

Chapter 9

Metals, Pesticides and Other Persistent Contaminants in Water, Sediments and Biota from Lake Malawi¹

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I. Persistent organochlorine chemicals in air and water from the Lake Malawi area: a preliminary report

Introduction

A critical question addressed by the Lake Malawi/Nyasa Biodiversity Conservation project was the state of water quality in the lake and trends in contaminants. Previous work has examined nutrients and basic water chemistry parameters on a lake wide basis but not microcontaminants such as PCBs and organochlorine pesticides. Import surveys for Malawi indicate that some of the persistent organochlorine (OC) pesticides continue to be used, e.g. aldrin, lindane (γ HCH) and endosulfan, or are used inadvertently because they are impurities in some widely used pesticides, e.g. DDT which has been found in dicofol, and hexachlorobenzene (HCB) which is found in chlorthal-dimethyl and lindane (Bailey 1998). DDT is still used in southern Africa for malaria vector control. Along with organochlorine pesticides, PCBs continue to be used as flame retardants in older (pre 1980's) electrical equipment and hydraulic systems. Organochlorine chemicals are very persistent in soil, air and water. They can evaporate from agricultural soils or building surfaces, move long distances in the atmosphere and be deposited in a region far from the original source. Because of their transport in the atmosphere, systems such as Lake Malawi may be receiving inputs of these pollutants from outside of its watershed and from direct inputs from usage in Malawi, Tanzania or Mozambique. The objective of this study was to analyse water, air and precipitation samples for persistent organochlorines in order to determine inputs to the lake from the atmosphere, the state of equilibrium between air and lake water, and possible sources of these contaminants.

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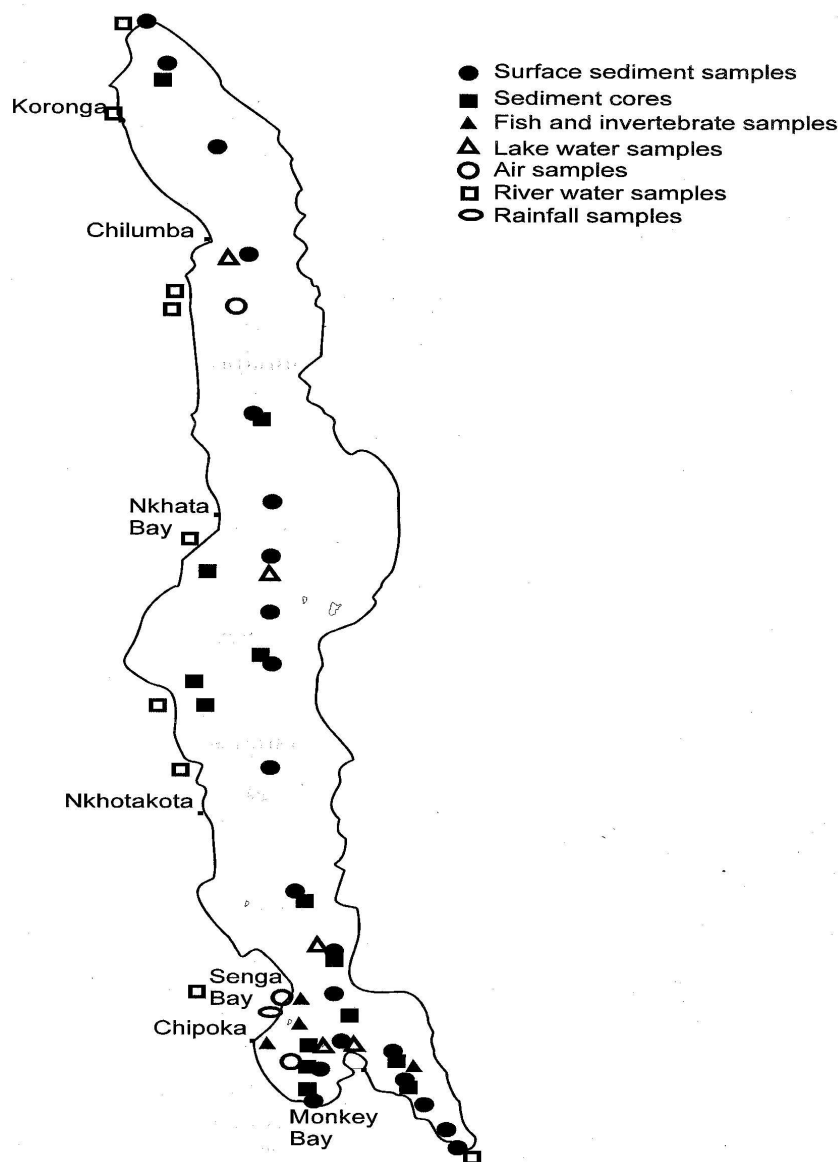


Figure 9.1. Locations for contaminant sampling in 1996 and 1997.

Methods

Water: Large volume water samples were collected from Lake Malawi during cruises in May 1996, February 1997 and May 1997 (see Figure 9.1). When time allowed, water surface approximately 1 m depth) was collected either directly using a submersible pump which pushed water directly through a filter (1 μ m glass fibre) and XAD extraction column at about 100 mL/min. Alternatively, surface water was pumped directly into 18 L stainless steel solvent-rinsed pepsi jars and then extracted through the filter and XAD column shortly thereafter. The extraction column was purchased pre-cleaned from AXYS Analytical (Sidney, British Columbia, Canada). Deep water samples (40 and 80 m depth) were obtained by mooring two automated Infiltrex samplers (AXYS Analytical) each equipped with a filter (1 μ m) and XAD column. All water sample volumes were 80 L. Blank or control samples consisted of XAD columns taken on the cruise and attached to the extraction apparatus but not used for sample collection.

Air: Samples were collected with a high volume air sampler (General Metalworks PS-1) using polyurethane foam plugs (PUF) preceded by a GF/A glass fibre filter to trap particulate matter. The sampler was set up at the Senga Bay research station and samples were collected from February 1997 until May 1998. Twenty-four hour air samples were also collected on two cruises (February and May 1997; see Figure 9.1). The PUF sample consisted of separate front and back PUFs in order to examine the extent of breakthrough of more volatile organochlorines at the relatively high air temperatures in Senga Bay. Filters and PUFs were pre-cleaned in Winnipeg and shipped to Senga Bay for sample collection. Filters were cleaned by heating for 18 hours at 265 °C. PUF plugs were pre-cleaned by Soxhlet with hexane for 24 h. Approximately 250 m³ of air was drawn through the sampling unit over a 24 h period every 13 days. Filters were placed in methanol rinsed tin foil and then into separate Whirlpak polyethylene bags, and sealed and stored at 4°C until extraction and analysis. Blank PUFs were placed in the sampler for 10 seconds and then into pre-cleaned glass jars with teflon lids for storage. Sample PUFs were stored in the same manner as the blank PUFs.

Precipitation: Rainfall was collected using an automated wet-only sampler (0.2025 m² collection area) (Meteorological Instrument Centre, Mississauga, ON) set up at Senga Bay. The sampler was equipped with an XAD column for direct extraction of OCs from the rain. Rain water was filtered through a glass wool plug at the bottom of the collection basin, for removal of large particles (e.g. leaves). Columns were prepared at NWRI (Burlington) with pre-cleaned XAD-2, sealed and then shipped to Senga Bay. The columns remained on the sampler until 10 cm of rain had fallen. They were then sealed and stored at Senga Bay for eventual return to Winnipeg or Burlington.

Extraction and quantitative analysis: All extraction and analyses of these samples were done either at the Freshwater Institute in Winnipeg, Manitoba or at the National Water Research Institute in Burlington, Ontario, Canada. The XAD columns for the large volume water samples were first eluted with methanol followed by dichloromethane (DCM). The combined elutions were evaporated to 5mL and diluted with water. The OCs were then partitioned into hexane. The hexane extract was cleaned up on a Florisil column which separated PCBs (hexane elution) from most OC pesticides (AXYS Analytical 1995). Internal standards of PCB30 and OCN were added to the column prior to elution. Blank XAD columns were processed in an identical manner. The extract was taken up in hexane and applied to a Florisil column (8 g, 1.2% deactivated with water) which was eluted as described for fish (see food web section). Florisil eluates were analysed by capillary gas chromatography (GC) with ⁶³Ni electron capture detection on a 60 m x 0.25mm DB-5 column using Varian 3400 or 3600 GC (Varian Instruments Palo Alto CA) and H₂ carrier gas. OC pesticides and PCBs were quantified using external standards. PCBs were quantified using a series of congener mixtures obtained from National Research Council of Canada (Halifax NS) and from Ultra Scientific (Hope RI). Total PCBs (Σ PCB) represents the sum of 100 individual PCBs (including co-eluting compounds) and is presented as totals, individual PCBs and homologue groups (groups with one through nine chlorines on the PCBs). We also quantified hexachlorobenzene (HCB; a microcontaminant in some pesticide formulations), the multipurpose pesticides chlordane (Σ CHL), hexachlorocyclohexane (Σ HCH), dieldrin, endosulfan, and Σ DDT. Concentrations of the main individual components found in Σ CHL (*trans*- and *cis*-chlordane), Σ HCH (α and γ HCH), Σ DDT (*p,p'*- and *o,p'*-DDT and breakdown product *p,p'*-DDE) of these pesticides are also shown.

Results and Discussion

Organochlorines in lake water: PCBs and OC pesticides were detected at low concentrations in surface and subsurface water from Lake Malawi. Table 9.1 presents results for samples collected in May 1996 and February 1997. Samples collected in May 1997 have not yet been analysed. PCBs were the major organochlorine in surface waters and ranged in concentration from 165 to 854 pg/L (uncorrected for blank contamination). Lower levels, 70-187 pg/L were found at 80 m depth. PCBs were also found in XAD blanks at concentrations of 59 to 165 pg/L. Therefore, it is likely that PCBs are below method detection limits (approximately 100 pg/L) in deep waters of Lake Malawi.

The PCBs in surface waters consisted mainly of tri- and tetrachlorobiphenyls such as CB 18, 31, 28 and 52 (Table 9.1). The profile of congeners in the blanks was quite different from lake water, and

consisted mainly of tetra, penta and hexachlorobiphenyls which indicates that contamination was probably from a different source, possibly introduced at the extraction step rather than in the field.

The OC pesticides were present at much lower levels than PCBs in Lake Malawi surface waters with the exception of the sample taken in south Lake Malawi in February 1997 which had relatively high DDE and chlordane (CHL) isomers (Table 9.1). Consistently higher levels of Σ DDT and Σ CHL were found in surface waters compared with 40 and 80m depths. Levels of Σ DDT and Σ CHL at 40 and 80 m were near or at levels in blank samples. With the exception of one surface water sample mentioned above, DDT isomers consisted mainly of the two insecticidally active components, p,p'-DDT and o,p'-DDT (Table 9.1) suggesting a new source of DDT. Blanks for DDT were low and did not resemble the pattern of isomers in lake water suggesting it may have been introduced during extraction rather than sample collection. Σ CHL consisted mainly of trans-chlordane, heptachlor and several minor hepta- and octachloro components of technical chlordane (MC1, MC2, MC3) (Dearth and Hites 1991) but low levels of nonachlor isomer. This pattern of components also implies a local source possibly of heptachlor.

Hexachlorocyclohexane (HCH) isomers were detectable at low levels in Lake Malawi at all depths with highest concentrations at the surface. Blanks for Σ HCH were very low. γ -HCH (insecticide lindane) was present at similar or higher levels than α -HCH in surface waters but was generally lower than the α -isomer at depth. This may imply recent use of lindane. α -HCH is a non-insecticidally active component of the older technical HCH product and also may be formed in the atmosphere from γ -HCH. Hexachlorobenzene (HCBz) was present at low levels in both surface and deep water samples and showed very little concentration change with depth. HCBz is an impurity in several pesticides that may be used in Malawi (e.g. chlorothal-dimethyl and lindane). Dieldrin also showed little change with depth. Much higher concentrations of dieldrin were observed in the 1996 water samples (11-14 pg/L) than in those collected in 1997. Dieldrin is a degradation product of aldrin which is known to be imported in to Malawi. Aldrin was not determined in these samples. Endosulfan was present at very low (sub pg/L) levels with the exception of a surface water sample from south Lake Malawi taken in February 1997 which had 12.6 pg/L. Several other insecticides e.g. methoxychlor, endrin and pentachloroanisole (a degradation product of pentachlorophenol) were tentatively identified in the Lake Malawi water samples but results require further confirmation by mass spectrometry.

Organochlorines may be present in water either freely dissolved or bound to particulates or dissolved organic matter. The results for OCs in lake water were based on filtered samples and therefore represent the fraction of these chemicals that are in the dissolved phase. Most of the OCs reported in Table 9.1 would be expected to be primarily in the dissolved phase in Lake Malawi waters due to very low particulate (POC) and dissolved organic carbon (DOC). POC and DOC levels averaged 140 ug/L and 80 ug/L, respectively in the February 1997 samples (Bootsma, H. pers. comm.). Assuming organic carbon partition coefficients equivalent to octanol-water partition coefficients (Mackay et al. 1992), less than 10% of the di-, tri and tetrachlorobiphenyls would be on the particle phase or sorbed to DOC at these low organic carbon concentrations (US EPA 1995). No attempt has been made as yet to analyse the particles on the filters because of the low mass of particles collected.

The concentrations of OCs in Lake Malawi surface waters were generally lower than reported for the Laurentian Great Lakes with the possible exception of PCBs (Table 9.2). The largest differences between Malawi and the Great Lakes, and indeed for lakes in the North America in general, are for α - and γ -HCH and dieldrin. Dieldrin is >100x lower than reported for the lakes Superior and Ontario and for Peter Lake, a remote lake near Rankin Inlet in the Canadian Arctic. Σ HCH is from 50 to 90x lower than levels in the same North American lakes. Overall, the PCB levels and DDT levels in Lake Malawi are similar or slightly lower (taking into account blank values) than those reported for the Laurentian Great Lakes. PCB levels in Lake Malawi are 2 to 3x lower than concentrations in waters from small lakes within forested watersheds in northwestern Ontario, Canada (Paterson et al. 1997; Jeremiason et al. 1997). Studies of Lakes McIlwaine and Kariba, and Hartbeespoort Dam in Africa have reported concentrations of DDT that are up to 400 ng.L⁻¹ (collected between 1974 and 1988; Matthiessen, 1985; Greichus et al. 1977; Mhlanga and Madziva, 1990), several orders of magnitude higher than the concentrations of DDT found in Lake Malawi water. The concentrations of DDT in other aquatic systems may have been considerably higher because samples were collected in areas of extremely high pesticide use or after chemical spills.

Table 9.1. Concentrations of major organochlorine pesticides and PCBs in filtered Lake Malawi water (pg/L.)¹

Location	Depth (meters)	Date	HCBz	α-HCH	γ-HCH	trans-CHL	cis-CHL	pp-DDE	op-DDT	pp-DDT	Dieldrin	Endo- sulfan	ΣHCH	ΣCHL	ΣDDT
South	1	Feb-96	2.25	5.37	3.17	0.37	0.35	3.02	12.5	5.82	13.7	4.96	10.5	5.4	22.2
South	1	Feb-96	1.51	5.86	3.15	0.52	<0.1	1.70	8.32	<0.1	11.2	6.03	10.2	2.4	10.0
South	1	Feb-97	3.83	<0.1	4.30	17.4	<0.1	83.2	<0.1	<0.1	<0.1	12.6	4.3	64.8	87.1
South	40	Feb-97	3.76	8.89	1.45	0.94	<0.1	2.07	3.14	2.66	1.2	0.11	13.1	3.8	8.1
Central	1	Feb-97	4.85	18.0	21.7	7.22	0.94	3.19	3.38	5.10	1.7	<0.1	52.5	25.0	11.7
Central	40	Feb-97	5.97	2.00	0.67	1.17	0.27	1.72	2.10	1.68	1.1	<0.1	4.8	4.2	6.9
Central	80	Feb-97	3.01	0.67	0.24	0.43	0.12	1.15	1.20	0.72	1.3	0.08	1.5	1.9	3.6
North	1	Feb-97	5.40	12.2	15.3	3.31	0.37	2.54	2.71	2.84	1.6	0.17	36.6	14.6	8.1
North	40	Feb-97	3.96	8.87	2.32	<0.1	0.36	3.17	3.81	2.12	1.5	0.14	14.3	3.0	9.1
North	80	Feb-97	3.75	2.26	0.59	0.32	0.70	2.65	2.77	0.70	1.7	0.16	4.3	2.1	6.4
Blank		Feb-96	1.49	0.77	1.65	0.19	<0.1	1.76	<0.1	2.32	3.0	5.47	2.4	7.3	4.1
Blank		Feb-97	0.68	0.22	0.27	<0.1	<0.1	2.06	<0.1	0.00	0.2	<0.1	0.5	1.1	2.2
Blank		Feb-97	0.37	0.43	0.38	<0.1	<0.1	1.28	<0.1	2.30	0.6	<0.1	0.8	1.8	3.6
di															
			ΣMono-	ΣTri	ΣTetra	ΣPenta	ΣHexa	ΣHepta	ΣOcta	ΣNona	ΣPCB	CB18	CB31	CB52	CB101
South	1	Feb-97	131	224	242	143	87.6	19.3	0.6	2.2	854	33.2	13.3	5.0	39.2
South	40	Feb-97	22.9	13.2	16.4	9.3	8.5	2.5	<0.1	<0.1	72.8	2.6	2.5	4.2	1.7
Central	1	Feb-97	73.8	50.4	54.9	55.7	30.2	10.6	1.2	0.9	278	8.3	12.9	9.1	9.6
Central	40	Feb-97	11.7	14.3	17.4	11.6	10.3	4.8	<0.1	0.0	70.1	1.6	2.5	2.3	2.0
Central	80	Feb-97	13.0	15.7	17.6	11.6	8.0	3.7	<0.1	<0.1	69.6	1.5	1.7	2.6	2.7
North	1	Feb-97	86.1	143	289	101	23.3	4.4	<0.1	<0.1	648	17.1	34.9	36.3	13.8
North	40	Feb-97	27.0	166	485	129	22.6	4.6	<0.1	<0.1	835	13.6	42.5	53.2	17.2
North	80	Feb-97	11.8	33.2	103	27.0	10.2	2.1	<0.1	<0.1	187	4.4	7.9	14.8	4.1
South	1	Feb-96	6.6	45.7	53.2	24.9	45.4	17.5	1.7	<0.1	196	5.2	10.4	24.0	3.4
South	1	Feb-96	3.9	74.7	53.0	23.7	43.1	17.5	0.8	<0.1	218	<0.1	38.3	38.3	3.3
Blank		Feb-96	7.5	34.6	71.5	11.7	25.3	12.7	1.2	<0.1	165	<0.1	8.4	50.1	2.0
Blank		Feb-97	1.4	4.8	19.6	15.9	28.6	11.0	0.9	<0.1	82.3	<0.1	1.5	7.2	3.5
Blank		Feb-97	1.9	3.7	10.6	10.1	19.8	12.3	0.8	<0.1	59.2	1.9	<0.10	<0.1	2.2

¹Results are not blank corrected in order to illustrate the extent of blank contamination

Table 9.2. Comparison of organochlorine pesticide and PCB concentrations (pg/L) in Lake Malawi surface waters with lakes in North America

Parameter	Mid-latitude and Arctic lakes				
	Malawi ¹	Superior ²	Michigan ²	Ontario ²	Peter ³
HCB	5	10	14	45	11
α -HCH	18	1100	1600	900	798
γ -HCH	22	400	340	360	177
dieldrin	2	260	na	320	193
p,p'-DDT	5	7	5	4	88
CB18	8	11	17	4	3
CB52	9	4	18	4	17
CB101	10	9	9	2	11
Σ PCB	278	180	360	18	261

¹ Results for central Lake Malawi, Feb 1997. Not blank corrected.

² Results summarized by Hoff et al. 1996 ³ From Kidd et al. 1998b

Organochlorines in air: Results for major OCs in air (blank and internal standard recovery corrected) are presented in Table 9.3. Air measurements at Senga Bay and over the lake (in February 1997) showed the presence of a wide range of chlorinated pesticides and PCBs. Background contamination due to sampling and extraction was relatively low as illustrated in the results for blank PUFs (Table 9.3), with the exception of PCBs on board ship where significant contamination of the PUF was picked up in comparison to Senga Bay. Additional blanks from Senga Bay and the ship-board collections (May 1997) are available but have yet to be analysed. Results for front and back PUFs are shown separately in Table 9.3 to illustrate the extent of breakthrough (movement of PCBs through first PUF to the second) of organochlorines at the relatively high prevailing temperatures (mean daily temp ranges from 22-27 °C at Senga Bay during the air sampling in 1997-98). Significant amounts of HCB, α -HCH and cis- and trans-chlordane and CB 8/5 and 18 (dichlorobiphenyls) were found on the back PUF as anticipated due to their relatively high volatility. The two PUFs together appear to have efficiently collected most OCs with the possible exception of HCB and CB8/5.

PCBs were the most prominent OCs in all air samples with concentrations at Senga Bay ranging from 210 to 910 pg/m³ from February 19 to May 29, 1997. Higher Σ PCB concentrations were found in a single sample collected on board ship on Feb 27. Although corrected for blank contamination there is nevertheless the possibility that the PCBs detected on the sampling cruise originated from oils, electrical components or paints on board the ship. Marine paints, for example, once contained PCBs although the production of these paints has been banned for about 20 years in North America and western Europe.

PCB concentrations did not correlate with mean air temperatures at Senga Bay which were relatively constant (22-27 °C) over the sampling period; concentrations varied only about 4-fold. These PCB concentrations are relatively high when compared to recent results from the Integrated Atmospheric Deposition Network (IADN) in the Laurentian Great Lakes region (Hoff et al. 1996). Annual mean Σ PCBs at four sites in the Great Lakes ranged from 170-360 pg/m³. The concentrations of Σ PCB and di- and trichloro- congeners found at Senga Bay most closely resemble those at Sturgeon Point, New York which is thought to receive PCB emissions from a nearby urban area (Hillery et al. 1997). The Senga Bay site may therefore also be influenced by local PCB sources similar to the ship-board samples.

The greatest variation over time in concentrations of OCs occurred for lindane and dieldrin. Lindane (γ -HCH) concentrations ranged from <0.1 pg/m³ in mid-March to 176 pg/m³ on June 21. By contrast α -HCH levels varied less and were not correlated well with those of lindane. Dieldrin levels in

Table 9.3. Concentrations of major organochlorines in air at Senga Bay and over Lake Malawi (pg/m³)¹

Sampling date	Location	Front/back PUF	HCBz	α-HCH	γ-HCH	trans-CHL	cis-CHL	pp-DDE	op-DDT	pp-DDT	Dieldrin	ΣCBZ	ΣHCH	ΣCHL	ΣDDT CODE
2/19/97	Senga Bay	front	5.6	12.4	5.8	3.4	2.4	6.7	6.0	12.8	72.6	7.4	18.6	18.2	30.9 MAL12
2/19/97	Senga Bay	backup	3.0	1.9	4.5	0.3	0.0	0.0	0.0	1.0	2.1	3.0	6.7	2.3	1.0 MAL14
3/4/97	Senga Bay	front	4.2	18.4	9.7	7.0	2.1	0.0	1.7	9.4	286	8.0	28.5	44.3	14.0 MAL25
3/4/97	Senga Bay	backup	4.9	21.5	0.0	0.0	0.4	0.0	0.0	0.6	1.0	12.2	22.5	15.4	0.6 MAL9
3/18/97	Senga Bay	front	4.7	0.3	0.0	0.0	0.0	3.9	2.9	0.0	2.6	30.2	0.3	38.6	6.8 MAL11
3/18/97	Senga Bay	backup	2.6	1.5	0.0	0.4	0.2	0.0	0.2	0.6	0.5	3.2	1.6	8.6	1.0 MAL13
4/20/97	Senga Bay	front	4.7	2.9	0.8	2.6	1.3	1.1	3.2	5.0	68.0	5.0	5.3	13.0	11.1 MAL15
4/20/97	Senga Bay	backup	2.7	1.8	0.0	0.7	2.2	0.0	0.0	0.7	2.4	3.2	4.9	6.1	0.8 MAL16
4/10/97	Senga Bay	front	4.3	4.8	0.0	1.3	0.6	0.0	0.0	1.5	70.1	3.7	14.6	20.3	11.7 MAL18
4/10/97	Senga Bay	backup	3.7	7.3	6.6	5.6	2.6	0.0	4.0	7.7	1.3	4.3	7.3	9.4	1.5 MAL17
5/3/97	Senga Bay	front	6.2	4.9	13.8	2.8	2.9	0.0	3.3	5.3	92.6	8.0	20.2	16.3	10.5 MAL19
5/3/97	Senga Bay	backup	3.6	1.1	0.0	1.5	0.4	0.0	0.0	0.5	0.4	5.0	1.1	2.8	0.6 MAL20
5/29/97	Senga Bay	front	12.0	6.4	161.8	2.3	1.7	0.0	6.3	7.5	98.0	23.5	169.9	15.0	16.2 MAL21
5/29/97	Senga Bay	backup	6.3	1.9	0.0	0.3	0.3	0.0	0.0	0.5	0.5	11.3	2.9	1.7	0.5 MAL22
21/06/97	Senga Bay	front	7.0	7.5	175.5	2.7	2.5	0.0	5.2	5.5	165	10.5	184.5	15.6	11.7 MAL23
21/06/97	Senga Bay	backup	3.9	1.0	0.0	0.2	0.8	0.0	0.0	0.5	1.2	10.0	1.7	2.8	0.8 MAL24
2/27/97	ship board	front	4.4	19.9	19.9	10.4	1.8	5.6	3.4	2.8	21.0	6.3	39.8	82.6	15.6 MAL10
2/27/97	ship board	backup	2.9	8.9	0.6	0.0	0.2	0.0	0.0	0.0	0.5	9.9	9.5	7.3	0.0 MAL26
Feb-97	Senga Bay	Blank PUF	0.61	0.50	4.46	0.00	0.00	9.59	0.95	0.00	0.0	2.3	5.0	0.7	10.5
Feb-97	Shipboard	Blank PUF	0.86	0.59	0.76	0.13	0.00	4.59	2.75	4.12	0.0	2.0	2.4	0.8	11.5

Table 9.3 continued

PCB congeners >>>		8/5	18	31	28	46	52	95/66	101	118	153	138	180	ΣPCB CODE
2/19/97	Senga Bay front	27.6	38.5	27.9	25.8	1.64	14.3	12.1	5.54	3.28	0.00	2.27	0.10	380 MAL12
2/19/97	Senga Bay backup	18.6	2.07	0.00	0.77	0.00	0.00	1.41	0.00	0.34	0.00	0.00	0.00	67.0 MAL14
3/4/97	Senga Bay front	12.7	29.1	38.3	36.1	2.80	32.7	25.0	22.14	36.18	20.54	39.62	3.70	801 MAL25
3/4/97	Senga Bay backup	11.3	21.3	4.58	4.43	0.00	0.00	1.43	1.33	0.35	0.00	0.00	0.00	110 MAL9
3/18/97	Senga Bay front	35.8	31.5	25.5	35.0	0.00	16.7	23.7	20.0	3.15	0.00	15.6	0.62	592 MAL11
3/18/97	Senga Bay backup	7.62	8.26	2.86	1.62	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	76.8 MAL13
4/20/97	Senga Bay front	4.24	5.54	9.83	7.42	0.62	6.78	10.8	3.85	2.31	0.00	0.15	0.00	160 MAL15
4/20/97	Senga Bay backup	2.61	6.51	0.70	29.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	84.0 MAL16
4/10/97	Senga Bay front	6.83	6.23	0.00	0.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	496 MAL17
4/10/97	Senga Bay backup	3.72	7.81	12.5	9.52	0.00	8.72	13.4	22.4	37.8	23.2	40.9	2.89	42.9 MAL18
5/3/97	Senga Bay front	7.49	7.72	9.33	7.83	0.28	7.42	9.72	4.84	4.61	0.00	2.11	0.19	182 MAL19
5/3/97	Senga Bay backup	1.89	1.30	1.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	26.6 MAL20
5/29/97	Senga Bay front	4.56	11.6	17.1	31.2	0.62	17.9	18.7	31.9	58.5	39.6	66.5	6.64	729 MAL21
5/29/97	Senga Bay backup	2.03	3.63	1.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	27.0 MAL22
21/06/97	Senga Bay front	3.58	10.6	14.6	11.5	0.80	0.00	19.9	28.1	58.5	38.3	71.5	5.85	618 MAL23
21/06/97	Senga Bay backup	3.19	4.33	1.58	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.00	30.6 MAL24
2/27/97	ship board front	75.2	43.6	45.0	54.3	2.34	33.7	32.8	26.89	40.26	25.2	51.8	7.20	1082 MAL10
2/27/97	ship board backup	4.73	6.66	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	32.7 MAL26
Feb-97	Senga Bay Blank PUF	0.64	0.93	0.00	2.78	0.00	2.23	4.20	4.43	6.96	11.1	10.9	3.03	114 Mal 3
Feb-97	Shipboard Blank PUF	2.18	4.09	2.08	4.78	0.00	6.23	12.3	20.9	37.9	38.7	46.3	7.28	439 Mal 4

¹Blank and IS recovery corrected concentrations. Blank results are shown for information only.

April, May and June paralleled those of lindane although a high concentration was also observed in early March. The results suggest local use of lindane and dieldrin when air concentrations are high. Locally applied pesticides typically show very large shifts in airborne concentrations related to the application period for the chemicals (Hoff et al. 1992; Rawn et al. 1998). Σ DDT did not show a major shift in concentration during the February-June sampling period. The high proportion of o,p'-DDT and p,p'-DDT in the gas phase concentrations of Σ DDT (Table 9.3) indicates a new DDT source. Endosulfan and pentachloroanisole were also detected in all air samples but did not vary greatly in concentration between February and June 1997.

The airborne concentrations of HCB and α -HCH were about 10x lower than observed in the Laurentian Great lakes region. For example, annual mean concentrations of HCB ranged from 80-130 pg/m³ at four IADN sites in 1994 and α -HCH from 79-160 pg/m³ (Hoff et al. 1996). Dieldrin levels were generally higher in Malawi also (3-287 pg/m³ compared with 14-34 pg/m³). Σ DDT in Malawi air site (8-32 pg/m³) was higher than at Eagle Harbour (Lake Superior) but lower than at three other sites in the Great lakes region in 1994 (25-106 pg/m³).

The state of air-water equilibrium for organochlorines in Lake Malawi: Organochlorines such as DDT and PCBs will move from air to water and from water to air, depending upon air and water temperatures, and upon the concentrations and properties of these chemicals. Using the air and water data collected to date, we calculated the direction of movement (flux) of selected OCs in Lake Malawi to determine whether the lake is a source or a sink of these pollutants. The Senga Bay air-sampling site, although not situated right on the lake, was judged representative of concentrations over the lake based on similar levels of most compounds found at the two sampling times in February 1997 (Table 9.3). Air-water equilibrium was evaluated using fugacity ratios (F_{WA}) and gas exchange fluxes for selected OCs (Table 9.4). Estimates of air-water gas exchange fluxes were made using the two-film model (Schwartzbach et al. 1993; see Table 9.4 for calculations).

These calculations suggested that lake waters were close to equilibrium (no net movement out or in to the lake) with the atmosphere in February, for α -HCH, p,p'-DDT, CB18, CB28 and CB52, i.e. F_{WA} values ranged from 0.4-1.3. Dieldrin and lindane had much lower F_{WA} (net movement into the lake) reflecting high air concentrations relative to water concentrations than would be expected at equilibrium. CB 101 and CB118 as well as Σ PCB had F_{WA} 's $\gg 1$ suggesting were undergoing volatilization out of the lake. Relatively high blank values for PCBs in both water and air make the equilibrium status for these compounds less certain.

Semi-volatile OCs such as PCBs, HCB and HCH isomers, undergo both gas absorption in to and volatilization from surface waters (Hoff et al. 1996). In the case of Σ PCBs in Lake Malawi, the net flux was estimated to be 48 ng/m² day export from the lake surface. Similar direction and magnitude of volatilization fluxes have been observed for PCBs in the Laurentian Great Lakes based on summer time temperatures and prevailing water and air-borne concentrations (Table 9.5). The direction and magnitude of net air-water fluxes of α -HCH and dieldrin differed between Lake Malawi and the Great Lakes (Table 9.5). α -HCH and dieldrin had net gas absorption under summer conditions (except in Superior) whereas they showed net gas absorption in Lake Malawi.

Conclusions

These results represent the first measurements of persistent OCs in Lake Malawi water or in air. The results are preliminary because additional samples and blanks need to be analysed. Further insight into the importance of atmospheric inputs to Lake Malawi will come from the precipitation samples which are currently awaiting analysis. Although results are limited some preliminary conclusions can be drawn from them:

1. PCBs appear to be important microcontaminants of Lake Malawi surface waters and air. PCB levels are below method detection limits (<100 pg/L) at 40 and 80 m. Future work needs to more thoroughly investigate sources of these PCBs.

Table 9. 4. Fugacities and fluxes of selected organochlorines in Lake Malawi - February 1997

Parameter	α -HCH	γ -HCH	dieldrin	p,p'-DDT	18	28	52	101	118	Σ PCB
Henry's Law Constant (H) ^a	0.87	0.07	5.90	2.36	30.0	20.0	20	9	5.1	20
Pa										
m ³ /mol										
Mass transfer coefficient (Kol) ^c	0.10	0.01	0.27	0.18	2.42	0.42	0.40	0.33	0.27	0.39
m/day										
Fugacity ratio ^b	0.4	0.06	0.04	0.30	0.45	1.3	1.0	3.61	1.67	3.21
Absorption ^d	3.9	3.45	8.55	2.64	1.52	1.37	0.71	0.5	0.5	21.7
ng/m ²										
day										
Volatilization ^e	1.7	0.21	0.38	0.80	3.68	1.8	0.7	1.8	0.8	69.6
ng/m ²										
day										
Net Flux ^f	2.2	3.24	8.17	1.83	-2.16	-0.4	0.01	-1.3	-0.3	-47.9
ng/m ²										
day										

^a Henry's Law constant at 25 °C, from Mackay et al. (1997) and Hoff et al. (1996)

^b Fugacity ratio = (C_w/Z_w)/(C_a/Z_a) where Z=fugacity capacity in water and air. Where C_w=water

concentration (dissolved) and C_a= air concentration. Both were blank corrected.

^c Kol = air-water mass transfer coefficient (m/day)(calculated according to Schwartzbach et al. 1993)

^d Absorption = Kol*Ca*RT/H (where R = gas constant (8.32 Pa m³/mol K), T = temperature Kelvin

^e Volatilization = Kol*C_w

^f Net Flux = Absorption - Volatilization (negative value indicates net loss from the lake)

2. There is evidence from air measurements that lindane (γ HCH) and dieldrin (or its precursor aldrin), as well as possibly heptachlor, endosulfan, and DDT, are currently being used in the region. Analysis of the remaining air samples would help to clarify the trends observed in the Feb-June 1997 sampling period.
3. Unlike many water bodies in the Northern Hemisphere, the direction of flux for current use compounds such as lindane and dieldrin is into the water suggesting that the lake has yet to reach equilibrium with these compounds. By contrast Lake Malawi appears to be degassing PCBs similar to what is observed in the Laurentian Great Lakes, although additional measurements are needed to confirm this because of high blank values.

Table 9.5. Comparison of air-water gas exchange of organochlorines in Lake Malawi with other Great Lakes (negative = volatilization)

Parameter	Net flux for each lake (ng/m ² day) ^{1,2}				Flux from Hoff et al		
	Malawi	Superior	Michigan	Ontario	Superior	Michigan	Ontario
	Feb-97	Summer	Summer	Summer	kg/yr	kg/yr	kg/yr
α -HCH	2.2	6.0	-9.9	-5.9	220	-210	-43
γ -HCH	3.2	0.6	32.1	2.2	22	680	16
dieldrin	8.2	-7.1	na	-5.8	-260	na	-42
p,p'-DDT	1.8	0.3	0.8	0.6	12	17	4.1
CB18	-2.2	-1.0	-2.5	-1.0	-36	-53	-7
CB52	0.01	-0.1	-2.2	-0.4	-4.5	-46	-3.1
CB101	-1.3	-0.7	-1.1	0.0	-24	-24	-0.3
Σ PCB	-48	-12.1	-45.3	-9.6	-440	-960	-70

¹ Calculated using the approach described by Hoff et al. 1996.

² Results for the Superior, Michigan and Ontario are based on results for 1994

II. Current use pesticides in tributaries of Lake Malawi/Nyasa: A preliminary report

Introduction

Assessment of time trends in water quality is a major objective of the Lake Malawi/Nyasa Biodiversity Conservation project. While the state of water quality has been examined in the lake as early as the 1950's and more recently in tributaries, the work has examined nutrients and basic water chemistry parameters but not microcontaminants such as pesticides. The objective of this component of the water quality project was to develop baseline information on levels of current use pesticides (insecticides, fungicides and herbicides) in tributaries of Lake Malawi.

Although agricultural use of pesticides is limited in Malawi because of cost factors, its usage is reported to be increasing. A survey of Malawi's pesticide imports in the early 1990's showed higher amounts of many products imported in 1992 compared to 1990. In currency terms, imports of pesticide types were K22,500,000 in 1992 and K20,600,000 in 1990. Fungicide and fumigant imports showed the greatest increases over the two year period (Figure 9.2). The products imported were for the most part, the same as those used in the US, Canada and western Europe.

Insecticides, mainly organophosphorus (OPs) and carbamate compounds, were the major pesticides imported. Major OPs were pirimiphos-methyl, disulfoton, fenitrothion, and dimethoate. Major carbamates were carbaryl, aldicarb and carbofuran. Among the herbicides and plant growth regulators, atrazine, metolachlor, chlorthal-dimethyl, butralin, MCPA, 2,4-D, glyphosate and paraquat were major imports. Among the fungicides used, major products were copper oxychloride and flutriafol. Major fumigants were methyl bromide, and ethyl dibromide.

To conduct this preliminary survey of pesticides in river water we first selected a series of chemicals to target that were being imported to Malawi in significant quantities, and that were appropriate for our methodologies involving solid phase extraction (SPE) of water and gas chromatographic (GC) analysis. The target compounds consisted mainly of neutral compounds such as OP insecticides, as well as herbicides. The SPE analytical methodology used in the study was the same as that used recently by the US Geological Survey in studies of pesticides in US rivers (Thurman et al. 1992; Burkhardt and Werner, 1994).

Materials and Methods

Sample collection: River water was collected in the Bua, Shire and Linthipe rivers in May and June 1996 (see Figure 9.1). Water samples (2L) were obtained by pumping the sample through a stainless steel filter plate (AXYS Analytical, Sidney BC) containing two GFF (Whatman) filters (10cm diameter) and into then into amber 1 L bottles. A portable generator was used to power the pump. Water was pumped from the river via a teflon tube placed 10-15 cm below the water surface and to the maximum extent of the tubing; about 2 m from the river bank.

Sampling resumed in December 1996 using the above procedure in the Linthipe, Songwe, Shire, Bua, Luweya, Dwangwa, Rhumpi, and Rukuru rivers. Sampling was done as near to the outflow of each river as possible where an accessible site on the river bank was available (Table 9.6). Road access was essential because a heavy generator was carried down to the sampling site. However difficulties were encountered with on site water filtration because of high suspended sediment loads which required long filtration and extraction times.

For the period February-March 1997, sample collection was modified to collect unfiltered 2L samples manually at 10-15 cm depth in each river. Samples were kept chilled after collection (2 day sampling program collected water from all 8 rivers) and returned to the lab for filtration. A subsample (10-100 mL) of unfiltered water was filtered to obtain total suspended solids and the remainder was filtered through GFF. Filters were wrapped in solvent rinsed aluminium foil and stored in plastic[®] Whirlpak bags in the freezer.

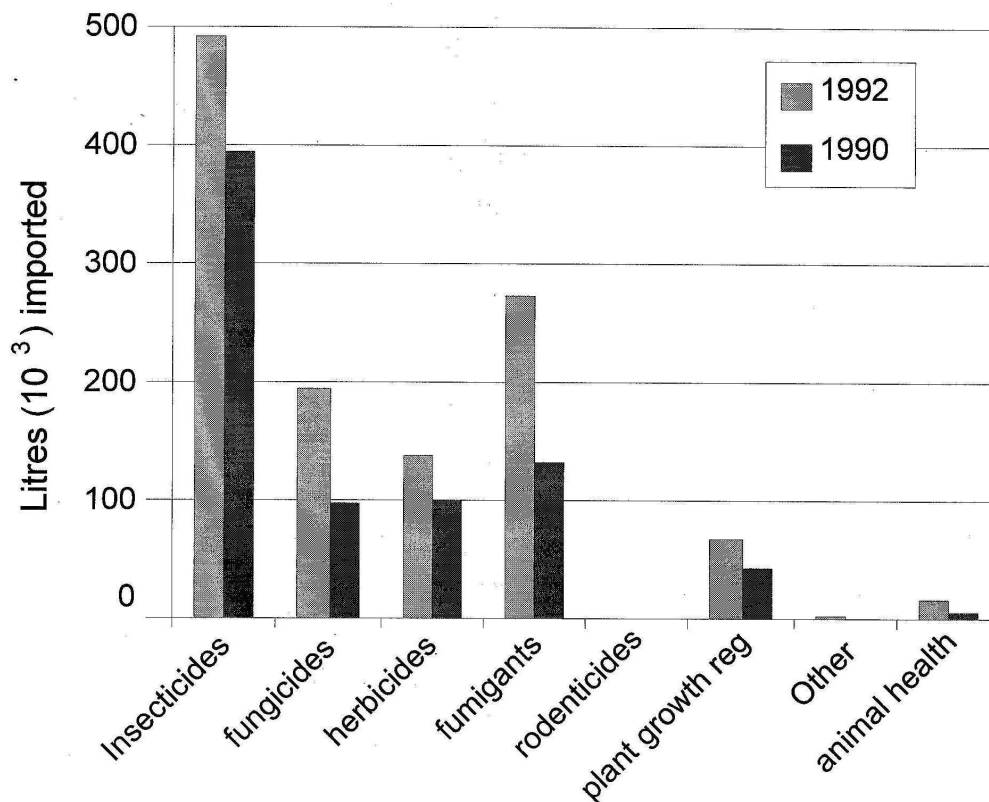


Figure 9.2. Pesticide imports in Malawi, 1990 and 1992 (Ministry of Agriculture and Livestock Development, Malawi).

Sampling was resumed in January 1998 and continued until late March. The same procedure was used for sample collection and filtration as was used in February-March 1997. For this period, samples were collected only weekly on the Linthipe River to examine temporal trends.

Sample extraction: Filtered river water samples were extracted following an adaptation of the USGS method for neutral and acidic pesticides (Burkhardt and Werner, 1994). This procedure uses solid phase extraction (SPE) cartridges packed with Carboxen B (Supelco Sigma-Aldrich Canada Ltd.). SPEs were pre-cleaned in Winnipeg or Burlington by eluting them with 6 mL 80:20 DCM:methanol and then sealed in individual bags for transport to Malawi. Internal standards (deuterated (D6)-fenitrothion, D10-diazinon or D5-atrazine (May 1996 only)) were added to water samples prior to elution through SPEs. An ascorbic acid solution (using HPLC grade water) was used to prepare the SPE columns just prior to use. Sodium chloride (10 g) was added to the 2L sample which was then pumped through the SPE. Sample SPE cartridges were labelled and stored in plastic bags at 4°C. Blank water samples were also prepared by passing HPLC grade water through SPE cartridges as described for the river water. SPEs were returned to the laboratory (Winnipeg or Burlington) and were first blown dry with nitrogen to remove excess water. They were then eluted sequentially with 1 mL methanol and then 6 mL 80:20 DCM:methanol to remove neutral compounds such as OP insecticides and triazine herbicides. Eluates were dried over sodium sulfate to remove trace water, filtered through 1 µm glass fiber paper, evaporated to about 100 µL and brought to 0.5 mL with toluene for GC analysis.

Table 9.6. Sampling Locations and Description.

River	Latitude	Longitude	Site location	Characteristics
Shire	14° 28.7'	35° 16.4'	West bank of river, 100m north of the M3 hwy at Mangochi bridge. Easily accessible	Sandy shore & river bed, water depth \approx 0.5 m, weeds nearby, clear and slow flowing.
Linthipe	13° 47.1'	34° 26.1'	North bank of river, 100m west of the M5 hwy. bridge, 2 km south of Salima town. Follow the dirt track leading from the bridge to the river's edge.	Muddy shore and river bottom, water depth \approx 1.5 m, turbid and fast flowing.
Bua	12° 47.3'	34° 11.7'	North bank of river, 25m west of the M5 hwy. bridge. Park at the north side of bridge, walk down to river's edge.	Sand/rock/weedy shore with rock and mud river bed, water depth \approx 0.5 m, turbid and moderately fast flowing.
Dwangwa	12° 30.9'	34° 06.9'	North bank of river, 200m east of the M5 hwy. bridge, adjacent to the Dwangwa sugar plantation. Turn on the dirt track at the north side of the bridge, Walk to water's edge.	Mud shore and river bed, water depth \approx 1.0m, turbid and moderately fast flowing. Upstream of plantation.
Luweya	11° 46.3'	34° 12.1'	South bank of river, 25m west of the M1 hwy bridge. Turn onto dirt track 1 km south of the bridge, cross the old bridge, and park at water's edge.	Mud/rock shore with muddy river bed, water depth \approx 0.5 m, moderate turbidity and flow.
South Rukuru	10° 45.8'	34° 07.3'	North bank of river, 25m east of the M1 hwy. bridge. Park at north end of bridge and walk to water's edge.	Sandy/rocky shore and river bed, water depth \approx 0.25m, moderate turbidity and fast flowing.
North Rhumpi	10° 41.4'	34° 11.1'	North bank of river, 15m west of the M1 hwy. bridge. Park at north end of bridge and walk to water's edge.	Sandy/mud shore and river bed, water depth \approx 0.5m, low turbidity and moderate flow.
North Rukuru	09° 55.0	33° 55.7'	South bank of river, 15 east of the M1 hwy. bridge. Turn onto dirt road, 1km south of bridge and follow to the river's edge.	Sand/rock shore with sandy river bed, water depth \approx 0.25 m, moderate turbidity and flow

GC analysis of pesticides: Sample extracts from river water collected in December 1996 and January 1997 were analysed by high resolution gas chromatography-low resolution mass spectrometry (Select Ion Monitoring) (Hewlett Packard 5971 MSD) using a 60 m x 0.25 m DB-5 column with helium as the carrier gas. Detection criteria were the correct ratios of two characteristic ions and retention times. Pesticides were quantified using external standard solutions and corrected for volume changes using PCB-104. The list of pesticides analysed by GC-MSD is shown in Table 9.7.

Sample extracts from 1996 and 1997 were also analysed by GC using a HP 5890 GC equipped with Nitrogen-Phosphorus specific detector (NPD) and a DB-17 column. Helium was used as carrier gas. The same analytes listed in Table 9.7 were determined with the exception of carbaryl, aldicarb and carbofuran which could not be determined using the N-P detector. This list of compounds was supplemented with an additional 11 organophosphorus pesticides.

Results and Discussion

All samples collected in May 1996 and December 1996-March 1997 have been extracted and analysed by GC-NPD (Table 9.8). A subset of the samples have been analysed by GC-MSD and results are presented in Table 9. 9. Difficulties were encountered analysing the samples with both

Table 9.7. List of pesticides analysed in Malawi river water samples

Compound	Gc-detector	Retention Time ¹	Ion #1 (m/z)	Ion #2 (m/z)	Ion #3 (m/z)
Aldicarb	MSD	8.51	41	39	86
Carbofuran I	MSD	12.36	164	149	
Carbaryl I	MSD	15.15	144	115	
De-ethylatrazine	MSD	17.04	172	187	
Dimethoate	MSD, NPD	18.14	87	93	125
Carbofuran II	MSD	18.18	164	149	
D5-atrazine (IS)	MSD, NPD	18.25	205	220	
Atrazine	MSD, NPD	18.3	200	215	
D10-diazinon	MSD, NPD	18.92	183	138	314
Disulfoton	MSD, NPD	19.4	88	97	89
Chlorothalonil	MSD, NPD	19.79	266	264	
Ametryn	MSD, NPD	21.14	227	212	68
Carbaryl II	MSD	21.17	144	115	
Alachlor	MSD, NPD	21.25	188	160	
D6-fenitrothion	MSD, NPD	21.93	131	283	115
Pirimiphos-methyl	MSD, NPD	21.95	290	276	305
Fenitrothion	MSD, NPD	22.02	125	277	10+
Metolachlor	MSD, NPD	22.87	162	238	
Chloropyrifos	MSD, NPD	22.98	199	197	97
Dicofol	MSD	23.26	139	111	75
Dacthal	MSD, NPD	23.3	301	299	332
Butralin	MSD, NPD	23.73	266	224	132
Pendimethalin	MSD, NPD	24.62	252	281	
Flutriafof	MSD, NPD	27.18	123	164	95
Hexazinone	MSD, NPD	35.21	171	83	252
Dibrom	NPD				
Phorate	NPD				
Cygon	NPD				
Turbofos	NPD				
Fonofos	NPD				
Disyston	NPD				
Methyl-parathion	NPD				
Malathion	NPD				
Ethion	NPD				
Imidan	NPD				
Guthion	NPD				

¹ Retention time on 60 m DB5 column used for MSD analysis.

detectors possibly because no additional “cleanup” was performed on the SPE eluate. Co-extractive material in the samples caused retention times to shift making absolute identification of the pesticides difficult, especially by GC-NPD. Thus results in Table 9.8 are reported only as detectable (with an “X”) and the relative amount by a series of X’s.

GC-MSD analysis confirmed the presence of the same group of compounds consistently detected by GC-NPD, i.e. atrazine, disulfoton, ametryn, carbaryl. Co-elution of disulfoton with diazinon and butralin with carbaryl on the GC-NPD instrument prevented confirmation of these compounds. Carbofuran and de-ethyl atrazine were also detected by GC-MSD but were not analysed by GC-NPD. GC-MSD results show that levels of all compounds were in the low ng/L range in samples collected in December 1996 and January 1997 (Table 9.9). These concentrations are very low for rivers flowing through agricultural areas. For example, in rivers in the US midwest, atrazine was detectable year-round at concentrations of 0.23 - 108 ug/L, many times higher than levels found in this study, and that were highest during the postplanting period, prior to harvest (Thurman et al., 1992).

The most consistently detected compound was ametryn, a triazine herbicide. Ametryn was the major triazine herbicide imported into Malawi in 1990 (14400L) although less was imported in 1992 (4225L). This herbicide is known to be very persistent in soils in temperate climates (Wauchope et al. 1992) which may explain its presence in the tributaries of Lake Malawi, despite declining use.

Table 9.8. Results of qualitative analysis of pesticides in Lake Malawi tributary samples by nitrogen-phosphorus specific detection.

Sample code	River	Sampling date	GC analysis date, 1997	atrazine	disulfoton/di azinon	ametryn	butralin/c arbaryl	penda- methalin
A5	BUA	MAY/1/96	19-Aug	XX		X		
A6	BUA	MAY/1/96	19-Aug	XX		X		
B3	BUA	DEC/28/96	19-Aug			X	X	
B4	BUA	DEC/28/96	19-Aug			XX	XX	
A4	BUA	JAN/8/97	15-Jul			XXX		
A5	BUA	JAN/17/97	15-Jul			XXX	XXX	
B5	BUA	JAN/29/97	20-Aug			XXX	X	
A6	BUA	FEB/14/97	15-Jul					
B8	DWANGWA	DEC/28/96	20-Aug			X		
B9	DWANGWA	JAN/8/97	20-Aug			XXX	X	
B10	DWANGWA	JAN/17/97	20-Aug			XX		
C1	DWANGWA	FEB/14/97	20-Aug	X		XX		
A3	LINTHIPE	MAY/1/96	19-Aug	XXX		X		
A4	LINTHIPE	MAY/1/96	19-Aug	XXX		X		
C2	LINTHIPE	DEC/19/96	20-Aug			X		
C3	LINTHIPE	JAN/2/97	20-Aug			XXXX	XXX	X
C4	LINTHIPE	JAN/2/97	20-Aug			XXXX	XX	X
B1	LINTHIPE	JAN/22/97	16-Jul			XXX		
C5	LINTHIPE	FEB/15/97	20-Aug			XX		
B2	LINTHIPE	MAR/5/97	15-Jul			X		
B6	LUWEYA	JAN/24/97	20-Aug			XX		
B7	LUWEYA	FEB/14/97	20-Aug	XX	XX	XXX	XX	X
C8	N RHUMPI	JAN/16/97	20-Aug					
C9	N RHUMPI	FEB/14/97	20-Aug					
C10	N RUKURU	JAN/15/97	20-Aug			XX		
D1	N RUKURU	FEB/14/97	20-Aug	X		X		
D2	S RUKURU	FEB/14/97	20-Aug		XX			
A1	SHIRE	MAY/1/96	19-Aug	XXX		XX		
A2	SHIRE	MAY/1/96	19-Aug	XXX				
A9	SHIRE	DEC/8/96	16-Jul			X		
B1	SHIRE	DEC/8/96	19-Aug					
B2	SHIRE	DEC/8/96	19-Aug			XXXX		
C6	SONGWE	JAN/16/97	20-Aug	XXX		XXX		
C7	SONGWE	FEB/14/97	20-Aug	XX		XXX	X	

¹X's indicate relative peak intensity. Identification with NPD is based on agreement of retention times of unknowns and external standards (+/- 0.01 min approximately) for major peaks

Conclusion

The apparent low or non-detectable levels of the large suite of pesticides on the target list reflects the persistence and use of these compounds in Malawi. Most pesticides examined in this study would be expected to degrade rapidly under tropical conditions. This is particularly the case for organophosphate insecticides which can undergo rapid degradation via several routes including hydrolysis and oxidation. With the exception of de-ethyl atrazine, we did not attempt to determine pesticide degradation products. Losses due to volatilization from plant and soil surfaces immediately after application are also a significant removal pathway especially under high temperature conditions. The combined effect of rapid degradation in both soils and runoff waters, as well as volatilization, may reduce the amount of pesticide found in surface waters in Malawi.

Table 9.9. Concentrations of pesticides (ng/L) in Lake Malawi tributary samples by GC-mass spectrometry

River	Sampling date	Carbofuran	carbaryl	atrazine	de-ethyl atrazine	ametryn	disulfoton
Shire	Dec-8-96	3.24	2.1	1.02	2.24	0.87	0.52
Shire	Jan-16-97	8.03	<0.5	2.5	2.66	2.58	1.18
Linthipe	Dec-19-96	2.06	2.39	9.93	<0.2	1.15	0.54
Linthipe	Jan-2-97	5.09	3.47	7.24	<0.2	<0.2	1.08
Bua	Dec-28-96	<0.5	3.04	1.97	3.49	3.69	1.47
Bua	Jan-8-97	0.74	<0.5	1.43	3.23	0.87	0.73

Highest concentrations of pesticides are found in surface waters during the periods when these chemicals are being used (Thurman et al. 1992; Rawn et al. 1998). Although we targeted major chemicals on the import list we did not have information on the typical application period nor on the location of the applications. It is therefore quite possible that we could have missed peak concentrations associated with runoff from recently treated cropland with the one to two week sampling frequency used in 1996-97. Additional sampling in January through May of 1998 using weekly and twice-weekly sampling in the Linthipe river may address the issue of low sampling frequency.

The levels of pesticides tentatively confirmed in the Bua, Linthipe and Shire rivers are well below accepted water quality guideline limits for these compounds (Table 9.10). Water quality guidelines are not available for ametryn, carbaryl or disulfoton.

Table 9.10. Canadian Water Quality Guideline values for some pesticides used in Malawi (Environment Canada 1995).

Chemical	Class/Use	Guideline Value (ng/L)
Aldicarb	Carbamate insecticide	1000
Atrazine + metabolites	Triazine herbicide	2000
Chlorpyrifos	Organophosphate insecticide	3.5
Carbofuran	Carbamate insecticide	1750
Chlorothalonil	Chlorobenzonitrile fungicide	180
2,4-D	Chlorophenoxy acetic acid herbicide	4000
Endosulfan	Chlorinated insecticide	20

III. Metals in Lake Malawi Sediment

Introduction

The issue of contamination of Lake Malawi, with the possible exception of nutrient enrichment, has received little scientific attention. Bootsma and Hecky (1993) pointed out the difficulty pollution can pose for this lake because its large volume and small outflow give it a long flushing time. Hence if the lake becomes polluted, it will remain in this state for a very long time.

Many metals and organochlorines bind to particulate matter in the water column of lakes. These particle-bound pollutants settle to lake bottoms and are preserved there, providing long-term archives of pollutant inputs to lakes. Sediment cores have often been used to reconstruct histories of inputs of contaminants such as polychlorinated biphenyls (PCBs), DDT, lead or mercury. It is possible to determine whether the inputs of contaminants to a lake are increasing or decreasing with such sediment core analyses. While there have been a number of previous studies of the sediments of Lake Malawi for limnological and geological insights (e.g. Pilskaln and Johnson, 1991; Owen and Crossley, 1992; Johnson et al., 1995), these studies have not included pollutant analyses. We initiated this study to assess the state of contamination of the lake sediments with a series of sediment grab samples and short cores collected in 1997. The objectives of these analyses were to determine the current state of pollutant levels in the lake, and to examine whether inputs of these contaminants are changing over time. An understanding of whether metal and organochlorine inputs are increasing or decreasing to Lake Malawi will also aid in predicting future contaminant concentrations in fish. In this report we present the results of metal analyses of the surface sediment samples.

Methods

In May and November of 1997, surface (top 5 cm) sediment samples were collected from 21 sites ranging in depth from 22 to 613 m in depth in Lake Malawi (Figure 9.1; Table 9.11) using a Ponar dredge. When dredges were retrieved, the sediments were emptied onto a plastic sheet and approximately the uppermost 5 cm of sediment was transferred, with a plastic spatula, to [®]Whirlpak bags which were retained on the ship until it reached port at Senga Bay. Bags were packed in insulated coolers but no refrigeration was available. After arrival at Senga Bay and storage at the laboratory for a few days, samples were shipped by air to Winnipeg. During shipment, the bags from the May collection leaked and some material was lost. The material remaining in the bags was taken to represent the original content of the bags. There was no leakage problem with the November samples.

At the Freshwater Institute in Winnipeg, sediment was freeze dried and analyzed for a series of metals (mercury, cadmium, lead, aluminum, titanium, iron, manganese, copper, zinc, arsenic, selenium, nickel and vanadium). Standard laboratory procedures were used for the extractions and analyses, and reference materials were also analysed for quality assurance and control. Mercury, cadmium and lead were digested with aqua regia; aluminum, titanium, iron, copper, manganese, zinc, nickel and vanadium were digested with a mixture of hydrofluoric, sulfuric, nitric and perchloric acids; selenium and arsenic were digested with a mixture nitric, sulfuric and perchloric acids. Mercury was analyzed by cold vapour atomic absorption; cadmium by graphite furnace atomic absorption, and lead, aluminum, titanium, iron, manganese, zinc, and vanadium by direct current plasma emission; copper and nickel by flame atomic absorption, selenium and arsenic using flame atomic absorption following borohydride reduction. National Research Council of Canada standard reference materials MESS-2 and PACS-2 were used in establishing the quality of the analyses and these results were within acceptable ranges.

Table 9.11. Locations, depths and size of cores collected from Lake Malawi between October 30 and November 5, 1997.

Core #	Latitude	Longitude	Depth (m)	Length (cm)	# of Slices
Mal-1	09 49.545 S	034 04.654 E	247	59	34
Mal-2	09 47.302 S	034 05.218 E	247		
Mal-3	11 12.153 S	034 26.848 E	613	59	37
Mal-4	11 54.088 S	034 16.717 E	285		34
Mal-5	12 15.074 S	034 28.087 E	363		32
Mal-6	12 21.171 S	034 11.658 E	150		29
Mal-7	12 27.384 S	034 15.967 E	161	47	32
Mal-8	13 18.265 S	034 37.503 E	192	41	
Mal-9	13 47.461 S	034 49.205 E	142	39	29
Mal-10	13 52.088 S	034 45.112 E	124	45	32
Mal-11	13 56.312 S	034 57.067 E	100	36	28
Mal-12	14 03.591 S	035 02.025 E	70	37	28
Mal-13	14 06.802 S	034 39.820 E	63	37	29
Mal-14	13 58.997 S	034 38.856 E	81	44	31
Mal-15	13 52.121 S	034 39.052 E	79	43	32

Results and Discussion

Surface sediment samples were collected from several locations in Lake Malawi and analysed for a series of metals including some of those most commonly found as contaminants in lakes. Mean, maximum and minimum concentrations of each metal are given in Table 9.12 and the distributions of mercury, cadmium, lead and aluminum in Lake Malawi are shown in Figure 9.3. Particle-size analysis is not available yet but the approximate nature of the material can be obtained from the facies map of Owen and Crossley (1992). Most of the samples were taken from areas of the lake where surface sediments were of fine-grained material but a few came from relatively shallow, sandy locations. Several metals (copper, zinc, arsenic and vanadium) were found at higher concentrations in samples collected from deeper sites, likely because these metals tend to associate with the finer particulates that are found at greater depths. With the exception of cadmium and vanadium, the concentrations of these metals were highly related at each site.

A very similar set of grab samples was collected from Lake Winnipeg, a large Canadian lake north of Winnipeg, Manitoba, in 1994 giving us the opportunity to compare metals in the sediments of these two very large but very different lakes (Table 9.12). The results were strikingly similar with the exception of cadmium which was several fold higher in Lake Winnipeg. While the cadmium in Lake Winnipeg may be partly the result of industrial inputs, there are also cadmium-rich soils in the watershed (Garrett, 1994) which may also contribute loadings to the lake. Mercury concentrations in the sediments of Lake Winnipeg are higher than in Lake Malawi, and the Lake Winnipeg fishery had to be closed for a time because levels of mercury in the fish exceeded levels considered safe for human consumption. Sediment core studies in the southern part of Lake Winnipeg indicate that mercury concentrations have approximately doubled from about 0.060 ug g^{-1} to about 0.13 ug g^{-1} over the past century (Lockhart et al., 1998). Based on these concentrations, if we reduce the current Lake Winnipeg concentrations of mercury by about half to reach the pre-industrial levels for the lake, the result is about the same as Lake Malawi in 1997. Very similar arguments may apply to lead. In the South Basin of Lake Winnipeg, lead levels in recent core slice are close to 20 ug g^{-1} but deep slices are in the range of $12\text{--}15 \text{ ug g}^{-1}$; both are within the range of lead levels in the samples from Lake Malawi.

Comparisons can be made between the measured concentrations of some metals (mercury, cadmium, lead, copper, zinc, and arsenic) in the sediments and the Canadian guidelines currently under development to protect freshwater organisms. These Sediment Quality Guidelines (SQL) are concentrations of metals in sediments that have rarely been observed to cause effects, such as reduced growth or reproduction, in sediment-dwelling organisms. Higher concentrations of metals that

Table 9.12. Comparison between ranges and mean levels (ug/g) of several metals in Lake Malawi in 1997 and Lake Winnipeg in 1994. Sediment Quality Guideline (SQG) values and Probable Effect Levels (PEL) are taken from draft Canadian guidelines, 1997.

Metal	Lake Malawi, 1997				Lake Winnipeg, 1994				Criteria	
	N	Min	Max	Mean	N	Min	Max	Mean	SQG	PEL
Mercury ug/g	21	0.015	0.073	0.046	31	0.028	0.161	0.084	0.17	0.486
Cadmium ug/g	21	0.013	0.096	0.050	31	0.107	0.978	0.413	0.6	3.5
Lead ug/g	21	5.7	29.6	14.6	31	10.39	30.3	20.5	35	91.3
Aluminum mg/g	21	30.7	118	82.3	31	21.0	91.2	77.5		
Titanium mg/g	21	4.09	8.49	5.22	31	1.22	4.26	3.46		
Iron mg/g	21	20.9	78.2	53.2	31	7.25	39.5	29.0		
Manganese ug/g	21	203	3820	1000	31	183	3650	874		
Copper ug/g	21	6.2	57.4	37.3	31	13.0	44.6	35.2	35.7	197
Zinc ug/g	21	40	126	96.8	31	21.8	137	105	123	317
Arsenic ug/g	21	0.22	3.42	1.37					5.9	17
Selenium ug/g	19	0.14	0.74	0.458						
Nickel ug/g	21	11.8	59.4	39.2	31	6.33	53.5	43.6		
Vanadium ug/g	21	43	203	119	31	41.3	221	153		

frequently have harmful effects on aquatic organisms are called Probable Effect Levels and have also been shown in this Table. It is recognized that these Canadian guidelines may be inappropriate for Lake Malawi, nonetheless, in the absence of local guidelines, the comparison is instructive. Copper and zinc were the only metals observed to exceed SQG in Lake Malawi sediments in 14 of 21 and 1 of 21 samples respectively. The remaining metals were at concentrations that are not expected to have effects on aquatic organisms.

Fifteen sediment cores were also collected from Lake Malawi between October 30 and November 5, 1997. The locations of these cores are shown in Figure 9.1 and were taken from sites ranging in depth from 63 to 613 m. Analyses of these cores have not been done but would provide valuable information on whether inputs of metals (and other pollutants like DDT) to the lake are changing. It is anticipated that future analyses of these cores will furnish that information and permit calculation of input budgets for metals and a number of organic contaminants.

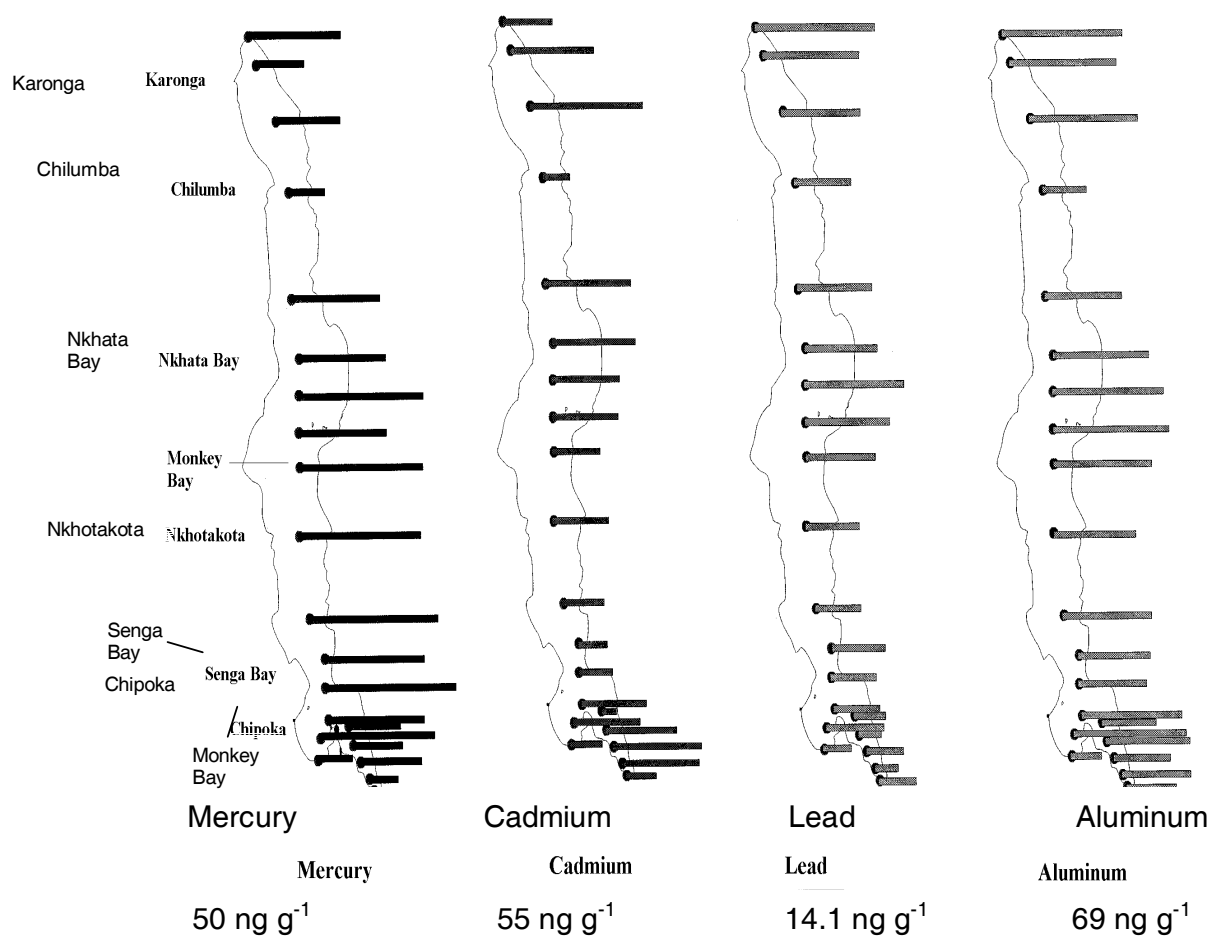


Figure 9.3. Distributions of selected metals in Lake Malawi surface sediment samples.

IV. Persistent Pesticides, PCBs, and Mercury in the Lake Malawi/Nyasa Food Web

Introduction

Persistent pesticides continue to be used in East Africa for the protection of human health (e.g. DDT and dieldrin to control malaria and sleeping sickness) and to meet the increasing agricultural demands [e.g. DDT, hexachlorocyclohexane (HCH) and dieldrin for cash crops]. It is estimated that Africa uses less than 5% of the world production of pesticides (Wikteliu and Edwards, 1997), although this may be changing due to increasing food production requirements. Although pesticide imports to East Africa peaked in the late 1980s (\$600 million US), they currently remain at a significant level of about \$500 million US per year (Wikteliu and Edwards 1997).

Some of these imported pesticides (such as DDT) do not degrade rapidly in the environment, and accumulate to significant and sometimes harmful levels in non-target organisms such as fish (e.g. Wikteliu and Edwards, 1997). Long-term exposure to some of these persistent pesticides is known affect the health of humans and wildlife. For example, the consumption of fish high in DDT is known to cause eggshell thinning in many species of birds (Kolaja, 1977).

Another pollutant of potential concern for humans and wildlife is mercury. Mercury is a natural component of the earth's crust but is also released into the environment by human activities such as coal and oil combustion and waste incineration (Hanisch, 1998). In lakes it is converted to an organic form, methylmercury, which accumulates through food chains and can be found at high concentrations in fish. Methylmercury is a neurotoxin (affect the central nervous system), and its toxic effects have been observed in humans and wildlife consuming fish with high concentrations of this contaminant (World Health Organization, 1990)

Little research has been done on pesticide and mercury contamination of fish and other organisms in East Africa. Because a large percentage of the animal protein consumed by the residents of Malawi is fish, it is important to determine whether the consumption of fish poses a significant risk to human health and to fish-eating wildlife. Prior to this study nothing was known about the levels of persistent pesticides and other contaminants in Lake Malawi.

Fish accumulate contaminants such as chlorinated pesticides and mercury mainly from their diet, and studies in cold-water lakes have found that fish that eat fish have higher concentrations of these pollutants than fish that feed upon insects or other invertebrates (Rasmussen et al. 1990; Kidd et al. 1995). Concentrations of these pollutants increase from insects to insect-eating fish to fish-eating fish, and this process is called biomagnification.

Aside from diet, other factors such as age and growth rate are known to affect the level of pollutants found in a fish. Older and slower-growing fish have much higher levels of pollutants than fish that have much shorter lifespans and those that grow quickly. These persistent pollutants have an affinity for fats and are found at higher concentrations in fatty tissues and in fatter organisms. The inputs of pollutants to a lake are also a determinant of the concentrations of contaminants in fish; higher inputs result in higher concentrations of pollutants in aquatic organisms. Because most of the previous work that has been done on colder-water systems, little is known about the fate of pollutants in tropical lakes. The main objectives of this study were to determine the levels of pollutants such as persistent pesticides and mercury in fish, and to understand the factors affecting the biomagnification of these pollutants through the Lake Malawi food web.

Stomach content analyses have often been used to characterize fish diets and feeding relations in a freshwater food webs. However, in warm climates it can be difficult to identify what a fish has eaten because its prey are rapidly digested. In this study we used a newer technique, stable isotope analyses, to determine the dietary habits of the fish and invertebrates of Lake Malawi. The elements of nitrogen and carbon have stable isotopes which differ only slightly in their mass; the ratio of these isotopes (^{13}C and ^{12}C for carbon; ^{15}N and ^{14}N for nitrogen; expressed as $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ respectively) in tissues from fish and other organisms is used to determine what source of carbon they are feeding upon, and their trophic level in the food web (Peterson and Fry 1989). The ratios of the heavier to lighter carbon isotopes ($^{13}\text{C} : ^{12}\text{C}$) do not change when food is assimilated into an organism and can be used to determine whether a fish feeds upon bottom-dwelling (benthic) or open-water (pelagic) invertebrates for example. Previous research on Lake Malawi by Bootsma et al. (1996) revealed that algae growing on rocks are much heavier in ^{13}C than the free-floating algae. Because fish in Lake Malawi are very specialized in their feeding habits, $\delta^{13}\text{C}$ can be used to distinguish the feeding habits of lower- and upper-trophic-level fish into those that are part of the nearshore (benthic) food web from those that are part of the offshore (pelagic) food web. In contrast, $\delta^{15}\text{N}$ measurements are used to determine an organism's trophic level because the heavier isotope of nitrogen (^{15}N) is retained to a greater extent than ^{14}N in a fish when compared to its diet. A predator typically has $\delta^{15}\text{N}$ values that are 3 to 5 parts per thousand (‰) greater than the prey (Peterson and Fry, 1989). These isotopic analyses provide information on the longer-term dietary habits of organisms, unlike stomach content analyses which represent an organism's most recent diet.

The objectives of this study are as follows:

- To understand the feeding relationships in both the offshore and nearshore food webs of Lake Malawi using stable carbon and nitrogen isotope analyses.
- To develop baseline information on the levels of mercury, PCBs and persistent pesticides in fish from Lake Malawi, particularly in those fish consumed by the residents of the riparian countries.
- To determine whether these pollutants are biomagnifying through the food webs of Lake Malawi.
- To determine whether pollutants accumulate differently in the offshore versus the nearshore food webs.
- To determine whether fish with rare dietary habits (such as scale, fin or egg eaters) are at greater risk of accumulating pollutants than fish with more common dietary habits.
- To determine whether some areas of Lake Malawi are more contaminated than others through the analyses of fish from several locations around the lake.

Methods

In May of 1996 and 1997, fish and invertebrates were collected from several locations in the southern part of Lake Malawi for pollutant and stable isotope analyses. The offshore species of fish were purchased from fishermen in the Senga Bay area and at the market in Salima, or from Maldeco commercial fisheries near Monkey Bay. In 1996 the field work focussed upon the open-water, offshore food web (zooplankton, lakeflies, usipa and offshore predators). In 1997 we used SCUBA to collect rock-dwelling fish (mbuna) and invertebrates that were associated with the nearshore food web of the Maleri Islands. The sampling locations are shown on Figure 9.1. Time limitations prevented us from collecting one species of fish from several locations around the lake to examine site to site differences in contaminant concentrations in fish.

Whenever possible a size range of fish were selected, and then the weights and lengths of these fish were determined. Most fish were frozen whole and shipped to the Freshwater Institute in Winnipeg for analyses. Muscle tissue and skin from the larger fish was removed and frozen in solvent-rinsed tin foil because these fish could not be shipped whole.

Stable Isotope Analysis: Muscle tissue from all fish or whole invertebrates (shells or casings removed) were dried in an oven at 60°C and ground with a mortar and pestle. Samples (1 to 2 mg for carbon; 2 to 4 mg for nitrogen) were weighed into tin capsules and analysed for stable carbon and nitrogen isotope ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$). The samples were combusted in a Carlo Erba NA1500

elemental analyzer. Sample gases were introduced into a VG Optima automated mass spectrometer with helium carrier gas, and water and carbon dioxide were cryogenically removed using magnesium perchlorate and an Ascarite[®] column respectively. All carbon and nitrogen isotope samples were standardized against carbon in PeeDee limestone and nitrogen in air respectively as follows:

$$\delta^{13}\text{C} \text{ or } ^{15}\text{N} \text{ ‰} = [(R_{\text{sample}}/R_{\text{standard}})-1] \times 1000$$

where $R = ^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$ and is expressed on a per mil (‰) or parts per thousand basis. Pharmamedium, a cottonseed protein, was used as a laboratory working standard and was run every 5 to 10 samples for both N and C analyses. Precision of the nitrogen and carbon isotope analysis was 0.4 and 0.3 ‰ (2 SD) respectively. One to 10 individuals from each of the 33 species or taxa was analysed for stable isotopes. Mean $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values only are shown. Results of these analyses were used to select fish and invertebrates for pollutant analyses.

Organochlorine Analysis: All organochlorine analyses were done at the Freshwater Institute in Winnipeg. Most fish were analysed whole for persistent organochlorines; muscle (including skin) was analysed for the larger fish such as the catfish. Prior to extracting the samples, whole fish or muscle was homogenized with dry ice and all invertebrate samples were freeze-dried. In brief, fish and invertebrates tissues were combined with 20 to 40 g of sodium sulfate and mixed until homogeneous. Samples were then extracted using an accelerated solvent extractor (2000 psi; 100 °C). Percent lipid in these tissues was determined gravimetrically using 1/10th of the extract. After removing the remaining lipids using automated gel permeation chromatography on SX-3 Biobeads with DCM:hexane, the extract was separated on Florisil (8 g; 1.2 % deactivated with HPLC-grade water) into three fractions: hexane (F1), hexane:DCM (85:15)(F2), and hexane:DCM (1:1)(F3). F1 contained all PCBs, and chlorobenzenes; F2 contained most of the hexachlorocyclohexane, chlordane and DDT compounds.

Florisil eluates were analysed by capillary gas chromatography (GC) with ⁶³Ni electron capture detection on a 60 m x 0.25 mm DB-5 column using a Varian 3400 or 3600 GC (Varian Instruments Palo Alto CA) under the conditions given in Kidd et al. (1998a). Concentrations of PCBs, chlorobenzenes (microcontaminants in many pesticide formulations), and the multipurpose pesticides DDT, chlordane and HCH were quantified using external standards. PCBs were quantified using a series of mixtures obtained from National Research Council of Canada (Halifax NS) and from Ultra Scientific (Hope RI), and ΣPCB represents the sum of 100 individual PCBs. ΣDDT is the sum of the parent compounds (*p,p'*- and *o,p'*-DDT) and metabolites (*p,p'*- and *o,p'*-DDD; *p,p'*- and *o,p'*-DDE). ΣHCH was quantified as the sum of αHCH , βHCH , and γHCH . The chlorobenzenes (ΣCBZ) detected in these fishes included 1,2,3,4-tetrachlorobenzene, hexachlorobenzene and pentachlorobenzene. Total chlordane (ΣCHL) was the sum of all chlordane-related compounds including heptachlor epoxide (shown only in Figure 9.5).

Quality assurance included the analysis of certified reference materials cod liver oil SRM 1588 (National Institute of Standards and Technology) or CRM-349 (BCR, Brussels, Belgium) every 20 samples. Reagent blanks were run with every 20 samples and showed only low levels of OCs. Results were not blank corrected.

Mercury Analysis: Muscle tissue from all fish, and whole invertebrates were analysed for total mercury [includes both organic (methylmercury) and inorganic (elemental mercury) at the Freshwater Institute. Methods for mercury extraction and analyses followed those given in Hendzel and Jamieson (1976). Tissues were digested in nitric and sulfuric acid at 180 °C, and the extracts analysed on an atomic absorption spectrophotometer. For quality control purposes, five certified reference materials and blanks were analysed at the same time as the Lake Malawi samples. Mercury results given herein were blank corrected.

Previous studies of fish from cold-water lakes have demonstrated that methylmercury makes up more than 90% of all mercury in fish (Bloom 1992). We are presently determining whether similar relations exist for tropical fish by analysing some of the Lake Malawi fish for methylmercury.

Results and Discussion

Food web relations: The dietary habits of all of the organisms that were collected from Lake Malawi in 1996 and 1997 were determined using stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope analyses. These results were used to identify organisms for pollutant analyses to ensure that biota from several different trophic levels (using $\delta^{15}\text{N}$) and from both the offshore (pelagic) and nearshore (benthic) food webs (using $\delta^{13}\text{C}$) were analysed. Mean $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values for most of the fish and invertebrates we collected from Lake Malawi are shown in Figure 9.4. Zooplankton, which feed upon free-floating algae had an average $\delta^{13}\text{C}$ value of -24.5‰ . In contrast, benthic algae had a much more enriched (less negative) $\delta^{13}\text{C}$ signal of -5.5‰ . We used these two endpoints to separate all other organisms into

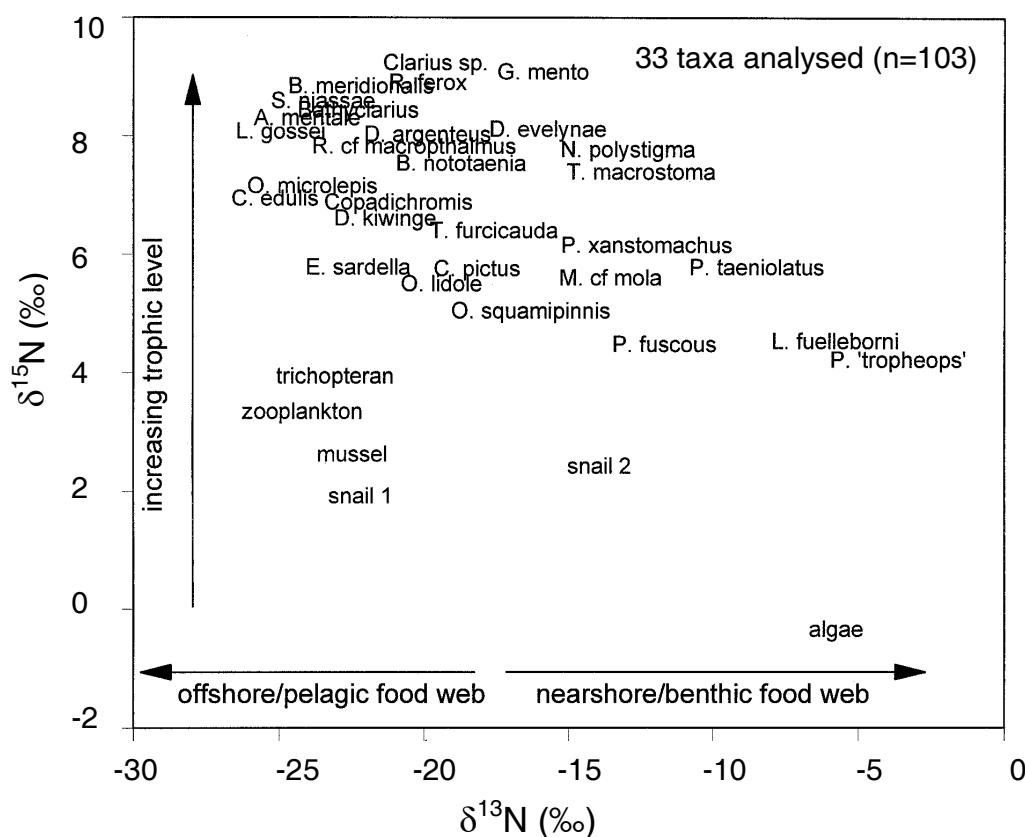


Figure 9.4. Food web relationships of organisms analysed for persistent organochlorines and mercury.

those that were part of the offshore food web ($\delta^{13}\text{C}$ values less than -18‰) and those that were part of the nearshore food web ($\delta^{13}\text{C}$ of more than -18‰).

In the offshore food web, the catfish (*Bagrus meridionalis*; *Clarius* sp.), *Synodontis njassae*, and cichlids (*Ramphochromis ferox*) were the top predators and had the highest $\delta^{15}\text{N}$ values (8.5, 9.1, 8.2, and 8.6‰). The $\delta^{15}\text{N}$ of these fish suggest that they fed mainly upon fish such as *E. sardella*. Fish that feed upon invertebrates such as zooplankton had the next highest $\delta^{15}\text{N}$ values between 5 and 7 ‰ (e.g. *Engraulicypris sardella*); zooplankton had the lowest mean $\delta^{15}\text{N}$ value of 3.2 ‰. Lake flies (*Chaoborus edulis*) are considered to be an important invertebrate link in the offshore food web (Irvine, 1995), and they had a mean $\delta^{15}\text{N}$ value of 7.12 ‰, a full trophic level higher than the zooplankton. The $\delta^{13}\text{C}$ of the lake flies (-24.0‰) was very similar to that of the zooplankton (-24.5‰), indicating that lake flies fed mainly upon zooplankton.

Fewer fish and invertebrates were collected from the nearshore food web than the offshore food web. The stable isotope analyses indicated that several of the mbuna fed directly upon the benthic algae, including *Labeotropheus fuelleborni* and *Pseudotropheus* sp. '*tropheops maleri* yellow' (shown as *P. tropheops* on Figure 9.4; mean $\delta^{15}\text{N}$ values of 4.4 and 4.3 ‰, respectively). Other rock-dwelling species such as the *Protomelas taeniolatus*, *Pseudotropheus xanstomachus* and *Mylochromis* cf. *mola* had higher $\delta^{15}\text{N}$ values (mean $\delta^{15}\text{N}$ values of 5.6, 6.0 and 5.4 ‰, respectively) consistent with a diet of invertebrates. Although very few top predators were collected from the nearshore food web, some of the upper-trophic-level fish included *Nimbochromis polystigma* and *Tyrannochromis macrostoma* (mean $\delta^{15}\text{N}$ values of 7.2 and 7.6 ‰).

Persistent pesticides and PCBs in fish and other aquatic organisms: Concentrations of persistent pesticides and PCBs in fish from Lake Malawi were low in all fish analysed (Table 9.13). The pesticides chlordane and DDT, and PCBs and chlorobenzenes were the most common contaminants found, and were generally higher in fish-eating fish than in invertebrate- or algae-eating fish. Of these, Σ DDT was the most predominant contaminant in top predators such as *Synodontis njassae* and was found at levels that were up to 60 times higher than any other pollutant measured (see Figure 9.5).

A fungus-eater (*Docimodus evelynae*) and a fin- and scale-eater (*Genyochromis mento*) were analysed to determine whether fish with unusual dietary habits were at greater risk of accumulating persistent contaminants than fish having more common diets. Concentrations of all organochlorines in these fish were low and comparable to those found in the algae-eating species (see Figure 9.5 and Table 9.13).

In relation to other studies on East African lakes, concentrations of Σ DDT in fish from Lake Malawi were much lower than results from Lakes Kariba and Mchinge, and similar to levels in fish from Lake Nakuru in Kenya (Figure 9.6). These comparisons to Lake Malawi have been made using studies by Berg et al. (1992), Mhlanga and Madziva (1990) and Greichus et al. (1978) and using species with similar dietary habits and sizes. High Σ DDT in fish from Lakes Kariba and Mchinge may be the result of more usage of this pesticide in Zimbabwe to control tse tse flies (Berg et al. 1992).

Concentrations of organochlorines in Lake Malawi fish were similar to what has been found in fish from Canadian lakes that are very remote from industries and that are contaminated solely from atmospheric inputs of these pollutants (Paterson et al. in press). In contrast, fish from the highly industrialized Laurentian Great Lakes have Σ DDT concentrations that are many times higher than what has been found in this study; for example, average Σ DDT concentrations in lake trout from Lake Ontario were 840 ng/g in 1992 and as high as 1900 ng/g in the late 1970s (De Vault et al. 1996). Σ PCB concentrations in lake trout from the least contaminated of the Laurentian Great Lakes, Lake Superior, are also many times higher (average of 450 ng/g in the early 1990s; De Vault et al. 1996) than what has been found in Lake Malawi fish.

Previous studies of cold-water lakes have found higher concentrations of organochlorines in fattier (Kidd et al. 1998a; Rasmussen et al. 1990) and larger (Kidd et al. 1998b) fish. In this study, we found that the concentrations of these contaminants were also higher in fattier fish, and we observed a significant relationship between DDT and percent lipid in all organisms from Lake Malawi (Figure 9.7). *Opsaridium* spp. (mpasa) and *Synodontis njassae* had the highest percent lipid (9.1 and 12.8 % respectively) and Σ DDT (Table 9.1) of all species analysed. Although not shown, the larger fish analysed for each species had consistently higher concentrations of organochlorines than the smaller fish. These results indicate that some of the same factors that affect contaminant concentrations in cold-water fish are also important for tropical fish.

In addition, Σ DDT concentrations in these organisms were significantly related to their trophic position ($\delta^{15}\text{N}$; Figure 9.8), indicating that fish at a higher trophic level have higher concentrations of pollutants. We also observed that Σ DDT accumulated to a greater degree through the offshore than nearshore food web; the slope of the regression between Σ DDT and $\delta^{15}\text{N}$ was twice as large for the offshore (slope = 0.26) than the nearshore food web (slope = 0.13; relations not shown). The higher accumulation of contaminants in the offshore food web appears to be related to the higher lipid content of these fish.

Previous studies have also found that contaminant concentrations in biota are significantly related to their trophic position ($\delta^{15}\text{N}$) in temperate (Kucklick et al. 1996) and arctic food webs (Kidd et al. 1995; 1998b). The slope of the relation between organochlorine concentrations and $\delta^{15}\text{N}$ can be compared among lakes and used to contrast the degree of contaminant biomagnification through food webs; for this study, we observed that *p,p'*-DDE (a metabolite of the active component of DDT) was accumulated through the Lake Malawi food web at a degree similar to that observed for Lake Baikal (Kucklick et al. 1996) and Lake Superior (Kucklick and Baker 1998) even though these lakes have very different species, with different growth rates and lifespans, and distinct seasonal temperatures.

Mercury in fish: Concentrations of total mercury were generally highest in muscle from fish-eating fish (0.02 to 0.16 ug/g), and lowest in fish that eat algae (<0.001 to 0.003 ug/g wet weight; Figure 9.9).

Table 9.13. Mean concentrations [ng (g weight wet)⁻¹] of the pesticides DDT, HCH and chlordane, and PCBs in fish from Lake Malawi (1996 & 1997).

Species	Common Name	Weight (g) and (# of Fish)	Tissue Analysed	ΣDDT	ΣPCBs	ΣChlordane	ΣHCH
<i>Bagrus meridionalis</i>	Kampango	1298 ± 1244 (4)	muscle	10.2 ± 11.7	0.9 ± 0.6	0.2 ± 0.2	0.03 ± 0.00
<i>Buccochromis nototaenia</i>		472 (2)	muscle	3.4	1.4	0.04	0.02
<i>Clarius</i> sp.		133 (1)	muscle	1.4	2.6	0.06	0.03
<i>Ctenopharynx pictus</i>		10 ± 9.4 (5)	whole	2.0 ± 0.9	1.9 ± 0.2	0.08 ± 0.04	0.1 ± 0.1
<i>Dimidiochromis kiwinge</i>		10 ± 9.0 (5)	whole	2.9 ± 1.3	1.5 ± 0.4	0.08 ± 0.04	0.08 ± 0.07
<i>Diplotaxodon argenteus</i>		48.5 (2)	whole	3.7	1.4	0.05	0.03
<i>Docimodus evelynae</i>	Mbuna	4.8 (1)	whole	1.1	1.9	0.05	0.06
<i>Engraulicyprus sardella</i>	Usipa	4.6 ± 2.1 (6)	whole	5.2 ± 3.3	4.6 ± 4.0	1.0 ± 1.2	0.16 ± 0.12
<i>Genyochromis mento</i>	Mbuna	13 ± 1.7 (5)	whole	1.1 ± 0.97	1.8 ± 0.45	0.05 ± 0.05	0.06 ± 0.05
<i>Labeotropheus fuelleborni</i>	Mbuna	20 ± 12 (6)	whole	1.2 ± 0.45	1.9 ± 1.3	0.06 ± 0.03	0.08 ± 0.04
<i>Nimbochromis polystigma</i>		28 ± 17 (3)	whole	3.5 ± 0.20	1.7 ± 0.53	0.09 ± 0.02	0.13 ± 0.07
<i>Opsaridium microlepis</i>	Mpasa	491 ± 153 (7)	muscle	34 ± 16	3.6 ± 1.8	1.1 ± 0.34	0.09 ± 0.09
<i>Oreochromis</i> spp. ¹	Chambo	633 ± 208 (6)	muscle	0.59 ± 0.38	0.41 ± 0.26	0.01 ± 0.01	0.05 ± 0.03
<i>Petrotilapia</i> sp. 'fuscous'	Mbuna	24.5 ± 11.1 (7)	whole	1.1 ± 1.0	1.4 ± 0.65	0.06 ± 0.05	0.08 ± 0.07
<i>Protomelas taeniolatus</i>	Mbuna	13 ± 2.8 (6)	whole	3.5 ± 1.1	2.1 ± 0.35	0.18 ± 0.06	0.20 ± 0.04
<i>Pseudotropheus</i> sp. 'tropheops'	Mbuna	16 ± 6.7 (6)	whole	1.3 ± 0.34	2.5 ± 1.6	0.07 ± 0.04	0.15 ± 0.15
<i>Pseudotropheus xanostomachus</i>	Mbuna	12 ± 6.8 (6)	whole	1.9 ± 1.3	1.5 ± 0.36	0.12 ± 0.08	0.10 ± 0.07
<i>Ramphochromis ferox</i>	Ncheni	516 (1)	muscle	8.3	1.7	0.07	0.02
<i>Synodontis njassae</i>		85.8 ± 35.9 (5)	whole	58 ± 39	6.6 ± 3.2	0.38 ± 0.16	0.07 ± 0.05
<i>Tyrannochromis macrostoma</i>		20.4 ± 10.7 (5)	whole	3.4 ± 3.3	1.4 ± 0.3	0.06 ± 0.03	0.09 ± 0.03

¹*O. lidole* and *squamipinnis*

An anomalously high concentration of mercury, 0.39 ug/g, was found in one of the *Ramphochromis ferox* (ncheni) analysed, but this result was still below the concentration recommended for the protection of wildlife of 0.5 ug/g (De Vault et al. 1995). Unlike the results for the organochlorines, larger fish did not have consistently higher mercury concentrations than the smaller fish.

Fish from Lake Malawi have concentrations of mercury that are comparable to or lower than what has been found in fish from other East African Lakes. Greichus et al. (1978a; 1978b) found mean concentrations of total mercury in several species of fish from Lakes Nakuru and McIlwaine of 0.044 and 0.046 ug/g wet weight, respectively. In similar studies of several dams in South Africa, Greichus et al. (1977) found average concentrations of total mercury that ranged from 0.13 to 0.06 ug/g wet weight. The studies by Greichus et al. gave an average mercury concentration for several species of fish rather than concentrations for each different species; for this reason it was not possible to directly compare results among lakes for species with similar dietary habit.

Human Health Impacts of Pollutants in Fish: To determine whether the pesticides, PCBs and mercury in Lake Malawi fish pose a health risk to humans, tolerable daily intakes (TDIs; the amount of pollutant that can be safely consumed on a daily basis over a person's lifetime) and concentrations of these pollutants in fish must be examined. These TDIs are based upon long term toxicity tests (lifetime exposures) on mammals, or upon observed effects of these pollutants on humans. For each metal or pesticide, the highest exposure that does not cause a toxic effect (No Observed Adverse Effects Level or NOAEL) is determined. This NOAEL is then divided by a safety factor of 100, which takes into account differences among humans, and the differences between humans and the mammals used in the toxicity tests, to determine

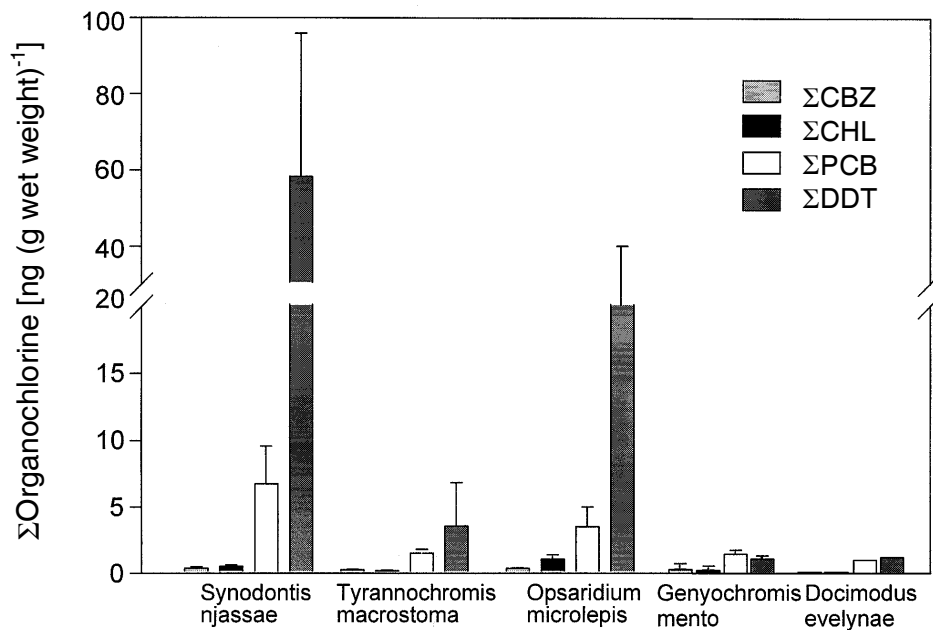


Figure 9.5. Concentrations of Σ chlorobenzene (CBZ), Σ chlordan (CHL), Σ PCB and Σ DDT in fish from Lake Malawi/Nyasa (1996-1997).

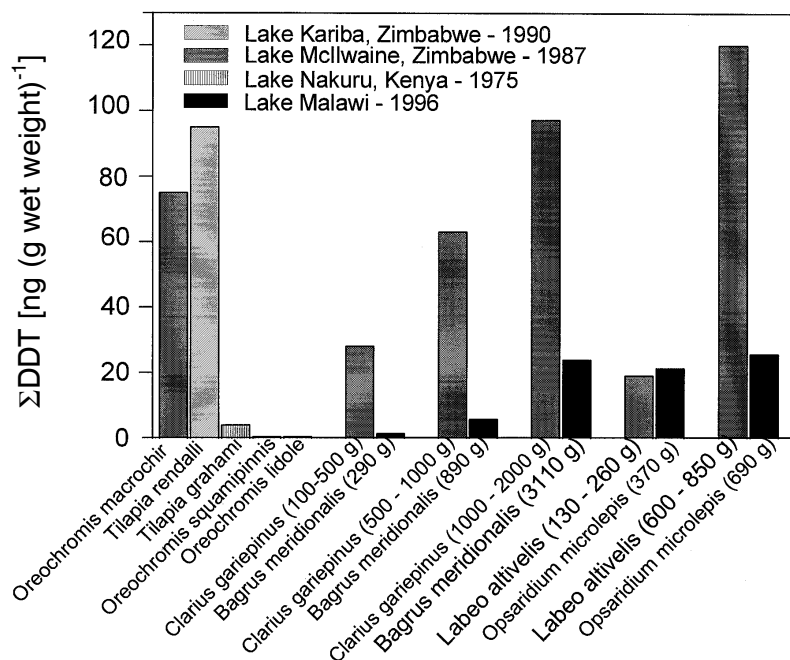


Figure 9.6. Concentrations of DDT in fish from East Africa (this study; Berg et al. 1992; Mhlanga and Madziva 1990; Greichus et al. 1978).

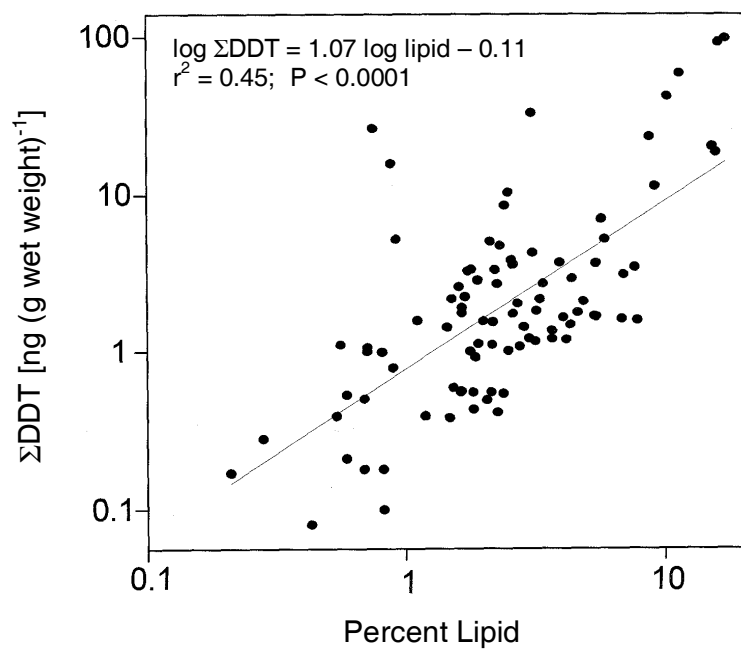


Figure 9.7. Concentrations of ΣDDT versus percent lipid in fish and invertebrates from Lake Malawi/Nyasa.

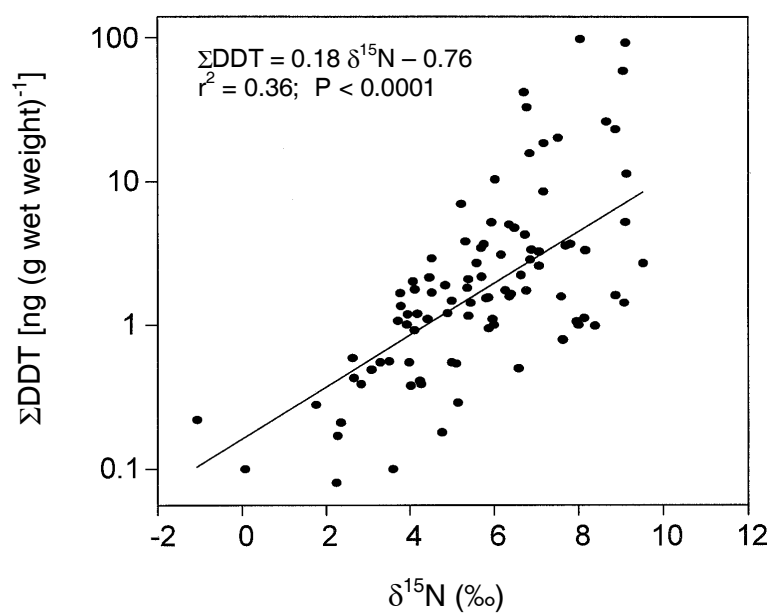


Figure 9.8. Concentrations of ΣDDT versus δ¹⁵N in biota from Lake Malawi/Nyasa.

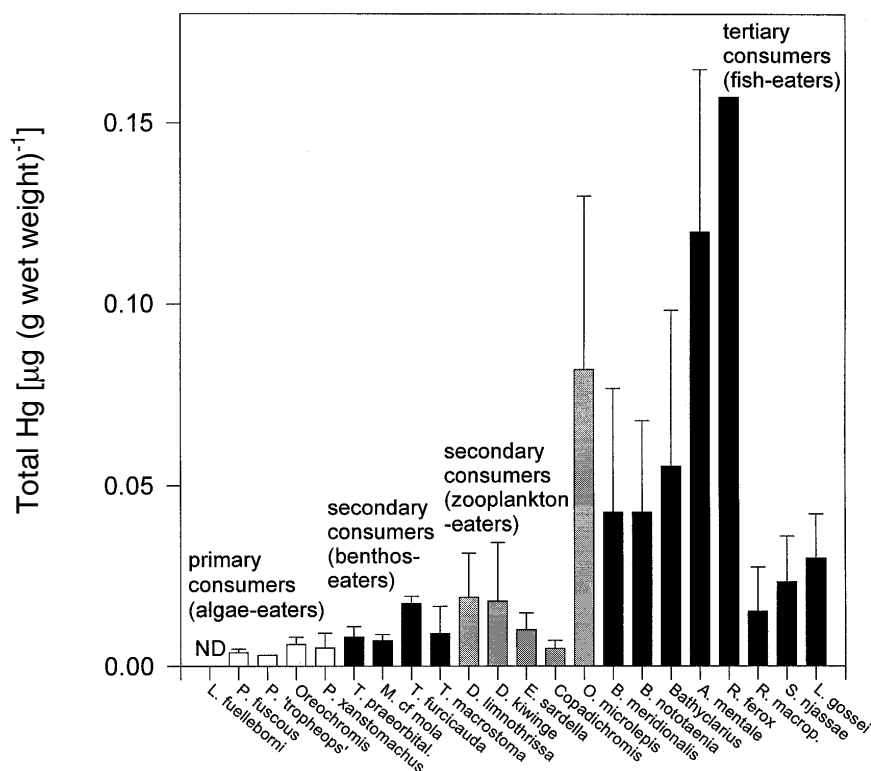


Figure 9.9. Mean concentrations (\pm SD) of total mercury in fish muscle from Lake Malawi/Nyasa, 1996-1997.

considerably. For example, a person can safely ingest about over 25 times more DDT than mercury based upon the TDIs shown in Table 9.14.

Some of the fish that are commonly consumed by the residents of Malawi are shown in Table 9.15. Using the average concentrations of some pollutants in these species of fish (Table 9.13), we calculated the maximum amount of either muscle or whole fish (wet tissue) that could be consumed safely on a daily basis over a person's lifetime (Table 9.15). For these calculations we assumed that the person weighed 60 kg and that they were not exposed to these pollutants through other food or non-food sources. These calculations should be adjusted for people heavier or lighter than 60 kg using the equation shown in Table 9.15. Based upon the TDIs for pesticides and PCBs, a person could safely consume between 3 and 235 kg of Lake Malawi fish per day depending upon the species. It is unlikely that one person would or could consume enough fish in a day to exceed these TDIs. However based on the mercury TDIs, considerably less fish can safely be consumed on a daily basis [330 g of ncheni or 350 g of mpasa if you assume that most of the mercury in fish is methylmercury (only 150 g for children, pregnant women and women of child-bearing age); Table 9.15], and these amounts are likely much closer to actual fish consumption rates in the riparian countries. Prior to making any conclusions it is necessary to combine these calculations with some fish consumption data for the region. It is also important to note that some fish, such as usipa, are eaten dried. This will lower the amount of fish that can be safely consumed per day because on a per mass basis, dried fish have higher concentrations of pesticides and mercury than fish that have not been dried.

Table 9.14. Tolerable daily intake (TDI) or acceptable daily intake (ADI) of environmental contaminants for humans (from Bureau of Chemical Safety, Health Protection Branch, Health Canada, Ottawa, Canada).

Contaminant	Canadian TDI/ADI (ug. kg body weight ⁻¹ .day ⁻¹)
Total DDT (includes DDE and DDD metabolites)	20
Total HCH (includes α -, β -, γ - and δ -HCH)	0.3
Total PCB (all congeners)	1.0 ¹
Chlordane (cis-, oxy- and trans-chlordane, cis- and trans-nonachlor)	0.05 ¹
Mercury (total Hg)	0.714
Mercury (methyl Hg)	0.471 ^{1,2}

¹under review; ²a provisional TDI (pTDI) of 0.20 ug methyl Hg per kg body weight per day is being considered by Health Canada for pregnant women, women of child-bearing age and infants.

Table 9.15. Quantity of fish that can be safely consumed by a 60 kg person on a daily basis over a lifetime using the mercury and pesticide TDIs given in Table 9.4 {calculated as [TDI (from Table 9.14) x body wt (kg)]/mean concentration of pollutant in species (see Table 9.13)}

Species	Common Name	Tissue Analysed ¹	Amount of Fish (kg/day)			Amount of Fish (kg/day)
			Total Hg	Methyl Hg ²	Methyl Hg ³	Pesticides or PCBs
<i>Bagrus meridionalis</i>	kampango	muscle	1.0	0.60	0.28	17.7 ⁴
<i>Bathyclarius</i> spp.	bombe	muscle	0.71	0.47	0.20	
<i>Copadichromis</i> sp.	utaka	whole	8.9	5.9	2.5	
<i>Engraulicyprus sardella</i>	usipa	whole	4.2	2.8	1.2	4.1 ⁴
<i>Opsaridium microlepis</i>	mpasa	muscle	0.52	0.35	0.15	2.9 ⁴
<i>Oreochromis</i> spp. ⁶	chambo	muscle	7.3	4.8	2.1	235 ⁴
<i>Ramphochromis</i> spp.	ncheni	muscle	0.50	0.33	0.14	34.6 ⁵

¹may not be the same as the tissue consumed, analyses of muscle includes skin; ²using TDI of 0.471; ³based on the TDI for children, women of child-bearing age and pregnant women of 0.2 ug/kg body weight/day; ⁴based upon chlordane TDI; ⁵based upon PCB TDI; ⁶*O. squamipinnis*, *O. lidole* and *O. karongae*

Potential Impacts of Pollutants in Fish on Fish-Eating Wildlife: Mammals and birds that consume fish may also be at risk from pollutants in their diet. For example, high levels of DDT in the diets of birds causes eggshell thinning and other such impairments to reproduction (e.g. Kolaja, 1977). Canadian tissue residue guidelines (TRGs) are the maximum concentration of an organochlorine that could safely be consumed by wildlife, and have been determined using toxicity tests on fish-eating birds and mammals. For the Lake Malawi fish, all *Opsaridium* and *Synodontis*, and one large *Bagrus* had tissue DDT concentrations above the TRG (14 ng/g). However most fish (71 of 84 analysed) had DDT concentrations that were much lower than the TRG (Table 9. 13). For this reason, it is unlikely that DDT poses a significant risk to wildlife that consume the fish from Lake Malawi. Concentrations of mercury in all fish were below the recommended levels for the protection of wildlife (0.5 ug/g; De Vault et al. 1995).

Conclusions

Based upon the results from this study, we conclude that:

- Concentrations of persistent pesticides, PCBs and mercury in most fish from Lake Malawi were low. DDT was the most predominant contaminant in many of the fish-eating fish.
- Concentrations of persistent organochlorines in a scale/fin eater (*G. mento*) and a fungae-eater (*Docimodus evelynae*) were low and indicated that fish with unusual dietary habits did not have a greater risk of accumulating contaminants than fish with more common diets.
- Concentrations of total DDT in fish from Lake Malawi are lower than levels found in fish from other East African lakes.
- Lipid is a significant predictor of organochlorine concentrations in fish from Lake Malawi. The offshore fish tend to be fattier and therefore also more contaminated than the nearshore fish we analysed.
- Trophic position (as determined by $\delta^{15}\text{N}$) is also a significant predictor of organochlorine levels in the food web from Lake Malawi. Based upon the slope of this relation, DDT accumulates at the same rate in this tropical food web as has been found previously in temperate and arctic food webs.
- DDT is accumulated at a greater rate (slope of DDT versus $\delta^{15}\text{N}$) through the offshore than nearshore food web of Lake Malawi, and this is likely due to the higher lipid content of the offshore top predators.
- Information on consumption rates are needed to assess whether contaminants in the fish may have human health impacts. It is unlikely that organochlorines would have any health impacts because a person would have to consume more than 3 kg of fish each day to exceed the recommended intake of these contaminants. However, mercury is a potential problem for humans since less of some fish species can safely be consumed (e.g. 140 g of ncheni or 150 g of mpasa for pregnant women, women of child-bearing age and children).
- The levels of organochlorines and mercury found in Lake Malawi fish are not likely to have detrimental impacts upon fish-eating wildlife.

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