Part B: Sediment Core Investigation

Chapter 7: Purpose

The purpose of the *Sediment Core Investigation* is to systematically assess chemical patterns within the Finger Lakes over time. Specific goals of the Study are as follows:

1. Assess spatial variations in chemical patterns between the Finger Lakes,
2. Assess temporal patterns of chemical inputs within each lake,
3. Evaluate chemical levels with respect to sediment quality assessment values,
4. Determine sediment accumulation rates.

A second, related study, termed the *Synoptic Water Quality Investigation*, involves long term synoptic water quality monitoring on each of the lakes and is discussed above (see Part A)
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Chapter 8: Design and Methods

The Finger Lakes Sediment Core Investigation involved the collection of a deep water sediment core from each of the 11 Finger Lakes, vertical segmentation of the core, radiometric dating of core segments, and chemical (organic and inorganic) analysis of core segments. The Sediment Core Investigation was designed as a one-time effort and was conducted between 1997-98.

Sample Collection

All sediment cores, with the exception of the Seneca Lake core, were collected from the New York State Department of Environmental Conservation (NYSDEC), Division of Water (DOW) sediment assessment vessel (Figure 8.1). The vessel, a 23 feet long aluminum pontoon boat, is equipped with a 19 feet tall tripod and electric winch. The deck of the vessel has a 4 x 3 foot opening to allow deployment of the sediment coring device.

Figure 8.1: NYSDEC sediment assessment pontoon boat

The Seneca Lake core was collected in cooperation with Professor John Halfman of Hobart and William Smith College (Geneva, NY) using their research vessel, which is stationed on Seneca Lake.

Sediment cores were collected with a modified Wildco Box Corer [model # 191-A15; dimensions 15.2 x 15.2 x 100 cm] – see Figure 8.2, and associated acrylic core liner. Factory modification involved lengthening the corer to accommodate collection of 1-meter cores. The corner seams of the liner(s) proved of insufficient strength (often splitting upon removal and/or core extrusion) and had to be reinforced with duct tape. Otherwise, the box corer worked well.

Figure 8.2: Wildco Box Corer

The core collection procedure is as follows: (a) the box corer is lowered to within approximately 2 meters of the lake bottom using an electric winch; (b) sufficient winch cable is spooled out to allow free-fall of the corer to the lake bottom; (c) the sample crew secures the spooled cable, and when in position they release the cable in unison; (d) immediately after core penetration, tension is reestablished on the cable to establish vertical stability of the corer; (e) the corer is retrieved using an electronic winch; (f) once on board the sampling vessel, the box corer is placed within a wash basin and the corer is lifted off the core liner; (g) water overlying the core is siphoned off to minimize disturbance of the upper core layers during transport to shore; (h) core length is measured; and (i) core is secured for transport to shore.

The core extrusion and segmentation procedure is as follows: (a) core liner is hoisted atop an extrusion apparatus (this consists of a wooden frame with an extruding surface area slightly smaller than the surface area of the core liner); (b) meter stick is affixed to the side of the liner to enable measurement of individual sediment segments; (c) sediment core is pushed upward by prescribed increment; (d) core segment is inspected and visually described; (e) core segment is sliced off and sub-sectioned for laboratory submission; and (f) steps c through e are repeated as necessary. Sediment cores are sectioned into 1–4 cm increments and analyzed for the following parameters: (1) radioisotopes, (2) organic compounds, (3) inorganic compounds, and (4) ancillary parameters.

All sediment cores were collected from deep water locations – either maximum lake depth or greater than 25 meters. Deep water locations are more likely to contain undisturbed sediment deposits than are shallower areas. Thus, in theory, deep water cores insure an intact sediment chronology – as will be discussed below, this proved only partially true. Sample locations and approximate water depths for each of the sediment cores are shown in Table 8.1.

Table 8.1: Sediment core sample locations

Lake	**Latitude**	**Longitude**	**Water Depth (m)**	**Landmarks (**latitudinal**)**
Otisco	42 51 24	76 16 37	20	South of Bay Shores
Skaneateles	42 53 33	76 24 08	35	Thornton Grove
Owasco	42 51 48	76 31 21	35	Burtis Point
Cayuga	42 32 50	76 34 01	65	Between Myers & Taughannock Points
Seneca	42 43 07	76 56 14	130	Sampson State Park
Keuka	42 25 58	77 11 00	45	Silvernail Road
Canandaigua	42 41 50	77 21 11	60	Just south of Long Point
Honeoye	42 45 05	77 30 42	8	California Point
Canadice	42 43 01	77 34 01	27	Mid-point of lake
Hemlock	42 42 26	77 35 37	27	3.8 km from south end of lake
Conesus	42 45 00	77 43 05	16	Cotton Wood Point

Analyses

Radioisotopes

Selected core segments were analyzed for radioisotopes (including ^{137}Cs, ^{210}Pb, ^{214}Bi, and ^{226}Ra) in an effort to establish time chronologies within the given core.

Samples were dried in a hood under a heat lamp and ground in a mortar with a pestle. Sub-samples were transferred to plastic vials and sealed for at least twenty days to allow the short-lived daughters of ^{226}Ra to grow into equilibrium. The sub-samples were analyzed for ^{137}Cs, total ^{210}Pb ($^{210}Pb_{tot}$), ^{214}Pb, and ^{214}Bi via gamma counting. ^{214}Pb and ^{214}Bi are short-lived daughters of ^{226}Ra (which is also the parent of ^{210}Pb). The mean equilibrium activity of ^{214}Pb and ^{214}Bi is equal to the supported ^{210}Pb ($^{210}Pb_{sup}$), the portion of $^{210}Pb_{tot}$ "supported" by the decay of ^{226}Ra in the sediments. Subtraction of $^{210}Pb_{sup}$ from $^{210}Pb_{tot}$ yields excess ^{210}Pb ($^{210}Pb_{xs}$) which was derived from the atmosphere and decays away in the sediments with a half life of 22 years. ^{137}Cs activities are reported in units of picocuries per kilogram (pCi/kg) while ^{210}Pb activities are given in decays per minute per gram (dpm/g). Dividing dpm/g by .00222 yields pCi/kg.

Radionuclide measurements were carried out using a gamma counter with an intrinsic germanium detector. Blank corrections were applied to each sample based on the analysis of empty sample containers. Background corrections were applied to each radionuclide based on the sample count rate at energies just above and just below each peak of interest. For ^{137}Cs, detector efficiency was calibrated using an NBS sediment standard (River sediment NBS 4350B), a liquid NBS standard (NBS 4953-C) that was used to prepare spiked sediments (G-standards), and secondary standards (D-standards) prepared at the Lamont-Doherty Earth Observatory and calibrated to NBS standards.

No major problems were encountered with the gamma counter: it remained stable during the entire period of counting.

Organic Chemicals

The suit of organic analytes measured during this study is shown in Table 8.2. These substances are termed organochlorines due to their composition (carbon and chloride molecules). All of these substances are currently either banned or restricted for usage within the United States. Thus, occurrence of these substances in the environment is likely the result of historical use and/or improper disposal. Unfortunately, from an environmental perspective, many of these substances are quite stable in aquatic environments and susceptible to biotic uptake and bioaccumulation. Thus, a number of these substances can remain in the environment for long periods of time and can increase in concentration within biota.

The analytical method used for organic analyses was EPA method 608/8080 [Organochloride Pesticides/PCB's (Dual column GC/ECD)]. Sediment samples were homogenized and a 5-10 gram aliquot was used for analysis. The aliquots were Soxhlet extracted for 16 hours using acetone/hexane (1:1). After extraction, the extracts were treated with anhydrous sodium sulfate and given further cleanup with gel permeation chromatography and Florisil. The analyses were performed using a 5890 Hewlett Packard gas chromatograph with a 60 meter DB-5 capillary column (J&W scientific), I.D. - 0.25 mm with a film thickness of 0.1 micron, using a Nickel 63 electron capture detector. The carrier gas was helium (0.8 mL/min) with nitrogen as the auxiliary gas (60 mL/min). The initial temperature of 90 degrees C was held for one minute, programmed to 150 degrees C at 25 degrees C per minute and held for 4 minutes, then programmed to 290 degrees C at 1.5 degrees C per minute. The final temperature was held for 40 minutes. Samples were also analyzed for total organic carbon using the Walkley-Black titration procedure.

Table 8.2: Organic analytes and usage (mostly historical).

Analyte	Description
HCH, alpha	Breakdown product of HCH, gamma
HCH, gamma	Hexachloro Cyclo Hexane; Insecticide - common name is lindane.
HCH, Beta	Breakdown product of HCH, gamma
HCH, Delta	Breakdown product of HCH, gamma
Heptachlor	Insecticide, restricted to underground termite control.
Heptachlor Epoxide	Formed by chemical and biological transformation of heptachlor.
Endosulfan I	Insecticide
Endosulfan II	Insecticide
Endosulfan Sulfate	Breakdown product of endosulfan
Aldrin	Insecticide
Dieldrin	Insecticide
Endrin	Insecticide
Endrin Aldehyde	Metabolite of endrin.
* 4,4'-DDT	Dichloro Diphenyl Trichloro Ethane; Insecticide
* 4,4'-DDE	Dichloro Diphenyl Dichloro Ethylene; breakdown product of DDT.
* 4,4'-DDD	Dichloro Diphenyl Dichloro Ethane; Insecticide
Methoxychlor	Insecticide
Toxaphene	Insecticide
Chlordane	Insecticide
Mirex	Insecticide and fire retardant.
* Total PCBs	
PCB Aroclor 1221	Hydraulics, plasticizers, adhesives, and electrical capacitors.
PCB Aroclor 1016/1242	Electrical capacitors and transformers, vacuum pumps, and gas-transmission turbines, heat transfer fluid, hydraulic fluids, rubber plasticizer, carbonless paper, adhesives and wax extenders.
PCB Aroclor 1248	Hydraulic fluids, vacuum pumps, plasticizers, synthetic resins, & adhesives.
PCB Aroclor 1254	Hydraulic fluid, rubber plasticizers, synthetic resins, adhesives, wax extenders, de-dusting agents, inks, cutting oils, pesticide extenders, sealants and caulking compounds.
PCB Aroclor 1260	Electrical transformers, hydraulic fluids, plasticizer, synthetic resins and de-dusting agents.

* Findings are presented below for these compounds

Inorganic Chemicals

Inorganic analytes are shown in Table 8.3. Analytical methods for inorganic analysis are: (1) SW-846 ICP method 6010 for total metals; (2) method 7740 for selenium; and (3) method 7470 for mercury.

The sediments are initially digested using SW-846 method 3050B. A representative aliquot of sample is weighed into a beaker and digested using nitric acid and hydrogen peroxide on a standard hot plate. Hydrochloric acid is used as a final reflux acid for ICP analyses. Nitric Acid is used as the final reflux acid for Graphite Furnace analyses. The samples are then analyzed by ICP-AES or Graphite Furnace Atomic Absorption (GFAA). The metals are analyzed on a Perkin Elmer Optima 3000XL Axial ICP using the internal standard, Yttrium, to help stabilize the "plasma environment". This axial ICP allows for much lower detection limits than the standard radial ICP, but the Linear Range is sacrificed to obtain lower level detection limits. Metals that do not need low detection limits and are known to have high concentrations, such as the Alkaline Earth metals (Ca, K, Na, and K) are analyzed on a Leeman PS3000 radial ICP. Any low level metals such as As, Se, Pb and Tl that do not fall within SW-846 6010B criteria, can also be analyzed by GFAA - performed on a Perkin Elmer 4100ZL. This furnace has a Zeeman Background Correction that is used to help overcome difficult matrix interference. The sediments are also digested and analyzed for Mercury using Cold Vapor Atomic Absorption (CVAA) using method 7471. A Perkin Elmer FIMS analyzer was used to determine Hg concentrations in the sediment samples.

Table 8.3: Inorganic analytes and potential sources

Analyte	Symbol	Comments and Possible Sources
Aluminum	Al	Possible sources include geology and mining
Antimony	Sb	
*Arsenic	As	Possible sources include geology and pesticides
Barium	Ba	
Beryllium	Be	
*Cadmium	Cd	Possible sources include metal plating, etc.
*Calcium	Ca	Possible sources include geology and agriculture
*Chromium	Cr	Possible sources include metals plating, wood preservation, etc.
Cobalt	Co	
*Copper	Cu	Possible sources include geology and plumbing
Iron	Fe	Possible sources include geology, mining, and plumbing
*Lead	Pb	Possible sources include leaded gasoline and paint
Magnesium	Mg	
*Manganese	Mn	Possible sources include geology and the production of steel and batteries
*Mercury	Hg	Possible sources include fossil fuels and incinerators
Molybdenum	Mo	
*Nickel	Ni	Possible sources include metal plating, etc.
Potassium	K	
Selenium	Se	
Silver	Ag	
Sodium	Na	Possible sources include geology and mining
Strontium	Sr	
Thallium	Ti	
Tin	Sn	
Titanium	Ti	
Vanadium	V	
*Zinc	Zn	Possible sources include metal plating, etc.

* Findings presented below for these elements