

Organochlorine Pesticides in Water, Sediment, and Fish of Paranoá Lake of Brasília, Brazil

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Paranoá Lake is a man-made reservoir, created in 1959 with the city of Brasília, the capital of Brazil. The lake has a surface area of 38 Km² and an watershed area of 1046 Km², of which approximately 8% is agricultural. Around 450,000 people live in the catchment area. Contamination of Paranoá Lake and other water systems with organochlorine (OC) insecticides has been reported (Dianese et al., 1976; Ministério da Agricultura, 1979; Gold-Bouchot, 1995), and is mainly due to the runoff of the chemicals applied in agriculture.

Although the use of organochlorine insecticides in agriculture was prohibited in Brazil in 1985, their illegal use continued for many years after. The chemical stability of these compounds, their high lipid solubility and toxicity to human and animals (Bouwman et al., 1990), have led government and researchers to be concerned with their presence in the environment. The aims of this work are to evaluate the level of Paranoá Lake contamination by OC compounds (insecticides and PCBs) and to assess the potential health risk posed to consumers from the exposure to OC through the ingestion of fish grown in the Lake.

MATERIALS AND METHODS

All solvents used were pesticide residue grade with no further treatment. Standards of pesticides (α , β and γ HCH, p-p'DDE, o-p'DDT, p-p'DDT, p-p'DDD, endrin, aldrin, dieldrin, endosulfan I and II, and endosulfan sulfate) and PCBs (tri, penta and hexachlorinated) were obtained from U.S. Environmental Protection Agency (EPA). The samples were taken from 10 points (A1, A2, B1, B2, C1, C2, D1, D2, E1, and E2) from 5 areas of the Lake, divided according to its limnologic characteristics (Figure 1). Water and sediment were sampled in July 1995 (dry season) and February 1996 (rain season). Fish samples were taken from August to October 1995 (dry season) and March to May 1996 (rainy season).

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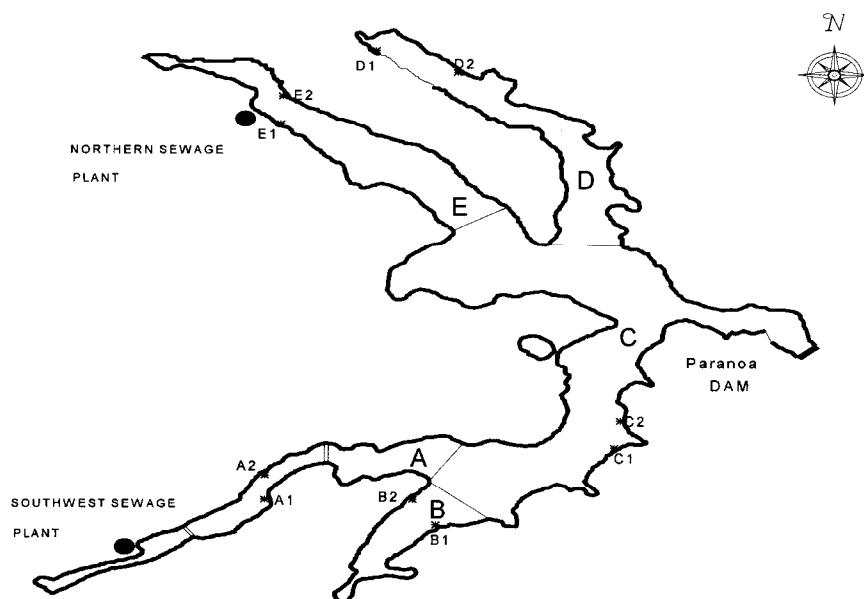


Figure 1. Paranoá Lake and the sampling points

One liter water samples were collected at the surface of the lake and at 1 meter deep into Kemmeder jars (40 samples) and kept refrigerated until analysis. Approximately 2 kg of sediment samples were collected using a Elkman dredge (20 samples). Sediment samples were dried at room temperature, ground, homogenized and kept at room temperature until analysis. Fish samples were captured (1-2 kg/sample, 120 samples), wrapped in aluminum foil and kept at -20°C until analysis. Size of individuals within the same specie did not vary significantly. Seven species were selected for this study: Readbreast Tilapia (*Tilapia rendalli*), Nilo Tilapia (*Oreochromis niloticus*), Carp (*Cyprinus carpio*), Tucunaré (*Cichla ocellaris*), Bagre (*Rhamdia sp.*), Saguiru (*Steindachnerina elegans*) and Traira (*Hoplias malabaricus*).

A modified APHA (1975) method was used for water samples extraction, using n-hexane/dichloromethane. Clear samples were injected directly into the GC, while others required a clean-up procedure with previously activated florisil. The sediment samples were extracted according to Steinwantder (1990). Water and sediment extracts showing a broad peak in the beginning of the chromatogram were treated with copper for the reduction of sulfur interferences (Wang et al, 1980). Sections of dorsolateral muscle of fish samples were prepared according to Steinwantdter (1982). To estimate the lipid content of the fish species, four

samples of each specie were analyzed for the extractable lipid, using petroleum ether in a Soxhlet apparatus.

All samples were analyzed in a Finnigan 9001 gas chromatograph with a 1.5% OV17 + 1.95% QF-1, 2 m packed column and electron capture detector (ECD) with Ni^{63} source. Positive samples were re-injected into a CG-Master gas chromatograph (CG Analitica Ltda, Brasil) with a 5% OV-210 packed column and ECD for confirmation. A standard curve containing the insecticides and PCBs was freshly prepared and run daily in both instruments. Limits of detection for the chlorinated compounds were in the range of 0.2 - 1.2 pg. Recoveries for sediment averaged $86.7\% \pm 14.9$ and for fish $92.8\% \pm 7.6$. All results for fish and sediment are based on wet and dry weights, respectively. Systat 5.0 for Windows was used to perform Univariate Analysis of Variance (ANOVA).

RESULTS AND DISCUSSION

PCBs, endosulfan, endrin or aldrin were not found above the limit of detection in any sample analyzed. Table 1 shows the range of HCHs, heptachlor epoxide and dieldrin found in the samples. Due to the low water solubility of the organochlorine compounds, it is expected that any OC present in the lake will be preferable adsorbed to sediment or bioaccumulated in fish. Indeed, only HCHs were detected in water, and the levels of these compounds were considerably higher in sediment and fish. Fish samples had more frequent detections and higher levels of heptachlor epoxide, dieldrin and DDTs than did sediment samples (Table 1). While only p-p'DDE was detected in sediment (60% of the samples), at levels ranging from 0.52 to 12.6 $\mu\text{g/kg}$, DDTs were present in 98% of the fish samples, at levels up to 77.7 $\mu\text{g/kg}$. Dianese et al. (1976) found dieldrin concentration in fish of the Paranoá Lake up to 700 times higher than in sediment. Gold-Bouchot et al. (1995) also found higher OC insecticides residues in biota (shrimp, oysters and mussels) than in sediment of the Palizada river, Mexico.

In fish samples where both a HCH and lindane (γ HCH) were detected, the first isomer represented, on average, 75.9% of total HCH. This result agrees well with the fact that technical HCH contains 55 - 70 % of a HCH (Brooks, 1974). Within the DDT series, p-p'DDE, the most stable isomer, accounted for 32.4 to 95.5% of the total DDT complex (79.6 % average), an indication of non-recent exposure. Zabik et al. (1995) also found that over 80% of DDTs detected in walleye and white bass harvest from Great

Table 1. Residue levels of organochlorine pesticides in Paranoá Lake

Matrix (samples analyzed)	H C H^{1,2}	Heptachlor hepoxide¹	Dieldrin¹
Water (40), µg/L	0.001– 0.052 (13)	nd	nd
Sediment (20), µg/kg	0.49 – 0.90 (2)	0.14 – 2.0 (7)	nd
Fish (120), µg/kg	0.20 – 17.6 (24) ³	0.94 – 6.0 (12)	1.3– 7.4 (2)

¹Number in parenthesis corresponds to positive samples; ²α HCH and/or lindane; ³β HCH was detected in one sample; nd = below the limit of detection

Table 2. Residue levels of DDTs' in fish from Paranoá Lake (µg/kg ww)

Specie	Total²	Dry ± sd (n)	Rainy ± sd (n)
Saguiru	16.2 ^a ± 18.1	25.8 ± 20.6 (10)	5.4 ± 3.4 (9)
Traira	2.6 ^b ± 2.5	3.0 ± 1.8 (6)	2.4 ± 2.8 (9)
carp	1.1 ± 4.7	10.4 ^c ± 3.7 (10)	3.6 ^d ± 3.1 (10)
Bagre	18.1 ^a ± 14.2	18.2 ± 2.1 (4)	12.5 ± 14.7 (6)
Tucunaré	16.9 ^a ± 18.3	18.8 ± 18.4 (9)	6.6 ± 3.0 (8)
Nilo tilapia	7.3 ± 7.1	13.5 ^c ± 6.1 (10)	2.1 ^d ± 2.1 (10)
Redbreast tilapia	4.5 ^b ± 2.8	5.8 ± 3.1 (10)	2.4 ± 1.3 (9)
All species		14.9 ^c ± 15.1 (59)	5.0 ^d ± 6.3 (61)

¹DDTs = p-p'DDE, o-p'DDT, p-p'DDT, p-p'DDD; ²samples from dry and rainy season; n=number of samples; a is significantly different from b; c is significantly different from d.

Lakes was p-p'DDE. On the other hand, the ratio between DDT and its breakdown products was high in fish collected in locations with recent history of aerial spraying of DDT in Lake Kariba, Zimbabwe (Berg et al., 1992).

There was no correlation between the level of residues in fish, sediment or water and sampling point or area in the Lake. However, total DDT levels varied significantly among fish species. The bottom feeder saguiri and the predatory bagre and tucunare had residues significantly higher than the herbivorous redbreast tilapia ($p=0.027$, 0.012 and 0.001 , respectively) (Table 2). This variation is probably due to different feeding and living habits. Predatory fishes might bioaccumulate OC compounds by eating other fishes, while the constant contact of bottom feeders with the sediment allows their continuous exposure to the adsorbed pesticides. Kent et al. (1974) found that Utah sucker (*Castomus ardens*), a bottom feeder,

contained the highest level of organochlorine compounds in the American Fall Reservoir. Berg et al. (1992) also found 3 to 10 times higher levels of DDT in the predatory tiger-fish than in the zooplankton feeding karpenta and the redbreast tilapia.

Data from the National Contaminant Biomonitoring Program in major US rivers and the Great Lakes found no differences between OC residues in bottom feeders and predators (Kidweel et al., 1995). The authors suggested that monitoring program costs can be lowered by conducting the studies using only one of the trophic guilds. However, in the Paranoá Lake, DDT residues in traíra, a predatory fish, were significantly lower than in the predatory bagre and tucunare ($p < 0.001$ and $p = 0.01$, respectively) and in the bottom feeder saguiri ($p < 0.001$). Furthermore, a decision on which species should be sampled in studies to assess OC contamination might depend on the water system.

All the water samples containing HCH and 50% of HCH positive fish and sediment were collected during the rainy season. On the other hand, 5 of the 7 sediment samples and all the fish samples of which heptachlor epoxide was present were collected during the dry season (Table 1). Within the DDT series, considering all species together, residues in samples collected during the dry season were significantly higher ($p < 0.001$) than the ones collected during the rainy season (Table 2). The same pattern was found individually for the species carp and nilo tilapia (Table 2). Factors that might explain these results include concentration of the pesticides, which can occur during the dry season, and different living habits of the fishes between the seasons. Fish moves less at lower temperatures, which occurs during the dry season in Brasília. This less mobile behavior can lead to an increase of fish body fat content and, consequently, to a greater OC uptake.

The average values of OC residues in fishes from Paranoá Lake found in this study are summarized on Table 3, with the results from two other studies conducted in the Lake (Dianese et al., 1976; Ministério da Agricultura, 1979). The levels of HCHs, lindane and dieldrin are comparable in the three studies, while the study reported in 1979 presented higher levels of DDTs. Although there was less agricultural activity in the Paranoá basin during the 1970's, OC compounds were widely used. After 1985, when the use of these compounds were no longer allowed, the situation changed, with increasing agricultural activity and decreasing of OC use.

Table 3. Average¹ of OC values found in Paranoá Lake fish².

Compound	1976 ³ mg/kg fat	1979 ⁴ µg/kg ww	This study µg/kg ww mg/kg fat ⁵		MRL ⁶ mg/kg fat
DDTs	2.1 ± 0.39 (3)	96.1 ± 105 (22)	9.9 ± 12.5 (114)	1.4 ± 1.9	5.0 ^{7,8}
HCHs		5.14 ± 6.7 (22)	1.8 ± 8.9 (24)	0.46 ± 2.8	
lindane	0.09 ± 0.12 (1)	0.34 ± 0.83 (9)	0.14 ± 0.52 (24)	0.02 ± 0.05	2.0 ^{7,9}
aldrin		1.63 ± 3.09 (14)	nd		
dieldrin	0.17 ± 0.20 (2)	1.1 ± 4.1 (2)	0.08 ± 0.71 (2)	0.02 ± 0.17	0.3 ⁷ , 0.2 ⁹
heptachlor		0.15 ± 0.68 (1)	nd		0.02 ⁷
heptachlor epoxide			0.46 ± 1.4 (12)	0.10 ± 0.34	0.2 ^{9,10}

¹Non detected was considered zero for average calculation; ²values in parenthesis correspond to number of positive samples; ³3 samples; ⁴22 samples; ⁵based on fat content (0.53 to 1.8%); ⁶except for EPA, all MRLs are for mammalian meat; ⁷Brazilian legislation; ⁸EPA; ⁹Codex Alimentarius; ¹⁰heptachlor +heptachlor epoxide

In assessing the potential health risk that dietary pesticides poses to consumers, four set of data should be evaluated: the local diet, the residues in food, the maximum residue level permitted (MRL) and the accepted daily intake (ADI) for the pesticide (Winter, 1992; WHO, 1997). The levels of DDTs, lindane, dieldrin and heptachlor epoxide found in fish of Lake in this study were below the MRLs for fish or mammalian meat established by Brazilian Legislation, Environmental Protection Agency (EPA, USA) or Codex Alimentarius (Table 3). The Maximum Daily Intake (MDI) of OC detected in this study from consumption of fish from the Lake can be estimated multiplying the maximum residue level found by the estimated daily consumption of fish in Brasilia (0.050 kg). When the MDI is compared to the ADI (%ADI) (Table 4), we find that consumption of Paranoá fish does not contribute significantly to the ADI of the OC compounds. The chemicals contributing to the highest percentage of ADIs, dieldrin and heptachlor epoxide, compounds which were detected in only 1.6 and 10% of the samples analyzed, respectively.

Table 4. Maximum intake of organochlorine insecticides through consumption of fish from Paranoá Lake

Compound	MDI (µg/person/day)	ADI¹ (µg/person/day)	% ADI
DDT	3.9	1200	0.32
lindane	0.25	480	0.05
dieldrin	0.37	6.0	6.2
Heptachlor epoxide	0.30	6.0	5.0

¹Codex Alimentarius (1996)

Recently, the Joint Meeting on Pesticide Residue (FAO/WHO JMPR) estimated the Theoretical Maximum Daily Intake (TMDI) of lindane, based on the Codex MRLs and total diet from 5 world geographic regions (FAO, 1998, not published). The %ADI varied from 381 in the African diet to 1236 in the European diet. The Latin American diet had a %ADI of 542, with cereal grains and mammalian meat contributing the most (200 and 145%, respectively). There is no Codex MRL established for lindane in fish. From the 37 pesticides studied, only 4 had % ADI higher than 100 in one or more diet, and lindane, the only persistent OC in the list, was the pesticide with the highest values. These results show that, although lindane has been banned for agriculture use in many countries, its level in food might be of a human health concern, necessitating the need for continued monitoring studies.

In conclusion, we found that the level of organochlorine pesticide contamination in the Paranoá Lake is relatively low, and it is unlikely that the ingestion of fish from this aquatic system will pose any health risk to consumers. However, monitoring programs should continue in order to control and maintain the quality of the Lake environment.

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