coastal waters in Ghana, FAO/WACAF 2 Newsl,Rome 2: 5

El Nabawi A, Heinzow B, Kruse H (1987) As, Cd, Cu, Pb, Hg and Zn in fish from the Alexandria Region, Egypt. Bull Environ Contam Toxicol 19: 889-897

FMHE, Federal Ministry of Housing and Environment (1981) The state of the environment in Nigeria: Industrial waste management, Monogr Ser no.1, Lagos, Nigeria, 87-100

Fodeke VA(1980) Heavy metal and microbial contamination of Tilapia species in

Lagos Lagoon. M Sc Dissertation, University of Lagos, Lagos, Nigeria
FAO/WHO, Food and Agricultural Organization/World Health Organization (1972) Evaluation of certain food additives and of contaminants Hg, Pb and Cd. 16th report, Rome, 84 p
Greichus Y, Greichus A, Draayer HA, Marshal B (1978) Insecticides, Polychlorinated biphenyls and metals in African Lake ecosystem II. Lake McLlwaine, Rhodesia. Bull Environ Contam Toxicol 19: 444-453
Kakulu SE, Osibanjo O, Ajayi SO (1987) Trace metal content of fish and shellfishes of the Niger Delta area of Nigeria. Environ Int 13: 247-251
Martin EA (1971) Nutrition in action. Holt, Rinehart and Winston Inc, New York, 133-160
McLeod BE, Robinson MF (1972) Dietary intake of manganese by New Zealand infants during the first six months of life. Brit J Nut 27:229-232
Nauen CE (1983) Compilation of legal Limits for hazardous substances in fish and fishery products. FAO Fish Circ. 764, Rome, 5-90
Okoye BCO (1991) Heavy metals and organisms in the Lagos Lagoon. Int. J Environ Stud. 37:285-292
Okoye BCO, Afolabi OA, Ajao EA (1991) Heavy metals in the Lagos Lagoon sediments. Int J. Environ Stud 37:33-41
Suffern JS, Fitzgerald CM, Szluha AT (1981) Trace metal concentrations in oxidation pond. J Wat Pollut Con Fed 53: 1539-1608
Twort AC, Law FM, Crowley FW (1985) Water supply. 3rd ed, Arnold Publ Co Ltd, London 222-223
Wandiga SO,Onyari JM (1987) The concentrations of heavy metals: Mn, Fe, Cu, Zn, Cd and Pb in sediments and fish from the Winam Gulf of Lake Victoria and fish bought in Mombassa town markets, Kenya J Sc Ser A 8: 5-18
Wilke BM, Duke BJ, Jimoh WLO (1984) Mineralogy and chemistry of harmattan dust in northern Nigeria Catena 11:91-96.
WHO, World Health Organization (1970) Requirements of ascorbic acid, Vitamin D, Vitamin B_{12}, folate and iron. Tech Rep Wld Hlth Org no 452, Rome, 75p.