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CHEMICAL STUDY OF THE INTERSTITIAL WATER DISSOLVED ORGANIC MATTER AND GASES IN LAKE ERIE, CLEVELAND HARBOR, AND HAMILTON HARBOUR BOTTOM SEDIMENTS - COMPOSITION AND FLUXES TO OVERLYING WATERS

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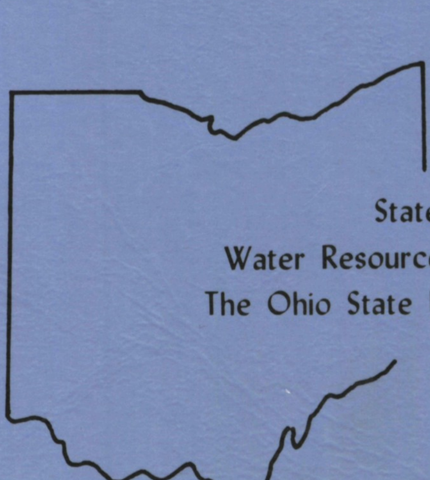

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FINAL REPORT FOR OWRT GRANT A-059-OHIO

CHEMICAL STUDY OF THE INTERSTITIAL WATER DISSOLVED ORGANIC MATTER AND GASES IN LAKE ERIE, CLEVELAND HARBOR, AND HAMILTON HARBOUR BOTTOM SEDIMENTS - COMPOSITION AND FLUXES TO OVERLYING WATERS

BY

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INTRODUCTION

During the summer and fall of 1979 and 1980 sediments from diver-obtained cores collected from Lake Erie's three basins, Cleveland Harbor, and Hamilton Harbour (on Lake Ontario) were analyzed for interstitial dissolved gases and dissolved organic carbon (DOC). The majority of 14 cruises taken during this two-year study were within the central basin of Lake Erie where investigations were conducted to evaluate compositional differences between the open lake environment and harbor sediments highly impacted by anthropogenic sources. Benthic chambers were also placed above the sediment surface at selected locations in the central basin of Lake Erie to retain evolved gases. In addition, sediments were collected from Lake Erie's central basin and Hamilton Harbour for removal of large quantities of interstitial water to characterize the chemical composition of organic compounds by gas chromatography/mass spectroscopy (GC/MS) and assess their molecular sizes. Sediment percent water and volatile solids were also measured at selected stations.

This represents the completion of these studies sponsored by OWRT and EPA and includes a data tabulation (in Appendix) as well as a selected bibliographic listing of papers dealing with gases and dissolved organic matter in aquatic systems. Further publications resulting from these studies will appear as journal articles and a report to the U.S.E.P.A. at Grosse Ile, Michigan and were presented as two M.Sc. theses (Fendinger 1981 and Deis 1981) at Wright State University. Dr. Adams should be contacted concerning these publications and other information dealing with these investigations.

THE STUDY AREA

Lake Erie

Lake Erie, the southernmost of the Laurentian Great Lakes, is located between $42^{\circ}45'$ and $42^{\circ}50'$ north latitude and $78^{\circ}55'$ and $83^{\circ}30'$ west longitude. The lake has a total area of 25,300 km^2, total volume of 470 km^3, length of 386 km, mean width of 17 km, and is divided into three major, distinct subbasins. The western basin is the shallowest with a mean depth of 11 m. The western basin is separated from the central basin by the Sandusky sill, an underwater rise composed of dolomitic limestone and coarse lag gravels extending from the Ohio shore at Marblehead to Point Pelee on the Canadian shore. The central basin is the largest basin in terms of area (16,317 km^2) and has a mean depth of 25 m. The central basin is separated from the eastern basin by a ridge composed of coarse sand and gravel extending southeastward from Long Point, Ontario on the Canadian shore to Presque Isle, Pennsylvania. The eastern basin is the deepest basin with a maximum depth of 64 m (Sly 1976 and Argonne National Laboratory 1978).

The shape and depth of Lake Erie's basin, as well as the composition of the Recent sediments, are strongly influenced by regional geology and geological events. The formation of the Great Lakes Basin is the result of Quaternary glaciation and the subsequent excavation of the basin during glacial recession. Differences in rock stress from the weight of the glaciers resulted in the relative differences in depth between the western and eastern basins of Lake Erie, however, the extent of this difference has decreased due to glacial infill and deposition of post-glacial muds.

The Sandusky sill and the islands area are extensions of the Findlay Arch, an upwarp of Lower Devonian dolomite. The Findlay Arch and the Appalachian geosyncline also influence the general west-southwest, east-northeast orientation of Lake Erie's basin (Sly 1976).

The texture of the surficial sediments of Lake Erie is similar to the sediments of the other Laurentian Great Lakes. The sediments can be divided into two major populations, sand-clay and fine silt-clay. Although the majority of both populations are derived from shoreline erosion, the relative distribution is directly related to the hydraulic energy of the depositional region (Thomas et al. 1976).

The western basin is characterized as being highly eutrophic and is predominantly fine-grained sediments (silt-clay) resulting from sedimentation of Detroit and Maumee River inflow under shallow water conditions (Thomas et al. 1976). There is evidence of sediment reworking by wave action and bioturbation (Jernelöv 1970). The estimated reworking rate for the top six cm of sediment is 0.8 years (Fisher 1979).

The central basin is classified as secondary eutrophic (Vollenweider et al. 1974). It is also dominated by fine grained muds, particularly in the central depositional areas of the basin. A west to east increase in grain size is due to increasing wave energy caused by the long fetch of the basin and prevailing winds (Thomas et al. 1976). Unlike the western basin deposits, the central basin sediments are in equilibrium with the available hydraulic energy. The top six cm of sediments are reworked and resuspended as a result of wave energy and biological activity approximately every eight years (Fisher 1979).

Eastern basin sediments exhibit a mean offshore decrease in grain size as a result of decreasing hydraulic energy with increasing water depth.

A population of coarse silt material found in the deepest portion of the basin is derived directly from erosion of Long Point. The material forming Long Point results from large scale erosion of the bluffs on the north shore of the Central basin (Thomas et al. 1976). The highest sedimentation rate of 13.4 mm yr^{-1} occurs in the deep areas of the eastern basin (Kemp et al. 1976). The lowest sediment reworking rate for the top six cm of sediment, 16 years, is also in the eastern basin (Fisher 1979).

Currents in the lake are generally variable outside the immediate influences of the Detroit and Niagara Rivers. The Detroit River plume dominates the current in the central area of the western basin. Outflow to the central basin occurs through the Pelee Passage with variable water movement in the islands area. Surface flow is then southeast from Point Pelee, Ontario, then eastward and to the right of the longitudinal axis of the Lake. Currents are mainly wind driven in the eastern basin except within the influence of the Niagara River where flow is drawn from the U.S. side of the basin (Hamblin 1971).

The northern shore of the lake is heavily agricultural with few population centers. There are few large tributaries entering the lake from the northern side; the primary source of sedimentary materials is shore erosion. The southern shore of the lake is heavily populated and industrialized. Several major tributaries enter the lake from this side, particularly the Maumee and Cuyahoga Rivers, and contribute large amounts of sedimentary materials. A major source of contaminants to the lake is the Detroit River and the industrial centers on the southern shore.

Settlement of the basin began in the 1800's on both sides of the lake. Water quality began deteriorating during this time in localized areas near population centers and escalated to a problem in the entire lake by the middle of the twentieth century. The problem of cultural eutrophication of Lake Erie became an internationally recognized problem in the 1960's and prompted the signing of a Great Lakes Water Quality agreement between the U.S. and Canada in 1972 (Sly 1976).

Cleveland Harbor

Cleveland Harbor is formed by an eight km long breakwater lying parallel 460 to 920 m offshore of the city of Cleveland, Ohio on the southern shore of Lake Erie. The opening used for commercial shipping (iron ore, limestone, sand, gravel, crushed rock and steel products) is near the mouth of the Cuyahoga River approximately two km from the western end of the harbor. Another opening for small boat passage is also located at the western end of the harbor near Edgewater Park where a marina and the West District sewage treatment facility for the city of Cleveland are situated (Hartley 1964).

The harbor is maintained by the U.S. Army Corps of Engineers' Buffalo District. During the period 1951-1972, approximately 1.7×10^7 m^3 (7.7×10^5 m^3 yr^{-1})of dredged material was removed from the harbor and disposed of in open lake dredge disposal sites. The entire amount of dredged spoil sampled in 1972 was considered polluted according to EPA guidelines for phosphorus, volatile solids, COD, Kjeldahl nitrogen, oil and grease, iron, mercury, lead and zinc. The harbor sediments vary from black organic muds to sandy-silty materials in areas of higher hydraulic energy (EPA 1974). The overlying waters receive both industrial and domestic treated wastewater and are used for recreational boating. Influences of waste-water disposal and the highly polluted Cuyahoga River make Cleveland Harbor one of the most polluted areas in Lake Erie.

Hamilton Harbour

Hamilton Harbor is a triangular shaped, enclosed body of water at the western end of Lake Ontario. The harbor is approximately eight km long and five km wide, contains 2.8×10^8 m^3 of water and has a mean depth of 13 m. It is connected to Lake Ontario by the Burlington Ship Canal which allows periodic exchange of water between the lake and the harbor. Hamilton Harbour receives drainage from a 500 km^2 watershed through several streams which drain directly into the harbor.

The highly industrialized south shore of the harbor recycles 26 m^3 sec^{-1} (490 mgd) of harbor water. The harbor is also used for shipping raw materials and finished products. In addition, harbor waters are the final receiver of wastes from three municipal sewage treatment plants (10.2 m^3 sec^{-1})and storm sewer overflow (0.1 m^3 sec^{-1}).The total annual flow into the harbor from all sources is 4.5×10^8 m^3 (OME 1977).

Hamilton Harbour sediments consist of gray to black organic muds in most areas of the harbor. Sandy or silty sediments are predominate along the north shore near the ship canal and the western edge of the harbor and near Dundas Marsh (OME 1977). These sediments are a sink for much of the pollutants discharged into the nearshore areas by industries and sewage treatment plants. Sediments analyzed by the Ontario Ministry of the Environment (OME 1974) were highly contaminated with heavy metals and PCBs. Organic substances deposited in the sediments are an important source of biological and chemical oxygen demand in the harbour. Most of the harbor sediment consist of silts and clays with fine sands near the channel area.

The water quality of Hamilton Harbour has been described as poor due to the quantity of urban and industrial effluent (Harris et al. 1980). Investigations of the water quality have been conducted yearly since 1974. An artificial aeration program, begun in 1975, has improved the dissolved oxygen concentrations in the bottom waters and increased the waste assimilation potential of the harbor (OME 1977).

METHODS AND MATERIALS

Field methodology

Normally, replicate sediment cores were obtained by SCUBA divers at three stations in the central basin of Lake Erie and at one location in the western basin (Figure 1). Because of depth, gravity coring was conducted in the eastern basin. Two stations were occupied in Hamilton Harbour (Figure 2) on the western edge of Lake Ontario, while Cleveland Harbor's bottom sediments were collected at one location (Figure 3). These stations were assigned codes either from previous studies (83, A-1 and C-11 in the central basin and HH-258 and HH-4 in Hamilton Harbour) or as a result of this investigation (WB for western basin, EB for eastern basin and CH for Cleveland Harbor). Stations C-11 and A-1 were located within 1.5 km of each other. EB was close to NOAA's station 28 at the deepest portion of the basin off Long Point. Information is provided in Tables 1-7 for each of the cruises and Table 8 includes the types of sampling activities.

Sediment cores were classified into four categories for separate types of processing: 1) measurements of dissolved gases and percent water, 2) measurements of dissolved organic carbon and percent water, 3) physical description and photography, and 4) chemical characterizations of dissolved organic compounds. Sediment volatile solids were usually measured on category 2) cores. Lengthwise halving of cores (category 3) was added later in the program; therefore information is available only for stations C-11 in the central basin, WB, EB and HH. Coring was done either with 6.5 cm i.d. Lexan 2000 (made of polycarbonate) or Benthos Inc., Falmouth, MA, gravity core liners. Gas core liners were modified by drilling 3 cm holes for subsampling at either

3- or 5-cm intervals. Holes were located at 90 degrees to each other to retain material integrity. During deployment the openings were covered with clear plastic tape. Overlying water was carefully removed on board ship by pushing a machined piston (containing a center hole fitted to a length of tubing) to the water-sediment interface. Sediment cores were stored in the dark, refrigerated, when possible, or kept cool until processing. Cores were subsampled or extruded under artificial light within 1-3 hours after collection; they were usually processed on board ship.

Cores for dissolved gases (category 1) were placed horizontally into a modified Hydrovoid (Air Control Inc., Norberth, PA) glove box under an atmosphere of helium. A YSI model 57 oxygen meter (Yellow Springs Instrument Co, Yellow Springs, OH) was used to monitor air contamination (<1.0 ppm oxygen, usually 0.5 ppm or less) during processing. Sediments were subsampled with 50-mL disposable plastic syringes with their Luer-lok ends removed. A 1-2 g aliquot was collected from each syringe for percent water determination. A measured amount of wet sediment was added either to a wide-mouth pint canning jar (ca. 480 mL) or an unaltered 50-mL disposable syringe. The canning jars were equipped with specially constructed double lids for sediment addition and mounting of a septum port. The jars contained 230 mL of degassed 10% salt solution and 40-50 mL of wet sediments. Lastly, the jars were waxed, inverted, and refrigerated until analysis. In the case of syringe storage for gas analysis, a measured amount (20-30 mL) of wet sediments were displaced from the open-ended syringe into an unaltered one. The plunger handle was machined smaller to allow for unresticted passage through the syringe barrel. A plastic Luer-lok cap, containing a septum, was attached and the front portion of the syringe was waxed. Recently, 50-mL glass syringes, modified by utilizing plungers from plastic syringes, were used for sediment storage before gas analysis. In addition, about 4-6 cm of hot wax was poured onto the back side of the plunger and allowed to cool within the syringe barrel. Syringes were refrigerated until analysis. Processing a core for gas analysis usually took 30 minutes within the glove box.

Sediment cores for dissolved organic carbon (category 2) were extruded vertically and sectioned every cm for the first 10 cm and at 2-cm intervals thereafter. A subsample from each interval was processed for percent water. The remainder was transferred to 25- or 50-mL polycarbonate centrifuge tubes, capped, and refrigerated. Processing of a 80-100 cm core usually took one hour.

A core liner was cut horizontally and taped for halving (category 3). Visual observations, subsampling, and photographic documentation were obtained within 1-2 hours after diver collections.

Two sets of samples were collected from Hamilton Harbour (HH-258) and the central basin of Lake Erie (C-11) in August 1980 for GC/MS identification and molecular weight size analysis of the sediment interstitial water dissolved organic components (category 4). The sediments were divided into 0-25 cm and 25 cm and deeper sections (normally 25-50 cm); these were labelled top and bottom. Sediments from HH-258 were obtained from diver-collected cores. Station C-11 bottom samples were collected by multiple Benthos coring while top sediments were obtained with a shipek dredge.* Upon receiving the samples on deck, the sediments were quickly transferred to quart mason jars which had been cleaned with chromic acid and heated in a muffle furnace at 450°C for 4 hrs. The containers were covered with pre-combusted aluminum

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*The depth of the surface sample at station C-11 would depend on penetration of the shipek dredge.

foil and sealed with a lid and retaining ring, leaving no headspace over the sediments. Samples were packed with ice and remained at approximately 4°C until returning to Wright State University where they were immediately refrigerated.

Two methods were employed to collect gases evolved from bottom sediments at stations A-1 and 83 in the central basin of Lake Erie: 1) a modified SOD (Sediment Oxygen Demand) chamber (Lucas and Thomas 1972) was placed on top of the sediments and 2) a gas collection funnel (Chau et al. 1977) was located at 0.15 m above the sediments. The SOD chamber was modified by installing a plastic septum support for SCUBA diver syringe sampling. Previously degassed water or 10% saline solution was filled into a gas cylinder located on top of the gas collection funnel. One or both of these gas collection devices were deployed six times during the summer and fall of 1979 (Table 9). The gas collection funnel worked on only one occasion; therefore information obtained from this device will not be included in this report.

Gas measurements

Mason jar samples were allowed to equilibrate at room temperature or 85°C after removal from cold storage. Samples were agitated for two minutes and a 20 mL headspace removed with a 50-mL gas tight syringe. Sediments stored in syringes were equilibrated at room temperature before addition of 10 mL degassed 10% salt solution and 30 mL helium head space. The sediment slurry was then agitated for two minutes before removal of a 2.0 mL aliquot of the equilibrated headspace. Syringes were treated slightly differently for the analysis of headspace CO_2 gas.

Argon, oxygen, nitrogen, methane, and carbon dioxide in the equilibrated headspace, or obtained from the gas funnel collection cylinders, were analyzed with a Carle model 311M gas chromatograph (Carle Instruments Inc., Anaheim, CA). Helium was used as the carrier gas. The chromatograph was equipped with four microvalves and three columns: (1) 370 cm x 0.32 cm with 50/80 mesh Porapak N, (2) 240 cm x 0.32 cm with 42/60 mesh molecular sieve 5A, and (3) 15 cm x 0.64 cm with 42/60 mesh activated coconut charcoal (Fig. 4). A thermal conductivity detector was used for routine operations. Although the chromatograph was fitted with a flame ionization detector and methanizer, the concentrations of carbon dioxide and methane encountered were beyond the linear response range of this detector.

Simultaneous analysis of the above gases was accomplished by maintaining the Porapak N column at 90°C in an external hot water bath and operating the chromatograph isothermally at 30°C. Initial valve positions were:

Valve 1 (V1) - Counterclockwise (CCW),
Valve 2 (V2) - (CCW),
Valve 3 (V3) - (CCW), and
Valve 4 (V4) - (CCW)

as illustrated in Figure 4.

Aliquots of syringe or mason jar headspace gases were introduced into the gas chromatograph through a 2.0-mL sample loop by switching V1 to the clockwise (CW) position. Argon + oxygen, nitrogen, and methane were passed onto the molecular sieve column and detained by activating V2 to the CW position. Carbon dioxide then bypassed the molecular sieve column and was detected. After elution of the CO_2 peak the remaining gases were released from the molecular sieve column by returning V2 to the CCW position (Fig. 5). Peak areas were recorded on a strip chart for permanent record and measured electronically with a Varian CDS model 111 integrator (Varian Instr. Co., Palo Alto, CA). Argon was usually in the range near the minimum detection limit for sediment samples and air equilibrated water. This situation can be improved by increasing the sample loop volume but results in less sample for replicate determination (Adams unpublished data). Total carbon dioxide gas was measured on a separate wet sediment syringe sample by adding degassed salt water, shaking, settling, filtering directly into another syringe, acidifying the filtered water, and equilibrating with helium headspace (Fendinger and Adams ms.)

Total methane dissolved in the sediment interstitial water was calculated using the observed concentration in the equilibrated headspace, a dilution factor, and sediment percent water data. Corrections were not made for gas remaining dissolved in the sediment-water slurry, which constituted less than two percent of the total methane present. Partition coefficients for nitrogen and argon were determined using methods described in McAullife (1971). The presence of dissolved oxygen was periodically assessed by engaging V4 to the CW position and measuring the argon peak (Fig. 6). Because the charcoal column absorbs O_2 irreversibly (Cooke 1973), any differences between this peak and the previous Ar + O_2 peak would indicate the presence of dissolved oxygen. Details are provided in Fendinger (1981).

The chromatograph was routinely standardized by pressurizing a certified gas mixture within the 2.0-mL sample loop. The previously described valve sequence was then used. Alternately, a pure gas was injected through the inlet with a 100 µL gas-tight syringe by placing V1 in the CW position and engaging the appropriate column. Detection limits for sediment interstitial water gases are listed in Table 10.

A one-dimensional numerical model applicable to dissolved species in sediment interstitial water (Tzur 1971, Berner 1975, and Billens 1978) was used to evaluate the sediment to water flux of methane and its net production (production minus consumption) within the surface (0-25cm) and deeper sediments at the open lake stations. Because the model can be applied only to dissolved species undergoing Fickian dispersion and not bubble transport, as calculated by in situ gas partial pressures, mathematical modeling of sediment methane distributions at the harbor stations was not conducted. The usefulness of this model to the calculations of sediment-water diffusive flux will be presented in the discussion section of this report (available in Fendinger's thesis).

Dissolved organic carbon measurements

Centrifuge tubes containing sediments for organic carbon analysis were centrifuged at 7000 rpm at room temperature for one hour. The supernatant water was withdrawn with a glass syringe and filtered directly through precombusted (450°C - 1 hour) glass fiber filter pads, mounted in a Swinney adaptor, into precombusted (500°C - 2 hours) glass vials. The samples were acidified with concentrated sulfuric acid, preserved with sodium azide (1 drop of 20 mg/mL solution) and refrigerated at 4°C until analysis.

Dissolved organic carbon in the interstitial water was measured with a Dohrmann DC-50 organic carbon analyzer (Envirotech Corp., Santa Clara, CA). DOC in the water sample is combusted at 850°C, using a MnO_2 oxidizer, to carbon dioxide. CO_2 is then reduced on a nickel catalyst to methane, which is measured in a flame ionization detector. The instrument was calibrated daily with a 180 mg/L potassium hydrogen pthalate (KHP) standard dissolved in low carbon water and checked periodically throughout the sample run with the standard to ensure stability of the detector. Detector response linearity was periodically assessed using a series of KHP standards in the zero (blank) to 1800 mg/L range. The blank was low carbon water purchased commercially (Sparkletts Drinking Water, Los Angeles, CA) or prepared as outlined in Strickland and Parsons (1972).

Dissolved organic compound identification by GC/MS

1. Sample preparation

A Sorval RC-5B centrifuge with a GSA rotor allowed for centrifugation of six 250-mL polycarbonate bottles filled with sediments (allowing for no air space). Centrifugation of sediments was performed at 9000 rpm and $4^{o}C$ for one hour. A 10-mL muffled glass vial with teflon lined cap was used to store an unfiltered water sample for analysis of purgeable organic compounds.

Centrifuged samples were quickly passed through a glass fiber filter, utilizing an all-glass Millipore filter holder, into a suction flask. About 600-800 mL of interstitial water were transferred into a separatory funnel and the pH of the water was raised to approximately 12 using 12 M NaOH. After 50 mL of CH_2Cl_2 were added, the funnel was agitated for five minutes. The formation of iron hydroxide precipitate created an emulsion that prevented removal of the CH_2Cl_2 layer. The mixture was allowed to settle for one hour, the emulsion was passed through another glass fiber filter, the hydroxides were washed with 30 mL of CH_2Cl_2, and the solvent and water mixture were again returned to the separatory funnel. The water was extracted further with two more 20-mL portions of CH_2Cl_2 and the extracts were combined as the "base-neutral fraction" of organic compounds. Due to the difficulty of filtering the hydroxides, some of the more volatile components may have been lost during the extraction sequence.

Extraction of the "acid fraction" of organic compounds followed adjustment of the pH to 2 with 12 M hydrochloric acid. Methylene chloride volumes were 30, 20, and 20 mL, with shaking for two minutes after each portion was added. Base-neutral and acid extracts were dried over sodium sulfate and refrigerated.

A Kuderna-Danish apparatus with 500-mL evaporative flask, a three ball macro-Snyder column, and a 10-mL collection tube were used for the initial concentration. The volume was reduced to approximately two mL and a three ball micro-Snyder column was used to reduce the volume to less than one mL. Concentrates were transferred to a 3-mL muffled glass vial with a solvent-washed Teflon lined cap and refrigerated until analysis.

Glassware used for the extraction was washed in dilute soap water followed by thorough cleaning with chromic acid. After washing with distilled deionized water the glassware was heated to 450°C for four hours. Muffled aluminum foil was used to wrap glassware during storage. Sodium sulfate was prepared by muffling at 450°C for four hours. Sodium hydroxide and diluted hydrochloric acid were prepared with low-carbon water. Pesticide grade methylene chloride (Burdick and Jackson, Muskegon, MI) was used for the extractions. The method blank involved each piece of glassware and started with low-carbon water.

2. Purgeable organic analyses by gas chromatography/mass spectroscopy

Three groups of samples were analyzed for purgeable organic compounds by the Bellar purge and trap technique (Bellar and Lichtenberg 1974) utilizing gas chromatography/mass spectroscopy (GC/MS) instrumentation. The first group of four samples from Lake Erie station C-11 was prepared for analysis during August, but the samples were not analyzed for over two months.* Upon examination, they did not reveal any purgeable organic compounds. The second group of samples was derived from Hamilton Harbour and Lake Erie station C-11 sediments which had been accidentally frozen during storage. Finally, a third group of samples based on refrigerated sediment that had not been frozen, but which was processed one day before GC/MS analysis, is described in greater detail.

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*The EPA recommends samples be analyzed within 14 days after storage for purgeable organic compounds.

For both refrigerated and frozen (thawed for analysis) Hamilton Harbour and Lake Erie station C-11 sediments, interstitial water was collected as described previously. Supernatant water was removed from the centrifuge tubes, spiked with internal standards [to yield a concentration of 400 ppb each of $BrClCH_2$ and $Cl(CH_2)_4Cl$] and sparged onto Tenax/silica gel. Volatiles were then sorbed onto a 0.2% Carbowax 1500 on 80/100 mesh Carbopak C column, 183 cm x 0.32 cm stainless steel, maintained at -40°C. The analysis was conducted by heating the column from -40°C to +220°C at 8°C/min followed by holding for 10 minutes at 220°C. This is the same program used in a validation study of purgeable priority pollutant organics for the EPA. A Hewlett-Packard 5983 mass spectrometer and data system was used to identify the column eluents. Two samples from previously frozen sediments and four samples from refrigerated sediments (two from Lake Erie station C-11, top and bottom sections; two from Hamilton Harbour station HH-258, top and bottom sections) were prepared and analyzed in this manner. GC/MS analytical procedures were the same regardless of the sediment storage conditions.

The purgeable samples were analyzed as follows:

File Reference Number (FRN)	Sample Descriptions	Coll.	Dates (1980 and 1981)* Prep.	Anal.
	Frozen Sediments			
11935	Station HH- 258	8/16	11/20	11/21
11936	Station C-11	8/18	11/20	11/21
	Refrigerated Sediments			
12368	Organic-free Water plus Internal Stds.	-	-	1/24
12369	Supelco Purgeable Stds A,B,C	-	-	1/24
12370	C-11 Top Sediments	8/18	1/23	1/24
12371	C-11 Bottom Sediments	8/18	1/23	1/24
12372	HH-258 Top Sediments	8/16	1/23	1/24
12373	HH-258 Bottom Sediments	8/16	1/23	1/24

*Dates for sediment collection, processing sediments for interstitial water (Prep.), and GC/MS analyses.

3. Base/neutral fraction extractable organic matter identification by gas chromatography/mass spectroscopy

The CH_2Cl_2 concentrates of the base/neutral extracts of interstitial water were analyzed using a modified Hewlett-Packard 5983 GC/MS system. A 2 mm i.d. x 183 cm length SP-2250DB glass column was used with programming from 50°C to 260°C at 8°C/min and holding at 260°C for up to 15 minutes. An internal standard, biphenyl-d_{10}, was used in each sample and quantitation was performed relative to a mixture of priority pollutant base/neutral (numbers 2, 3 and 4) standards from Supelco (Supelco Inc., Bellefonte, PA).

The base/neutral samples were analyzed as follows:

File Reference Number (FRN)	Sample Descriptions*	Conc. Factor	Dates (1980) Coll.	Extr.	Anal.
12155	Supelco base/neutral 2,3,4 Standards	-	-	-	12/13
12156	C-11 Top Sediments	1150	8/18	8/28	12/13
12158	C-11 Bottom Sediments	1460	8/18	9/6	12/13
11108	HH-258 Top Sediments	-	8/17	8/27	9/10**
12157	HH-258 Bottom Sediments	860	8/17	9/7	12/13
12159	Method Blank			9/10	12/13

* See text for collection procedures at each station
** Data lost from computer tape

The method blank contained biphenyl-d_{10} internal standard, dialkyl adipate and dioctyl phthalate. Unfortunately, the computer tape which held data for the extract from the top 25 cm of Hamilton Harbour (HH-258) was damaged by the tape recorder so that information was no longer accessible. Only the chromatogram and eight mass spectra, copied at that time, were available for interpretation.

4. Acid fraction extractable organic matter identification by gas chromatography/mass spectroscopy

Although the extraction of the acidified interstitial water should yield most of the acidic organic components, the analytical procedure followed was primarily designed for phenolic components. The methylene chloride extracts were injected onto a 2 mm i.d. x 183 cm length SP-1240DA glass column, programmed from 50° to 220°C at 8°/min with a 10 minute final hold, in the same way as the analysis for E.P.A. phenolic priority pollutants. A modified Hewlett-Packard 5983 mass spectrometer was used to identify the components. Each chromatogram was normalized to the tallest point in its set of data.

The acid extractable samples were analyzed as follows:

File Reference Number (FRN)	Sample Descriptions	Conc. Factor	Dates (1980) Coll.	Extr.	Anal.
12043	C-11 Top Sediments	1120	8/18	8/28	12/6
12044	C-11 Top Sediments	1500	8/18	8/31	12/6
12045	C-11 Bottom Sediments	2060	8/18	9/6	12/6
12046	HH-258 Bottom Sediments	970	8/17	9/7	12/6
12048	HH-258 Bottom Sediments	1080	8/17	9/9	12/6
12047	Blank acid fraction		-	9/10	12/6
12042	Supelco Priority Pollutant Phenol Standard		-	-	12/6

Molecular weight size fractionation of sediment interstitial dissolved organic matter

Bulk sediment samples from stations C-11 and HH-258 collected for size fractionation by ultrafiltration were processed in a nitrogen-filled glove box to reduce changes in organic matter caused by oxidation (Templeton and Chasteen 1980). The sample jars were placed in the glove box, and following flushing with nitrogen, the lids of the jars were removed. The top two cm of sediment were removed with a spatula and discarded. The bulk samples were homogenized and a subsample withdrawn and transferred to polycarbonate centrifuge bottles with O-ring sealing caps. The bottles were immediately transferred to a refrigerated centrifuge and centrifuged at $4^{\circ}C$ for 30 minutes at 7000 rpm. Following centrifugation, the bottles were transferred to the glove box which was again flushed with nitrogen.

An Amicon (Amicon Corp., Lexington, MA) model 12 (10 mL capacity) stirred ultrafiltration cell was used with 25 mm Diaflo ultrafiltration membranes. The membranes used were UM2 (1000 MW), UM10 (10,000 MW), and UM20 (20,000 MW), where molecular weight cutoffs are listed in parentheses. Diaflo membranes are permselective ultrafilters cast from non-cellulosic polymer solutions which, while retaining solutes larger than their "cut-off" at the skinned surface, allow microsolutes and solvent to pass freely. The UM series membranes possess both hydrophilic and low adsorption characteristics and a net neutral charge (Amicon 1980). Before use, the membranes were soaked in glass distilled water in precombusted, covered glass beakers similar to the method suggested by Wheeler (1976). The membranes were rinsed in the cell by passing two volumes (20 mL) of low organic carbon water (prepared by the method in Strickland and Parsons 1972) at 40 psi N_2 pressure. A water blank was collected in a precombusted glass vial after 15 mL of water had passed through the membrane.

Supernatant water was withdrawn from the centrifuge bottles in the glove box with a 30 mL glass syringe. Samples were passed through each membrane in the following order: C-11 top sediment, C-11 bottom sediment. Hamilton Harbour top sediment, and Hamilton Harbour bottom sediment. Approximately 15 mL of the sample was passed through the membrane at 40 psi N_2 overpressure before the sample was collected in a precombusted glass vial.

A sample of the supernatant sediment interstitial water withdrawn from each centrifuge bottle was filtered directly through precombusted glass fiber filters into a precombusted glass vial. This sample was used to represent "total DOC" for each sediment section. Each of the samples and blanks were preserved with sodium azide and refrigerated at 4°C until analysis of dissolved organic carbon.

Other measurements

Percent water (% H_2O) was determined by drying the sediments to constant weight at either 110°C or by freeze drying. Percent water was calculated by weight difference. Porosity was determined by the following formula (Berner 1971):

$$\text{Porosity} = \frac{\omega \rho_s}{\omega \rho_s + (1 - \omega)\rho_{H_2O}} \tag{1}$$

where ω = sediment percent water expressed as a fraction = $\frac{\%H_2O}{100}$

ρ_s = sediment density (a value of 2.5 was used), and

ρ_{H_2O} = density of interstitial water (a value of 1.00 was used).

Sediment volatile solids were determined by heating the dried sediments to 540°C for one hour. The difference in weight was the percentage of sediment lost as a result of combustion.

RESULTS

This study of the composition and distribution of dissolved gases and organic matter in the Recent sediments of Lake Erie and two nearby harbors has resulted in considerable data. A listing of the complete data set is provided in the Appendix. Most concentrations are listed in units of mass, molarity or volume per liter (L) of sediment interstitial water.

Sediment interstitial dissolved gases

A total of 16 sediment cores were analyzed for interstitial dissolved methane gas. In addition, this gas was analyzed in water collected from an *in situ* equilibration device (peeper) at station A-1 in the central basin of Lake Erie. Sediments from the open lake stations usually contained less dissolved methane than was observed for the two polluted harbors (Figures 7-13). Station 83 in the central basin (Fig. 1) exhibited the lowest values, ranging from 1.05 to 9.73 mL/L* CH_4 gas. Highest concentrations for open lake stations were observed in the sediment interstitial water of the eastern basin where the range of 59.9 to 81.6 mL/L was similar to values measured in sediments from the polluted harbors. Concentrations of dissolved methane gas for the other open lake stations fell between stations 83 and EB (Table 11). Harbor sediment values were usually higher where methane ranged from 36.1 to 135.7 mL/L for two cores from Cleveland Harbor (CH), 16.2 to 181.4 mL/L at station HH-258 in the central portion of Hamilton Harbour, and 7.2 to 68.7 mL/L at HH-4, a station near the ship canal and sewage waste water outfall (see Fig. 2).

*Sediment interstitial gases are expressed either as mL/L or mM = mmoles/L; conversion factors were (mM/L) (22.414) (298/273) or (mM/L) (22.414).

A total of ten sediment cores were analyzed for interstitial dissolved nitrogen gas. The lowest (8.9 mL/L) and highest (74.9 mL/L) concentrations were measured in the harbor sediments (Table 11). As discussed later, this range was probably due to very active gas production (both methane and nitrogen gases) in the polluted harbor sediments and removal of N_2 gas by gas stripping through methane ebullition. Sediment N_2 gas concentrations for the open lake stations were all nearly the same, with values ranging from a low of 11.9 mL/L at WB to a high of 37.0 mL/L at C-11. Three cores were processed at station C-11 to evaluate reproducibility at the same site. About 60% of the N_2 concentrations were above saturation, some as high as 2-3 times normal saturation calculated for winter conditions of maximum N_2 gas solubility in water overlying the sediments (16.6 mL/L at $4^{\circ}C$; Murray et al. 1969).

Because of procedural difficulties, total CO_2 gas (ΣCO_2) was measured in the sediment interstitial water of only six cores (Table 11). Of the open lake stations, the western basin (WB) exhibited higher sediment concentrations (118 to 299 mL/L) than seen at the other two locations, where values ranged from a low of 50 mL/L at C-11 in the central basin to a high of 130 mL/L in the eastern basin (Table 11 and Figures 7-13). Hamilton Harbour sediments exhibited the greatest range and highest concentration of all interstitial water samples, 92.2 to 356 mL/L, while there was little variability in the down-core data for Cleveland Harbor sediments, 190-254 mL/L.

Sediment interstitial dissolved organic carbon

A total of 17 sediment cores were analyzed for dissolved organic carbon. This resulted in 347 measurements, which probably provides the largest DOC data bank for interstitial water (Table 12a). One core was collected 400 m north of Rattlesnake Island in the Lake Erie islands area; gases were not measured at this location. With the exception of stations 83 in the central basin, EB, and HH-258, DOC exhibited a highly significant (>99%) linear increase with depth at each of the other locations (Figures 7-13). This was also evident at station HH-258, as shown in Figure 12, if data from the unusual distribution seen in the 1979 core were not used. Therefore, in almost 90% of the stations sediment interstitial DOC exhibited a significant (> 99%) increase in concentration with depth.

DOC average values for open lake stations ranged from 5.8 mg/L at station 83 in the central basin of Lake Erie to 21 mg/L for station EB. The harbor stations had higher concentrations of sediment interstitial DOC with averages ranging from 29 mg/L for Cleveland Harbor to 38 and 76 mg/L for HH-258 and HH-4, respectively, in Hamilton Harbour (Table 12a). Considering the entire data collection, concentrations ranged from as low as 2.0 mg/L at station 83 in Lake Erie to 257 mg/L at station HH-4 in Hamilton Harbour. As will be discussed later, there was, with few exceptions, a high correlation between sediment volatile solids and interstitial DOC, sediment porosity and DOC, and dissolved methane and DOC.

Composition of sediment interstitial dissolved organic matter

1. Purgeable fraction of organic compounds by GC/MS.

The results of two sediment samples that were accidentally frozen, thawed and centrifuged for analysis of organic compounds by GC/MS (gas chromatography/mass spectroscopy) are summarized in Table 13. The concentrations of benzene, toluene and ethylbenzene were small and not much above the detection limit (≥ 1 mg/L) for the GC/MS system. Dichlorodifluoromethane in the central basin sample was probably a contaminant resulting from Freon leak-checking of the system. Dichloromethane at such high levels, along with trichloromethane, were unusual. Even though the blanks did not contain amounts of halocarbons even close to these, additional samples yielding the same constituents would be necessary in order to validate these results. Since the base-neutral fractions of interstitial water extracts showed greater levels of aliphatic hydrocarbons of higher molecular weight, the appearance of hexane would be expected in the purgeable fraction. A chromatogram of purgeables of sediment interstitial water collected at station C-11 in the central basin of Lake Erie is shown in Figure 14. The mass spectrum of hexane, tentatively identified from this chromatogram, is provided in Figure 15, while Figure 16 illustrates the mass spectrum of a purgeable compound from Hamilton Harbour interstitial water (tent. identified as C_3-benzene).

Four refrigerated (unfrozen) samples were also analyzed for purgeable organic compounds; these were from station C-11 and HH-258 (Table 14). Compounds given in Table 14 were corrected for concentrations in the water blank. Quantitation was based on Supelco purgeable standards. Comparisons of the gas chromatograph traces are shown in Figures 17 and 18. It is evident from Figure 18 that the C-11 samples were much lower in purgeable organic compounds than those from Hamilton Harbour. Bottom core samples for Hamilton Harbour were also richer in higher molecular weight organic compounds than the top 25 cm of the same core.

The large quantities of chloroform (and lesser amounts of methylene chloride) in the C-11 samples in the absence of significant quantities of other organic compounds was suspicious. It was probably attributable to the processing period, where chloroform might have been present in the laboratory at the time the samples were centrifuged and transferred to storage vials. A substance present in varying amounts in all chromatograms at 31.2 minutes had major ions

207, 208, and 209 and was evidently a silicone artifact in the GC/MS system.

A series of alkyl benzenes, C_2-benzene, and C_3-benzene were also observed as well as relatively large amounts of indan or methylstyrene (mass spectra are shown in Figure 19). In complex natural samples, such as the present ones, it is very typical to find homologous series of components rather than isolated species. The concentrations observed were in the low ppb (μ g/L) range; these represent the levels present in the interstitial water and would no doubt increase dramatically if the sediment were sonicated, purged or extracted. Mass spectra taken at random locations in the unresolved hump between 30 and 40 minutes in the Hamilton Harbour samples suggest a mixture of compounds including aromatics and alkenes or cycloalkane, with no significant amounts of normal alkanes.

2. Base/neutral fraction of organic compounds by GC/MS.

The interstitial water samples from station C-11 in the central basin of Lake Erie were almost free of base/neutral constituents whereas the Hamilton Harbour HH-258 sample had a relatively large amount and variety of organic components (Figure 20). The method blank contained three major components: biphenyl-d_{10} internal standard at 14 minutes, dialkyl adipate (tent.) at 25.7 minutes and dioctyl phthalate at 27.7 minutes. Two minor peaks at 29.5 and 31.2 minutes were most likely phthalates (major ion m/e = 149). The peaks at 25.7 and 27.7 minutes were also seen in station C-11 bottom (25-50 cm) sample but not in the C-11 top (0-25 cm) or HH-258 samples. They must be considered as contaminants in C-11 bottom sediment interstitial water, even though it was not clear why they did not appear in the other two samples.

Examination of the data indicated that the surface 0-25 cm section of station C-11 was free of any base/neutral components in the interstitial water except for two small peaks at 19.5 and 20.7 minutes. These were also in the method blank but were too low in intensity to be identified. Interstitial water from the bottom sediments (25-50 cm) at the same station contained phthalate and adipate (tent.) peaks - most likely contaminants as discussed above - plus small, unidentifiable peaks at 19.5 and 20.7 minutes, which were found in the blank and the surface sediments. In addition to these were a series of peaks all of which yielded typical saturated hydrocarbon spectra. Although a hydrocarbon standard was not analyzed along with these samples, the boiling points of the base/neutral standards used during these analyses suggest that hydrocarbons eluting in this group were from the C_{28} - C_{36} range. The estimated qualitative concentrations listed in Table 15 were obtained using the ratio of the m/e 71 area for alkanes to the m/e 164 area of the biphenyl-d_{10} internal standard.

Interstitial water from the 25-50 cm depth for cores collected from Hamilton Harbour station HH-258 contained not only a number of hydrocarbon components but also a variety of substances including PNA's. An expanded presentation of the Figure 20 HH-258 chromatogram is shown in Figure 21. There were numerous compounds not resolved by the chromatographic procedure. Even so, many peaks were identified as alkanes. In addition, heterocyclic and aromatic compounds were observed. Findings from the HH-258 chromatogram are provided in Table 16 and background mass spectra at 17.9 and 28.7 minutes are shown in Figures 22 and 23, respectively.

Higher molecular weight PNA's were specifically sought in the interstitial water sample from station HH-258; these were not found, indicating that, if present, they must have concentrations less than about 1 μg/L. The concentrations of the the PNA's were much lower than the estimated concentrations of the alkanes. Chlorinated compounds were also not observed in any of the mass spectra obtained from HH-258.

One other interstitial water sample from Hamilton Harbour was analyzed by GC/MS. This was from the surface 0-25 cm depth interval of the sediments and yielded a chromatogram similar in general appearance to the bottom 25-50 cm section (Figures 20 and 21), but with fewer distinct peaks. Unfortunately, the computer tape containing this set of data, along with the corresponding standards runs, was damaged by the tape reader so that the information is no longer accessible. Only the chromatogram (Figure 24) and eight mass spectra copied at the time are available for analysis. Inspection of these data revealed that (1) a series of alkane components were present in that sample, (2) some peaks were definitely more aromatic or heterocyclic in character than aliphatic, (3) the nature of the background mixture became decidedly less aliphatic as longer elution times were reached, and (4) the general level of organic compounds was probably about the same order of magnitude as that observed in the other HH-258 sample for the bottom of the core.

3. Acid fraction of organic compounds by GC/MS.

The most obvious feature of the chromatograms shown in Figures 25a and 25b was the very low levels of organic components in the interstitial water sample extracts. The following explanations are possible for this behavior: (1) the sediment interstitial waters were very low in phenolic components, (2) organic compounds in the sediment interstitial waters were not thoroughly extracted by this procedure, (3) even though the CH_2Cl_2 extracts were stored in the refrigerator the acidic components were lost, or (4) the analytical procedure discriminated against these compounds. Since the Supelco phenol standards were readily identified, this fourth situation does not appear to be the case at least for the phenolic materials. The analysis of carboxylic acids by this technique is a separate issue for at least some acids, such as benzoic, are known to pass through the gas chromatographic column. Whether simple aliphatic carboxylic and dicarboxylic acids would also elute at very low levels has not been studied. A careful examination of the chromatograms revealed that the phenolic priority pollutants were not present in these samples above the detection limit, which was in the range of 0.5–20 µg/L in the aqueous sample (including concentration factors of 970 to 2060 from sample to extract).

Of the peaks on the chromatograms, four were tentatively identified as p-cresol and three phthalates (Table 17). One would like to attribute the high phthalate concentration and possibly the adipate in FRN 12045 to the storage container, but this sample was stored in a screw-capped vial with an unpunctured Teflon liner which was unlikely to introduce this contamination. Since the concentration factors of the extracts from the interstitial waters were typically 1000 or greater, the values in Table 17 correspond to a few parts per billion in the original water sample. Thus, the content of the phenolic fraction of the interstitial water was very low, aside from the three phthalate - adipate peaks. The unspecified phthalate eluting at 17.1 minutes was likely a contaminant introduced in the sampling-extraction procedure, except for sample FRN 12048 (HH-258 bottom sediments).

Molecular weight size fractions for dissolved organic matter in the sediment interstitial water

The results of the ultrafiltration of sediment interstitial water dissolved organic matter (DOM) from two stations are listed in Table 18, where total concentrations of DOM and percentages of the DOM retained by each molecular weight cutoff are provided. The two stations selected for this study, Lake Erie central basin C-11 and Hamilton Harbour HH-258, differed in the types and sources of organic matter. Most of the DOM from station C-11 was retained by the UM20 membrane (20,000 molecular weight cutoff). Dissolved organic matter from station HH-258 was retained by the lower molecular weight cutoff membranes, indicating differences in DOM composition between the open lake and harbor stations. The amount of DOM retained by the higher molecular weight cutoff membranes also increased down core at station HH-258.

Other variables

Percent water and sediment volatile solids were measured on 24 and 9 cores, respectively. Porosity was calculated from percent water using equation (1). Station 83 in the central basin of Lake Erie exhibited the lowest average porosities while the highest were observed at station A-1, also in the central basin (Table 19). Sand layers were penetrated at HH-4 in Hamilton Harbour which resulted in very low percent water measurements and porosity calculations.

Station 83 also exhibited the lowest values for sediment volatile solids, which averaged 2.73 percent sediment dry weight (Table 20). With the exception of station C-11 in the central basin, which averaged 9.2 percent, highest sediment volatile solids were observed in the harbors. Station HH-258 in Hamilton Harbour exhibited the highest measurement of 20.7 percent with an average for the entire core of slightly less than 14 percent.

DISSCUSSION

The study of Lake Erie's recent sediments and two nearby polluted harbors was divided into three research efforts: (1) elucidation of dissolved gas cycles and associated sediment-water exchange processes, (2) determination of relationships between sediment oxygen demand and sediment-water transport of reduced chemical components, and (3) characterization of the quantity and quality of dissolved organic compounds and DOC within these surficial deposits. Even though these were distinctly separate areas of investigation, there was a great deal of overlap between the three efforts in trying to clarify the sedimentary geochemical processes involving carbon and nitrogen in these Recent depositional environments which are natural (portions of Lake Erie) and perturbed (two harbors with high loading from antropogenic sources). The sedimentary distribition of most of the variables discussed in this section are provided in figures 7-13*.

Dissolved gas cycles and sediment-water exchange processes

The importance of gas production/consumption in the carbon and nitrogen cycles of freshwater lakes has been reviewed by numerous authors (Koyama 1955, Overbeck and Ohle 1964, Kuznetsov 1968, 1970, Hutchinson 1975, Bott 1976, Ward and Frea 1980, Fallon et al. 1980, Ohle 1980, and Rudd and Taylor 1980, to mention a few). The cycling of gases within the water column and bottom sediments and their exchange across the sediment-water and water-atmosphere interfaces will affect whole lake metabolism and probably exert a major impact on oxygen budgets (Anagnostidis and Overbeck 1966, Keeney et al. 1971, Rudd et al. 1974, 1976, Andersen 1976, Reeburgh and Heggie 1977, and Rudd and Hamilton 1978). Furthermore, Ohle (1978) suggested that gas evolution from lake sediments bears a close relationship to primary productivity and perhaps may be used as an indicator of lake trophy (Ohle 1958). While this is probably true, Rudd and Hamilton (1979) pointed out that there may not be a simple or direct relationship between trophic status and gas production because only the more recalcitrant algal detritus, which avoids epilimnetic recycling, is refueling sediment gas production. Presley (1974, cited in Rudd and Taylor 1980) calculated that 40% of the organic carbon flux to Cariaco Trench sediments remains as recalcitrant material, while Rudd and Hamilton (op. cit.) estimated that 25% of produced

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*Sediment interstitial gases are expressed either as mL/L or mM = millimoles/L; factors were (mM/L) (22.414) (298/273) or (mM/L) (22.414).

particulate carbon in Lake 227's epilimnion will reach bottom deposits and Ohle (1980) showed values of 0.6 to 10.2% for Plusssee and Schohsee, respectively. Regardless of loss from the epilimnion, the importance of deposited organic detritus (and its organic carbon content) to biogenic gas production is fundamental in understanding microbial oxidation-reduction reactions, the amount of free energy made available to organisms, and the environmental conditions which mediate such processes (Hallberg 1973, Claypool and Kaplan 1974 and Mechalas 1974). The decomposing organic matter acts as a source of energy for bacterial metabolism resulting in the reduction of dominant electron acceptors, such as oxygen, nitrate, nitrite, sulfate, carbon dioxide, organic compounds occurring with carbon in intermediate oxidation states, and ferric and manganic oxides/hydroxides (Stumm and Morgan 1970). Therefore, evaluation of gaseous reactants and products and relationships between gases and their precursors serves as an important tool for understanding basic concepts of organic matter diagenesis in Recent sediments and the ecology of lake systems.

1. Dissolved methane gas

Sediment interstitial dissolved methane usually increased with depth in the sediment interstitial water at each of the stations (Table 21) with the exception of the harbor stations and the eastern basin of Lake Erie (station EB). This was not readily evident at station 83 because of the low concentrations, yet CH_4 increased from 1-3 mL/L in the surface samples to 9.7 mL/L at a depth of 57 cm. The shallow 1-21 cm depth interval for two cores at station C-11 did not allow for such an assessment although the normal increase with depth about 0.5 km away was observed in the third core (A108803; 3-45 cm depth interval).

With the exception of station C-11 and one core at HH-258 (H208803), the depth sampling interval for cores was usually five cm or greater. Therefore resolution of gas profiles near the sediment-water interface for calculating diffusive flux to overlying waters was tenuous at best. Cores at C-11 (A108801 and A108802) were designed to sample closer to the sediment-water interface. This was also possible using an in situ equilibrator, or peeper (Hesslein 1976a), at station A-1. Near-surface CH_4 maxima were seen only in cores designated as A108801 (13.3 mL/L at 7 cm), A108802 (17.9 mL/L at 8 cm), and A10979P (P = peeper, 23.6 mL/L at 5 cm) but not for core A108803

A CH_4 maximum was also observed for one core, H208803 (150 ml/L at 9 cm), in the harbors when close interval sampling was employed. Fick's first law modified for sediments (Berner 1971, 1980 and Li and Gregory 1974),

$$F_i = -D_i' \left. \frac{\partial C_i}{\partial z} \right|_{z=0} \qquad (2)$$

where F_i is the flux of specie i, D_i' is the effective diffusion coefficient (or D_s' for sediments) and C_i is the concentration of specie i, was used for indirect flux calculations. D_i', which was adjusted for a porosity to tortuosity squared (ϕ/θ^2) ratio of 0.75 (assumed to be constant), was taken as 7.95×10^{-6} cm^2 sec^{-1} at 8°C (Lerman 1979). In most cases the gas profiles (CH_4 gradients) were determined from the uppermost portion of the sediments (usually the top few centimeters or at most the 0-43 cm depth interval). A departure from this approach was a one-dimensional numerical advection-diffusion model applied to the entire CH_4 gradient (Fendinger 1981).

The one-dimensional advection-diffusion model was basically a mathematical treatment similar to that developed by Berner (1975), Billen (1978) and Tzur (1971);

$$\frac{dc}{dt} = D_s \frac{d^2C}{dz^2} - W\frac{dC}{dz} + P(t), \qquad (3)$$

where D_s was determined using an equation from Lerman (1979),

$$D_s = D_o \phi^2 , \qquad (4)$$

W is the sedimentation velocity and P is the net production rate (Berner 1975). By assuming steady state and a negligible advection term because of the relatively low sedimentation rate (Tzur 1971), the solution to equation (3) becomes:

$$0 = \frac{dC}{dt} = D_s \frac{d^2C}{dz^2} + P_{(z)} \qquad (5)$$

The production term (P) was allowed to float while the diffusion coefficient and the limiting methane concentrations were determined from experimental data. The best fit of the model generated data to the experimentally determined concentration profiles was established by least squares analysis (Fendinger 1981). The model profiles agreed very well with the field collected and measured dissolved methane profiles for the top 0-20 cm of sediment (Figure 26, where concentrations are expressed in mM). Methane fluxes calculated from the model for Lake Erie open lake stations are given in Table 22. Gradients for indirect flux calculations were determined from the one-dimensional advection-diffusion model (equation 5) and the linear regression fit of the methane concentration data versus depth over specified depth intervals determined by visual inspection of the profiles. Depth intervals, linear regression correlation coefficients (for CH_4 versus depth) and the number of data pairs used for the flux calculations are given in Table 22 for each station.

Indirect CH_4 flux estimates for station 83 were lowest, while calculations for stations A-1 and C-11 agreed by a factor of 4 or 5 with each other (120 to 530×10^{-6} moles m^{-2} day^{-1}) depending on the equation or the CH_4 profile interval employed. The only discrepancy was the flux estimate using peeper data. As suggested in Adams et al. (1982c), the measured near-surface CH_4 maximum was probably smeared by the thickness of the depth sampling interval used with the cores at station A-1. Therefore, the higher flux calculations could be actual values which are a result of rapid recycling of labile carbon in the surficial sediments, as suggested by other authors (Zeikus and Winfrey 1976 and Jones and Paynter 1980). Cappenberg (1974) also reported highest CH_4 values (7-13 mM/L or 157-291 mL/L) within the 2-6 cm interval in Lake Vechten deposits. Core data probably underestimate the CH_4 flux because of both disturbance during procurement and the greater and deeper depth sampling intervals.

Station 83 was located approximately 20 km west of stations A-1 and C-11. This station is situated about 40 km southwest of the Pelee Passage and is in a direct line with the major outflow of water from the western basin (Hamblin 1971). As a result, this area would be affected by stronger overlying water currents than would be seen at stations A-1 and C-11. Fendinger (1981) commented that sediments from station 83 consisted of glacial clay based on visual observations. The composition of sediments and pore water at these two locations confirm these interpretations. Interstitial methane and DOC were the lowest at station 83 as compared to any of the six Lake Erie stations (Deis 1981 and Fendinger 1981). Other parameters were also lowest at station 83 (Matisoff et al. 1981 and Adams et al. 1982c): mean porosity (0.7-0.8 at station 83 versus 0.9 at station A-1), volatile solids (2.7% versus 9.2%), total carbon (3.3% versus 6.7%), total phosphorus (26.6 uM/g versus 46.0 uM/g), and total Kjeldahl nitrogen (1.7 uM/g versus 4.5 uM/g). Even though they are both located in the central basin, these two locations have very little in common because of the differences in their sedimentary environments. It also illustrates the inherent risk in using limited data from few stations in developing lake-wide or basin-wide models.

As described earlier, methane maxima were observed within the surficial sediments in some of the cores where gas samples were collected at close depth intervals. This probably represents the fast recycling of labile organic materials. In freshwater environments where cultural eutrophication has contributed to excessive organic loading, the demand for electron acceptors usually results in rapid oxygen depletion and the establishment of a diverse heterotrophic bacterial community within these surface sediments. The dominant microbial processes involved in the breakdown of organic substrates will be largely anaerobic, where degradation of deposited carbon and nitrogen usually results in the accumulation of NH_4^+, N_2, CH_4 and CO_2 as dominant end-products, during a complex sequence of fermentative and reductive respiratory processes. Since the zone encompassing the sediment-water interface is probably responsible for the greatest amount of benthic remineralization of recently deposited labile organic debris, the microbial environment will include all types of respiratory metabolism. The transport of these dissolved decomposition end-products such as methane, from the sediments to overlying waters is dependent upon the rates at which this material is decomposed and accumulated in sediment interstitial water, i.e., the magnitude of the produced concentration gradient, and the mechanisms of sediment-water exchange. A recent study by Martens and Klump (1980) showed that the transport of methane to chambers overlying sediments was greater than what would be calculated from flux using interstitial water gradients and theoretical sediment molecular CH_4 diffusitivities. The discrepancy was most noticable during the summer months for their study area, an organic-rich coastal marine basin. They suggested that macrofaunal bubble tubes could enhance methane concentration gradients by bringing overlying water closer to the zone of methane saturation. This hypothesis was verified with field radon flux measurements (Martens et al. 1980). Another hypothesis suggested by Martens and Klump (op. cit.) to explain this discrepancy was for greater carbon recycling and methane production at the sediment-water interface or slightly below the interfacial boundary. However, they minimized the importance of this hypothesis because Martens and Berner (1974) previously demonstrated limited methane production in the presence of sulfate. Most likely, upward diffusion of methane would be consumed in this zone of intense sulfate reduction (Reeburgh 1981). Therefore, a process which might be of little importance in marine systems could be one of the dominant mechanisms for carbon recycling in freshwater environments. The depth concentration gradient of methane for sediment cores carefully collected by SCUBA divers at station A-1 in the center of the central basin provided for a calculated diffusive loss of 0.30 mmole m^{-2} day^{-1} (Table 22) when data for the top 0-40 cm depth interval were fitted to a linear regression equation ($r = 0.95$; $n = 12$). An experiment with a sediment "peeper" at the same station indicated a zone of maximum methane production at about the five-cm level; diffusive flux between this depth and the surface would be approximately 1.88 mmole m^{-2} day^{-1} or about six times higher than previous calculations using core data. This suggests that recycling of labile organic material might be extremely important in the gas budgets of lake systems.

The methane profile for Lake Erie's eastern basin was an anomoly for open lake stations (Figure 27.). Average interstitial water methane was 71 mL/L. Unlike the methane distributions observed in the other two basins, the maximum methane concentration of 81.6 mL/L occurred only 7 cm below the sediment-water surface and decreased to concentrations as low as 61 mL/L at 51 cm. Probable reasons for this anomalous distribution are the relatively fast accumulation of sediment in this particular area of the eastern basin (Kemp et al. 1976) and the reasonably slow sediment turnover by bioturbation. At locations in the other basins where conditions of relatively slow sedimentation and fast sediment turnover by hydraulic energy and bioturbation exist, methane oxidation would probably occur at an accelerated rate in the upper few centimeters of sediment. The sediment methane profiles determined at stations located in the western and central basins were typical of profiles measured in other freshwater environments (Table 21), where the upper 10-15 cm generally have linear methane concentration gradients (Reeburgh and Heggie 1977). The conditions of slow bioturbation and sediment turnover in the eastern basin, 0.08×10^{-2} cm^{-2} day^{-1} as compared to $0.34\text{-}2.4 \times 10^{-2}$ cm^{-3} day^{-1} for the remainder of the lake (Fisher 1979), possibly inhibited the methane consumptive processes in the upper layers of the sediment. This situation, combined with favorable conditions for methane production because of the rapid deposition of organic-rich sediment, allowed for methane to accumulate near the sediment-water interface. Similar methane distributions were reported by Reeburgh and Heggie (1977) in the sediments of Ace Lake, Alaska.

Dissolved methane concentrations in Cleveland Harbor sediments reflected the high organic loading to the harbor from local industry and a municipal sewage treatment plant (Figure 28). Profiles also illustrated the mixing processes from shipping and dredging within the harbor as well as possible losses due to gas ebullition. Methane concentrations increased from 51 mL/L near the sediment surface to as much as 118 mL/L at depth in one core and 136 mL/L in another. Average dissolved methane was 78 mL/L in these sediments, which is even higher than Lake Erie's eastern basin. At a nearby station Ward and Frea (1979a) reported methane ebullition of 38 mL m^{-2} hr^{-1} (40.5 mM m^{-2} day^{-1}), suggesting high rates of gas loss from the sediments in the form of bubbles. Even though diffusion could be a small portion of methane loss from these sediments to overlying harbor waters, these calculations are included in Table 22 as a comparison for open lake stations. The greatest diffusive flux of 0.5 mmole m^{-2} day^{-1} was one percent of bubble loss reported by Ward and Frea (op. cit.). This will be discussed later.

The two stations in Hamilton Harbour (HH-258 and HH-4) also had enriched methane concentrations as compared to the open lake sampling locations. These values were also variable with depth, again suggesting disturbance from shipping and dredging activities combined with rapid and variable sedimentation. Average interstitial methane at station HH-258 was 38 mL/L in May and 112 mL/L in August, 1980. Station HH-4 averaged 48 mL/L for two cores collected in May; at one place concentrations decreased from 64 mL/L to 7 mL/L within a 3 cm interval because of a sand layer at 27 cm. The presence of this sand layer was also reflected in rapid changes in percent water, sediment porosity and percent volatile solids (Figure 25). Although Deis (1981) reported DOC concentrations greater than 200 mg/L for this station, the high organic content of the sediments was not reflected in high methane concentrations in the interstitial water. As will be shown later, it was suspected that the character of Hamilton Harbour sediment interstitial dissolved organic matter was probably different enough from the open lake sediments that bacterial production of methane was either inhibited or the formation of precusor organic subtrates necessary for methane fermentation was significantly reduced. Whatever the reason, it was substantiated during the processing and visual inspection of the cores collected at both stations in Hamilton Harbour that the sediments contained a large amount of black organic oozes that resembled oil. This ooze no doubt contributed to the high DOC concentrations of the sediment observed by Deis (op. cit.) but its effect on methane production, as described previously, is unknown.

Diffusive flux was calculated for two stations in Hamilton Harbour; at one station (HH-258) sediment methane was measured during two different seasons when water temperatures changed from 9.5°C (May) to 20°C (August). The indirect flux increased by 7 to 9 times during this period (Table 22). Since there was such a large seasonal change in diffusive transport, bubble ebullition observations conducted by Snodgrass (1977) for July 5 to November 2, 1975 at station HH-4 (157 mg CH_4 gas m^{-2} day^{-1} = 9.8 mmole m^{-2} day^{-1}) could not be compared to the May 1980 data. However, Snodgrass measured methane bubble loss at station HH-270 near HH-258 during a similar season (Oct. 14 - Nov. 2, 1975). Gas ebullition averaged 87 mg m^{-2} day^{-1} (5.4 mmole m^{-2} day^{-1}), or about 70-80% of indirect flux calculations (6.3-7.5 mmole m^{-2} day^{-1}) for August 1980. The gas bubbles contained 63.4% CH_4 and 35.4% N_2 by volume.

2. Dissolved total carbon dioxide

Carbon dioxide gas was measured on acidified filtered interstitial water samples, so the reported values represent total carbon dioxide. The accumulation of total carbon dioxide in the interstitial water of sediments seemed to be closely related to source components, these being mainly from the decomposition of organic matter and dissolution of deposited carbonates. As a result, the sediment concentration profiles at the different sampling stations differed widely. Total carbon dioxide in sediment interstitial water at station C-11 located in the central basin of Lake Erie decreased with depth while gradients were different in the other two basins (Figure 29). For open lake stations reasonably distant from sources of detrital carbonates, total carbon dioxide content averaged between 106 mL/L (4.2 mM) at station EB and 56 mL/L (2.3 mM) at station C-11. Concentrations of total carbon dioxide determined at these two open lake stations are comparable to measurements in Lake 227 (0.2-3 mM; Hesslein 1976b) and Grane Langso in Denmark (2-5 mM; Anderson and Anderson 1972), while they were slightly less than concentrations observed in the terrestrial influenced environments of the White Oak River Estuary (2-10 mM; Martens and Goldhaber 1978).

Interstitial water total carbon dioxide concentrations were singificantly higher at stations located in Cleveland Harbor, Hamilton Harbour (Figure 30) and the western basin of Lake Erie. The total carbon dioxide profile observed in Cleveland Harbor was highly variable with depth and had a mean concentration of 219 mL/L (8.8 mM). At the western basin sampling station the total carbon dioxide concentration increased from 161 mL/L to 231 mL/L at a depth of 39.5 cm in the sediment (Figure 29); an average value for the core was 183 mL/L (7.5 mM). The observed behavior of the concentration profiles at this depth may be caused by a shell layer. Carbonate analyses were not conducted to substantiate this concept; however, some shell fragments were observed in the physical description of this core. A similar profile was observed in Hamilton Harbour sediments of station HH-258. The total carbon dioxide content increased from 192 mL/L to 355 mL/L over an interval of 6 cm at 37.5 cm in the sediment. A change was also observed in percent water and percent volatile solids data at the same depth. The average total carbon dioxide concentration for this core was 217 mL/L (9.20 mM). It is suspected that the difference in concentration over such a short depth interval can be explained by a change in the historical sedimentary environment of the harbor. More information concerning the history of the harbor and a thorough chemical analysis of the sediments is needed to adequately explain the anomalous trend observed in this profile.

Total carbon dioxide concentrations in sediments from Cleveland and Hamilton Harbors and the western basin of Lake Erie were from two to six times greater than concentrations observed in the sampling stations located in the eastern and central basins. These differences could possibly be caused by terrestrial influences such as influx of detrital carbonates or antropogenic loading of organic materials. Similar explanations were given by Whelan (1974) for differences in total carbon dioxide content observed between stations located in different types of environments in a Louisiana salt marsh. Those in the northern part of the marsh, where the sediments were strongly influenced by terrestrial additions had enriched concentrations of total carbon dioxide when compared to the southern area where tidal flushing was predominant.

Concentrations found in Cleveland and Hamilton harbors and western basin sediments were similar to those observed by Whelan (op. cit.) and by McCaffrey et al. (1980) for sediments of Naragansett Bay, but are approximately two times less than concentrations observed in the marine influenced environments of the White Oak River Estuary (Martens and Goldhaber 1978).

It appears that carbon dioxide concentrations reflect the sediment characteristics at a location rather than the rate or intensity of organic decomposition. Nissenbaum et al. (1972) and Koyama (1964) suggested that methane can be generated from the reduction of carbon dioxide while Mah et al. (1977) stated that 70% of methane is usually derived from acetate decarboxylation with 30% from CO_2 reduction. However, a significant correlation between total carbon dioxide and disolved methane concentration gradients was not observed at the stations examined during this study. Comparsions of average methane and average total carbon dioxide concentrations between stations also did not exhibit any meaningful relationships.

Using Fick's first law modified for sediment interstitial water (see equation 2), the indirect flux of dissolved total carbon dioxide was calculated from the concentration profiles within the sediments or from the gradient between the concentrations of dissolved total carbon dioxide in the overlying water (assumed to exist at 1 cm above the sediment water interface) and its counterpart measured in the interstitial water just below the sediment interface (depth varied between 2 cm in the eastern basin to 3.5 cm in the western basin). An overlying water concentration from Burns and Ross (1972; average of 2 mM = 44.8 mL/L) for the volume weighted average total CO_2 for Lake Erie's central basin hypolimnion was used for all three basins, and a D_o of 1.26×10^{-5} cm^2 sec^{-1} at 10°C was taken from Lerman (1979) to determine the diffusion coefficient D_s' of 9.45×10^{-6} cm^2 sec^{-1} for the sediment interstitial water. As with the methane indirect flux calculations, when possible the ΣCO_2 gradient was determined by fitting the dissolved total carbon dioxide concentration profile versus depth over specified depth intervals, as calculated by visual inspection of the profiles, to a linear least squares equation (Table 23a). Estimated fluxes ranged from 1.5 in the central basin to 8.7 mM m^{-2} day^{-1} in the western basin. Using changes in hypolimnetic total CO_2 of 11.9 and 18.3 mM m^{-2} day^{-1} during oxic and anoxic conditions, respectively (Burns and Ross 1972), the indirect flux of carbon dioxide from the sediments would account for about 10% of the CO_2 budget for the central basin of Lake Erie. A comparison of data in Tables 22 and 23a will illustrate that the calculated diffusive loss of CO_2 was always greater than methane for the open lake stations. A comparison of the upward flux of carbon as CO_2 and CH_4 to recent sedimentation of organic carbon calculated by Kemp et al. (1976) indicated that the loss of these gases could represent 7-45% of carbon influx to the sediments (Table 23b). Fisher et al. (1982) pointed out that the calculations of organic carbon sedimentation determined by Kemp et al. (op. cit.) ignored decomposition of particulate material; therefore recent sedimentation rates of organic matter (both carbon and nitrogen) listed in Table 23b would be high and the percentage of gas loss would be somewhat more. Of course, some of these gases will be recycled back to the benthos in the form of bacterial and plankton detrital material, so it is difficult to estimate complete losses from the lake's ecosystem.

Diffusive losses for open lake stations were less than the total carbon dioxide flux of 20 mM m^{-2} day^{-1} calculated by McCaffrey et al. (1980) for the sediments of Narragansett Bay. Factors accounting for this difference may in part be related to sulfate reduction in the sediments of Narragansett Bay. It was proposed by these authors that sulfate reduction accounts for most of the total carbon dioxide dissolution and that the reduction of oxygen was considered negligible. In the case of Lake Erie sediments, where carbonate dissolution and oxygen reduction probably play a more important role, further research needs to address the different production/consumption compartments for CO_2: (1) generation and utilization from methane oxidation and production, (2) decomposition of deposited organic matter, (3) respiration and (4) dissolution of carbonates.

3. Dissolved nitrogen gas

Depth distributions of nitrogen gas in the sediment interstitial water at the different stations can be classified into two distinct types: harbor and open lake sediments. Concentrations of nitrogen gas in the sediment interstitial water were compared to calculated N_2-saturation values for the overlying water. This value was determined from the solubility data of Murray et al. (1969) at the in situ temperature at the time sediments were collected or at 4°C when bottom waters would exhibit their maximum density. From this comparison it was determined that nitrogen gas concentrations in the surficial layers of harbor sediments were as high as 3.5 times saturation values calculated for the overlying water. Interstitial concentrations were highly variable with depth and usually above calculated saturation for the entire length of the cores (Figures 31 a-c). These averaged 1.4 - 1.5 times saturation ($n = 41$ measurements) at 4°C for both Hamilton and Cleveland harbors.

The second type of dissolved nitrogen gas profile was observed for open lake sampling stations. Interstitial water N_2 gas profiles for sediments in the western, central and eastern basins of Lake Erie had values that were highly variable with depth in the surface 0 - 20 cm but generally approached N_2-saturation values deeper in the sediments (Figures 32 a-b). Sediment concentrations in the central basin were on the average as supersaturated as the harbor sediments (1.46 times saturation for 23 samples), while this was not the case for the eastern (1.26 times saturation) and western (1.08 times saturation) basins.

The observed concentrations raise several questions about factors affecting nitrogen gas distributions in sediments. Atmospheric contamination of the samples can be ruled out because this would have been reflected in anomalously high argon concentrations and the detection of oxygen during gas analysis. The distributions of dissolved nitrogen gas appear to be controlled by biological denitrification rather than physical processes as suggested by Reeburgh (1969) for Chesapeake Bay sediments.

In the case of the dissolved gas profiles in the harbor sediments it can be speculated that anthropogenic nitrogen loading is much greater than at stations located in the open lake stations. It is also expected that sediment mixing would be more rapid as a result of shipping and dredging activities, wave action, and bioturbation. It is believed that these processes produce a layer of active denitrification in the top 0 - 20 cm of sediments where enriched dissolved nitrogen gas concentrations were observed. The source of nitrate as a necessary precusor for denitrification in the upper layer of the sediments can be derived from both advection from the water column and nitrification of ammonium in an aerobic surface layer in either the sediments or the overlying water. These compounds (nitrate and nitrite) are transported from surficial layers by diffusion, physical mixing of the sediment downward into lower layers of active denitrification, or through organism irrigation (Christensen et al. pre-publication manuscript).

Dissolved nitrogen gas profiles for the Lake Erie sampling stations suggest active denitrification at various depths in the sediment; therefore the presence of nitrate must be considered. Dissolved nitrate was determined at depth in the sediment of Lake Mendota as a result of ground water seepage (Brezonik and Lee 1968), however this source is unlikely in Lake Erie because of postglacial clay deposits (Kemp and Mudrochova 1972). It is suspected then that nitrification may occur in micro-environments as deep as 50 cm in the sediment to produce the nitrate needed to generate the nitrogen gas concentrations observed. Even though Adams et al. (1982a) did not attempt to measure nitrate in the interstitial water, Harris (1977) reported $NO_2^- + NO_3^-$ concentrations ranging from 0.001 to 1 mM for the central basin of Lake Erie; increases with depth (0-60 cm) were observed in half of her 16 cores. Kemp and Mudrokova (1972) also measured $NO_3^- + NO_2^-$ (ranged from 10-20 mg/kg of dry sediment) in the 50 to 100 cm depth interval in Lake Ontario. Assuming that water at this depth was about 40 percent of the sediment composition, the concentration of $NO_2^- + NO_3^-$ would be approximately 1-2 mM. Calculated interstitial water concentrations would have been 0.1 mM or less (for 80% water content) in the upper 5-50 cm of their core, or values which were in the same range as reported by Harris (op. cit.) for Lake Erie. It is suspected that because these sediments exhibited slightly negative to positive redox conditions (Kemp et al. 1976) and were not highly reducing as would be expected for nearshore marine sediments exhibiting sulfate reduction, dissolved nitrate could possibly exist throughout the sedimentary column as a result of <u>in situ</u> ammonium oxidation or some other biochemical process. These reactions were further substantiated by the presence of nitrifying and denitrifying bacterial populations which were anomolous and possibly represented microzones of dominant populations at depths of up to 20 cm in cores collected from Lake Erie (Dutka et al. 1974). Another avenue for the introduction of nitrate into subsurface sediments would be through burrow tubes, termed organism irrigation. Even though the mixed depth by tubificid oligochaetes was about 8 cm from laboratory studies (Fisher et al. 1980) greater mixing depths of up to 83 cm were reported for other environments (Matisoff 1982). Contrary to previous opinions which suggested only near-surface aerobic nitrification, it is suspected that denitrified N_2-production also occurs deeper in the sediments. The reason that these sediment distributions were different than reported by other authors, such as Reeburgh (1969) and Barnes et al. (1975) for marine sediments, could be the absence of an intense zone of sulfate reduction in the lake environment. The latter authors found N_2 values only 10% above saturation for California borderland surficial deposits while Reeburgh (op. cit.) found concentrations less than saturation in Chesapeake Bay sediments.

The formation of N_2 gas during denitrification can represent a major "sink" for lake nitrogen cycles (Brezonik and Lee 1968). The decomposition of organic nitrogen compounds to ammonium, with aerobic nitrification to nitrate and nitrites, represents a method for recycling nutrients back to the benthos and lake waters. With the exception of N_2-fixation, the formation of N_2 gas represents a loss of N from the lake's ecosystem. In a literature review, Tirén (1977a) reported that this loss varied from 11 to 60 percent of the annual nitrogen loading for 12 lakes. A recent study by Seitzinger et al. (1980) for Narragansett Bay nearshore marine sediments showed that conversion to N_2 and subsequent loss to overlying waters represented 29% of the total N flux from sediments (NH_4^+ was the highest at 59%). Even though ^{15}N is usually employed for such studies (Chen et al. 1972, Tirén et al. 1976, Chan and Campbell 1980 and others) some investigators employed benthic chambers to trap and measure the flux of N_2 from sediments (Tirén 1977b and Kaplan et al. 1979 as examples) or determined sediment depth distributions of nitrogen gas (Reeburgh 1969 and Barnes et al. 1975). Denitrification is probably not important in terms of carbon recycling (Kaplan et al. op. cit.) because the reduction of one mole of nitrate to N_2 results in the production of only 1.25 moles of inorganic carbon (Richards et al. 1965):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.4\ HNO_3 = 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 42.2\ N_2 + 148.4\ H_2O \qquad (6)$$

Even though methane is much less soluble than nitrogen gas, loss of N_2 from lake sediments has been observed as a portion of evading gas bubbles (Chau et al. 1977, Snodgrass 1977, Ohle 1978, and Ward and Frea 1979a). Reeburgh (1969) proposed that N_2 was lost as a result of methane supersaturation and bubble formation; such conditions would aid in stripping these gases (N_2, Ar and CO_2) from sediment interstitial water. Gas ebullition rates and the composition of evolved bubbles for various environments is given in Table 24. As will be shown later, gas stripping was probably an important process in the harbors but was most likely not evident in the open lake sediments.

Since N_2 gas was higher in the sediments than would be expected for overlying water, the existing gradient would provide for a diffusive loss from the sediments. Using a D_o of 1.3×10^{-5} cm^2 sec^{-1} at 10°C (Lerman 1979), an effective diffusion coefficient (corrected for a porosity to tortuosity squared ratio of 0.75) of 9.8×10^{-6} cm^2 sec^{-1} was used in equation (2) to calculate the indirect flux of nitrogen gas from the sediments to overlying waters. When possible, gradients for indirect flux calculations were determined from the linear least squares fit of the sediment dissolved nitrogen concentration data versus depth over specified depth intervals determined by visual inspection of the profiles. The diffusive transport of N_2 gas was calculated with the assumption that overlying water (1 cm above the sediment-water interface) exhibited maximum density and was saturated with nitrogen gas (4^oC = 16.6 mL/L; Murray et al. 1969). Warmer water temperatures would contain less N_2 gas and exhibit a greater calculated flux; therefore these estimates for N_2 loss from the sediments are probably conservative. If a sediment gradient could not be accurately determined because of scatter in the data (western and eastern basin stations), the indirect flux was calculated between overlying water and the first measurement below the sediment-water interface (usually at a depth of 1 to 4 cm). The greatest indirect flux for the open lake stations was 1.79 mmole m^{-2} day^{-1} (core A108801) in the central basin; calculations ranged from this high value to a computed flux as low as 0.42 mmole m^{-2} day^{-1} for another core (A108803). The western basin exhibited the lowest flux of 0.17 mmole m^{-2} day^{-1} while the eastern basin (0.59 mmole m^{-2} day^{-1}) was intermediate (Table 25a). These values were similar to an average N_2 flux of 1.2 mmole m^{-2} day^{-1} (range of 0.2 to 2.5) for Narragansett Bay sediments (Seitzinger et al. 1980).

Even though diffusive loss of N_2 gas from the sediments of the harbor might be a small portion of the transport to overlying waters, i.e. bubble ebullition perhaps being of greater magnitude, these calculations are included in Table 25a as a comparison for open lake stations. Snodgrass (1977) determined N_2 gas ebullition at station HH-270 near HH-258 during the same season (Oct. 14 – Nov. 2, 1975) as these indirect flux calculations (August 1980). Gas ebullition rates (68 mg m^{-2} day^{-1} = 2.4 mmole m^{-2} day^{-1}) was more than ten times greater than diffusive flux

(0.22 mmole m^{-2} day^{-1}). This is discussed in greater detail below.

If recent particulate nitrogen sedimentation rates from Kemp et al. (1976) are used for the three basins, the loss of nitrogen as N_2 from the sediments to overlying waters represented about 13% of the total N-sedimentation budget in the western basin to 23% for the eastern basin. The calculated N_2 flux for the central basin varied between 44% to slightly greater than the total N-sedimentation (Table 25b). As pointed out by Fisher et al. (1982), the sedimentation rate of organic nitrogen determined by Kemp et al. (op. cit.) would be high because they failed to include post-depositional decomposition of nitrogen compounds; therefor the percentage of gas loss reported in Table 25b would be somewhat more. Tirén (1977a) reported that in 12 lakes in Sweden, Denmark and the U.S. the loss of N_2 gas can be as great as 61% of the annual loading of nitrogen (Table 26). In addition to being an important parameter in the sediment-water exchange budget, it is obvious that denitrification and N_2 production represents a significant sink of fixed nitrogen for Lake Erie as well as these other lakes.

4. Gas transport across the sediment-water interface

The transport of gases from sediments to the overlying water column can be either through (1) molecular diffusion, (2) bubble formation and ebullition, (3) bioturbation including irrigation, and/or (4) physical disturbance. The molecular diffusion of gases within the sediments and upwards to the sediment-water interface, as a result of greater gas concentrations in the sediment interstitial water, was described in previous sections. The processes associated with items (3) and (4) will not be discussed in great detail except that mixing of the sediments by organisms would certainly occur at all of the stations with the harbor locations being disturbed the most by these and other activities such as dredging, stirring from ship's propellers, and bottom-induced turbulance from wind and wave action.

The formation and loss of bubbles from bottom sediments can be significant and, as shown earlier, ebullition will in some cases exceed molecular diffusion as the major mechanism of gas loss. In one study Strayer and Tiedje (1978) showed that methane diffusive flux from sediments (10-46 mmole m^{-2} day^{-1}) was about twice that lost by bubble ebullition (21 mmole m^{-2} day^{-1}) during the summer for a hypereutrophic hard-water lake in Michigan, while Martens and Klump (1980) reported opposite findings - bubble evasion was eight times greater than diffusive flux for their June-October sampling period. Methane bubbles moving upwards through the sediment will selectively strip other dissolved gases from interstitial water. The total partial pressures of all the gases dissolved in the interstitial water must equal the sum of the hydrostatic and atmospheric pressures in order that bubbles will form. Because of this relationship, bubble formation will probably limit the maximum dissolved gas content of sediment interstitial water.

The partial pressures of methane and nitrogen gas were calculated using solubility data from Wiesenburg and Guinasso (1979) and Murray et al. (1969). The sum of the partial pressures wss then plotted against the water depth at each station (Figure 33). Total pressure (in atmospheres) was calculated from the equation (Hesslein 1976b):

$$\text{Total Pressure} = 0.1\,(X) + 1, \qquad (7)$$

where X is the water depth in meters, 1 is the atmospheric pressure and 0.1 is a factor for obtaining the hydrostatic pressure from the water depth. The sum of the partial pressures must be above the total pressure line in Figure 33 for bubbles to form in the sediments. Therefore, bubble transport was likely only at stations CH in Cleveland Harbor and HH-258 in Hamilton Harbour. It is also possible that bubble formation may control the maximum pore water concentration of dissolved gases at these stations. However, nitrogen and methane gas profiles at these two stations do not exhibit any effects of gas stripping as a result of rapid bubble loss from the sediments. In fact, all of the above mentioned stations have nitrogen gas concentrations well above saturation in the uppermost sediments where the effects of bubble stripping would be the most noticeable. This does not mean that bubble ebullition does not exist at these stations, because Ward and Frea (1979a) measured bubble evasion rates as high as 2,640 ml m^{-2} day^{-1} (118 mmole m^{-2} day^{-1}) for Cleveland Harbor and Chau et al. (1977) reported gas loss of 224 ml m^{-2} day^{-1} (10 mmole m^{-2} day^{-1}) from Hamilton Harbour station HH-258 sediments. It is possible that such gas production would occur at an accelerated rate because of the increased loading of nutrients to these harbor sediments. The rapid biogenic production of gases may mask the effects of bubble formation and loss; if this were not the case dissolved methane and nitrogen concentrations in the sediments would become rapidly depleted as a result of bubble formation and gas stripping.

Bubble formation and loss is a mechanism by which significant amounts of carbon and nitrogen can be lost from lake ecosystems. In one study Martens and Klump (1980) calculated that 85 percent of rising bubbles escapes to the atmosphere from a water depth of 8-10 m. Considering that approximately 45-95 percent of the bubble is composed of methane (Table 24), only 6-14 percent of the bubble's volume of methane is retained by the water column. The remainder would be lost to the atmosphere of North Carolina. If the remainder of the bubble is composed of nitrogen (5-55%) then less than eight percent of the bubble volume of nitrogen gas is retained by the water column. In another study Snodgrass (1977) showed that a much larger percentage (52% at station HH-4 and 56% at station HH-270 in Hamilton Harbour) of methane was lost to the water column at water depths ranging from 10-21 m than reported by Martens and Klump (op. cit.). Both the water depth and greater utilization by methane oxidizers in the water column of Hamilton Harbour as compared to an unpolluted, tidally flushed coastal embayment off North Carolina resulted in a higher loss of methane between the sediments and atmosphere of Hamilton Harbour. Methane oxidation from rising bubbles accounted for 30% of the average hypolimnetic oxygen demand for Hamilton Harbour (Snodgrass op. cit.).

Sediment oxygen demand and the flux of reduced chemical constituents across the sediment-water interface

Benthic deposits in lakes and rivers have long been known to have a significant influence on the cycle of dissolved oxygen in overlying waters. These deposits may account for as much as 50% of total oxygen consumption in rivers (Hanes and Irvine 1968) while in Lake Erie's central basin this was estimated at 80 percent during the 1970 Project Hypo study when a 2-3 cm thick layer of algae was deposited on the basin floor in July (Burns and Ross 1972). The contribution of sediment oxygen demand (SOD) to total hypolimnetic oxygen consumption in lakes is complicated, however, by a variety of factors, the most important of which are productivity, hypolimnion thickness, temperature and lake mixing processes (Charlton 1980).

After thermal stratification, hypolimnetic oxygen consumption may be characterized by two components: water oxygen demand (WOD) and sediment oxygen demand (SOD). The downward flux of organic matter from the epilimnion is either stored or decomposed within the hypolimnion. Oxidative decomposition of this organic matter occurs within the water column (WOD) or sediments (SOD); the unoxidized remainder is buried in the sediments where it may be stored or utilized further by microbial processes. Hargrave (1973, 1975) has shown that more organic matter would contribute to SOD and sediment storage as the thickness of the water column decreases because the settling material would have little time for oxidation within a shallow water column.

SOD is usually divided into two components: biological and chemical oxygen demand (Bowman and Delfino 1980). The biological term accounts for all living organisms dwelling in the sediments, sometimes separated into microbial and macrobial (infaunal macrobenthos) respiration. Chemical SOD refers to reduced substances in the sediment, such as divalent iron and manganese and sulfide, which can quickly oxidize in the presence of O_2 and produce an oxygen demand. Chemical SOD can be further divided into oxidation of reduced solids or oxidation of dissolved reduced chemical species.

Several investigators attempted to determine the total sediment oxygen demand by examining and modeling oxygen profiles in sediments (Bouldin 1968, Murray and Grundmanis 1980, Revsbech et al. 1980,and Revsbech, Jorgensen and Brix 1981). These workers assumed that the oxygen concentration in sediments (and hence the total sediment oxygen demand) is the result of a balance between the diffusive flux of oxygen across the sediment-water interface and removal by reaction or respiration. Models for SOD which account for removal as respiration include those which assume that the consumption reaction is zeroth order in oxygen concentration (Bouldin 1968, Revsbech et al. 1980, and Revsbech, Jorgensen and Brix 1981), first order in oxygen concentration (Bouldin 1968) and first order in solid organic carbon concentration (Murray and Grundmanis 1980). Bouldin (1968) also detailed models for SOD which account for removal by reaction with a reductant. He compared oxygen fluxes for various models with measured values for lakes and salt marshes and found that more realistic results were obtained for models which incorporate diffusion of reductant(s). Even though there are differing opinions on the relative importance of chemical and biological SOD terms to total sediment demand, Wang (1980) found chemical SOD as the major component for two Illinois impoundments. With the exception of Wang's study, few attempts have been made to assess the importance of the different reduced chemical components to overall SOD.

A program was conducted with G. Matisoff who determined sediment interstitial manganese, ammonium and iron concentrations and fluxes, and these investigations of dissolved methane to evaluate SOD measured at the same locations by W. J. Snodgrass (published in Adams et al. 1982c). The upward flux of dissolved reduced chemical constituents (Fe^{2+}, Mn^{2+}, NH_4^+ and CH_4) were related to their oxygen consumptive properties. Near surface interstitial water profiles, determined from in situ techniques, allowed for minimal disturbance of natural conditions at the interface, and therefore accurate calculations of maximal SOD attributed to the oxidation of effluxing dissolved reduced compounds could be determined.

Two different methods were used to collect sediment interstitial water for measurements of dissolved reduced chemical constituents: a sediment peeper (Hesslein 1976a) and diver-collected cores. The peeper was allowed to equilibrate in the sediment for one month. The entire 1-m length of the peeper was subsampled by sequentially piercing the 0.2 μm Nucleopore membrane with syringes. Sediment cores were diver-collected near the peeper for either dissolved gases or dissolved inorganic components. Sampling for dissolved methane was previously described. A second core was placed into another glove box filled with nitrogen gas, sectioned into ten segments and the interstitial water expressed for analyses of Fe^{2+}, NH_4^+ and Mn^{2+} using a Reeburgh-type squeezer (Reeburgh 1967). Sampling details for this core are provided in Matisoff et al. (1980) and Matisoff, Fisher and Lick (1981). In situ measurements of SOD were made using a specially constructed apparatus consisting of either a dark or clear plexiglas hemisphere (0.31 m radius) sited on the sediment surface and enclosing an area of 0.29 m^2. A stirrer and dissolved oxygen probe, located in the top of the hemisphere, were connected by a cable to an underwater cannister containing a battery pack, dissolved oxygen meter and chart recorder. The oxygen concentration was recorded continuously.

Hemispheres were lowered to and placed on the sediments from a small boat maintained at a near stationary position. A clear hemisphere was inspected by divers one and two days after emplacement. The macroinvertebrate community was active and there seemed to be an equal density of macroinvertebrate tubes within the chamber as on its outside. The amount of sediment disturbance during emplacement was also observed. The chamber water appeared to be quite clear. Analysis of water samples taken from inside the chamber a few hours after emplacement and two days later showed essentially no difference in turbidity. The rate of oxygen consumption was somewhat more rapid during the first hour than succeeding 24 hours. The initial rapid rate may be caused by disturbance of particles but is more likely due to the impact of the hemisphere causing displacement of some interstitial water which contains reduced chemical constituents.

The mixing regime inside the chamber was investigated in the laboratory using a dye tracer. The chamber was nearly uniformly mixed within 2-3 minutes and completely mixed in 10 minutes. Visual inspection suggested that currents were within the laminer to turbulent range of water flow. It is still unknown how well the mixing regime inside the chamber simulates that of Lake Erie bottom waters, which typically exhibit bottom currents of 1-5 cm sec^{-1} (F. Boyce, personal communication). During three different cruises a total of four chambers (two clear, two dark) were placed primarily at station A-1 for periods ranging from 24 to 90 hours. Since sunlight penetrates to the bottom of the central basin of Lake Erie (23 m), it has been hypothesized that oxygen production by benthic algae can strongly affect the oxygen budget of the central basin; hence the clear chambers were used to evaluate net oxygen production at the sediment surface. However, although both clear and dark chambers were used to evaluate net oxygen consumption at the sediment surface, the results were not significantly different. This would probably not have been the case during an "algal rain" event.

The dissolved oxygen probe mounted within the SOD hemisphere was calibrated in the laboratory by placing the measuring surface at a fixed distance (ca. 1 cm) from the stirrer. With this procedure, probe drift was minimized and calibration maintained for one week at ±0.2 mg/L. Greater errors were observed in meter drift near the end of battery life than in changes in calibration. The lack of consistent stirring of water past the probe would result in the largest error.

Diffusion coefficients used for calculating the flux of dissolved reduced chemical constituents are given in Table 27. Concentration gradients were determined from data listed in Table 28 for each individual reduced chemical specie. Using equation (2), the flux across the sediment-water interface was calculated for both peeper and core data at station A-1 and only for core data at station 83 (Table 29). Even though SOD was not measured at station 83 with the in situ hemisphere, this station is used to illustrate the variability expected for flux calculations. As described previously, the depositional environments of the two stations (A-1 and 83) have very little in common and therefore should not be compared. For example, CH_4 concentrations at station 83 were the lowest of the six coring locations sampled in Lake Erie's three basins. Because Mn^{2+} data were not available for station A-1, the flux computations for this constituent at station 83 were used in the calculations of chemical SOD at station A-1. Judging from measurements of other reduced chemical species, it is suspected that the calculated Mn^{2+} fluxes at station 83 are probably lower than would be expected for station A-1 (compare calculated fluxes for Fe^{2+} and NH_4^+ in Table 29, for example). In any case, the inclusion of Mn^{2+} flux in the calculation of chemical SOD represents a small ($\leq$ 2%) correction.

The calculated fluxes of iron and ammonium are greater using core data as compared to peeper samples. This appears to be real at least for this one experiment, for fluxes calculated for other species from the same samples show similar patterns (Matisoff, Fisher and Lick 1981): bicarbonate (867 $\mu M\ m^{-2}\ day^{-1}$ from core samples versus 410 $\mu M\ m^{-2}\ day^{-1}$ from peeper samples), soluble reactive phosphate (25 $\mu M\ m^{-2}\ day^{-1}$ versus 10.2 $\mu M\ m^{-2}\ day^{-1}$) and soluble reactive silicate (976 $\mu M\ m^{-2}\ day^{-1}$ versus 200 $\mu M\ m^{-2}\ day^{-1}$). The reason for this consistent deviation is not known but an examination of the concentration profiles provides some clues. Peeper samples are time averaged with heavily damped short-term fluctuations. Frequent disturbance of the sediment surface by waves and organisms will mix interstitial and bottom waters and lessen observed concentration gradients, and hence calculated fluxes. The magnitude of the differences ranges from a factor of 2.2 (iron) to 25 (ammonium). Species (iron) that are removed from solution rapidly in oxygenated bottom water would probably show less difference than those that are removed more slowly (ammonium).

Using the plexiglas hemispheres, oxygen uptake near the sediment-water interface was measured. The rate of oxygen depletion decreased slowly throughout the measuring period yet over successive 12-hr periods the rate was approximately constant. The decrease in rate has been noted by others and modelled by Walker (1980) using Monod type kinetics with an effective half-saturation constant (K) of

1.2 mg/L. This means that SOD is proportional to [DO]/(K + [DO]) where [DO] is the oxygen concentration. Using data from station A-1, it was difficult to observe any dependency between initial oxygen concentrations in the range of 2-9 mg/L and SOD because of variability in the calculated SOD rates. Oxygen demand at A-1 and nearby stations suggest that the variability in sediment composition would mask any oxygen dependency effects on SOD rates until very low concentrations are reached. Monod type kinetics suggest a substantial decrease in rates only below 1-2 mg/L.

The average rate of oxygen consumption for A-1 and nearby station A-2 was 0.3 g m^{-2} day^{-1} (9.4 mmoles m^{-2} day^{-1}); this value will be used for further calculations. Substantial differences in SOD rates between the two stations or between the three cruises in June, July and August were not observed. This rate is below the integrated daily SOD range of 0.4 to 0.7 g m^{-2} day^{-1} observed by Lucas and Thomas (1972) for five stations occupied in 1970 and located in a grid near station A-1. Since most of their measurements were for periods of 2-4 hours, their data include periods influenced by sediment disturbance; these periods were rejected in this study. Blanton and Winklhofer (1972) reported SOD rates of 0.28 and 0.35 g m^{-2} day^{-1} for two 6-7 day experiments in August 1970 at a nearby station in the central basin; site locations were within 9 m of each other. Their data and time period were similar to those given in this study.

During stratification when the hypolimnion is still oxygenated, it is possible that a majority of the dissolved reduced chemical constituents lost from bottom sediments are oxidized at the sediment-water interface. Of the many possible pathways for oxidation, the following equations were used to compute potential oxygen utilization by the major reduced chemical constituents:

$$4\ Fe^{2+} + O_2 + 6\ H_2O \rightarrow 4\ FeOOH + 8\ H^+ \quad (8)$$

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2\ H^+ \quad (9)$$

$$2\ Mn^{2+} + O_2 + 2\ H_2O \rightarrow 2\ MnO_2 + 4\ H^+ \quad (10)$$

$$CH_4 + 1\text{-}1.8\ O_2 \rightarrow 0.3\ CO_2 + \text{cellular material} + H_2O \quad (11)$$

Overall metabolic requirements for a cultured methane oxidizer (Naguib, 1975) were used for methane oxidation calculations. Naguib (1976) showed that this obligate strain utilized O_2 in a ratio of 1 CH_4:1-1.2 O_2 during exponential growth and 1 CH_4:1.4-1.8 O_2 when in resting stage. An oxygen consumption ratio of 1 CH_4:1.5 O_2 was used for oxidation calculations in this study; this ratio is similar to that used by Rudd and Hamilton (1978).

Using equations (8-11), the hypothetical SOD resulting from the upward flux of dissolved reduced constituents (Table 29) was calculated for station A-1 (Table 30). The molar ratios of reduced substrate to potential O_2 utilization are also listed.

Because the peeper was processed in the open where oxidation could rapidly occur as evidenced by the dissolved ferrous iron profile it was suspected that dissolved methane would have been lost during sampling (Hesslein 1976a). However, the upper 30 cm data from three cores (two cores obtained one month earlier, one core near the peeper) practically match the peeper gradient with two exceptions: the peeper data exhibited greater variability and a near-surface methane maximum (1.1 mM) at 5 cm was evident. The variability might be representative of <u>in situ</u> conditions, as shown by Deis (1981) for sediment interstitial water DOC profiles, or could be an artifact of sampling techniques. The estimated CH_4 flux for the peeper data was calculated from the surface 1-cm sample to the zone of maximum concentration. It is suspected that the wide depth spacing of core samples (see Table 28) precludes measuring any surface CH_4 maximum. As described earlier, three cores were collected 1.5 km north of station A-1 in 1980 for the purpose of sampling the sediment-water interface; depth spacing was kept to 3-cm intervals. Two of the cores exhibited methane maximum zones at 7 cm (0.6 mM) and 8 cm (0.8 mM). Average interstitial concentrations were 0.36 mM. Therefore, flux calculations for methane at station A-1 were probably underestimated when using core data because of the depth sampling interval.

The percentage of SOD exhibited by indirect flux calculations of each dissolved reduced chemical constituent is also provided in Table 30. Approximately a third of the measured <u>in situ</u> SOD (0.3 g m^{-2} day^{-1} = 9.4 mmoles m^{-2} day^{-1}) can be accounted for by fluxes of reduced chemical constituents calculated from either the peeper or core data. The fraction of chemical SOD may be higher due to possible analytical problems with sampling methane and ammonium; it will be lower if the actual SOD is greater than measured by the enclosed plexiglas hemisphere. This would be the case only if bottom currents significantly affect the rate of SOD at the sediment-water interface.

Characterization of the quantity and quality of dissolved organic compounds and DOC within sediment interstitial water

Many studies have been made on the nature and concentration of organic carbon in marine and freshwater environments. However, the composition, concentrations and chemical and biological interactions of dissolved organic carbon (DOC) in the interstitial waters of sediments has rarely been investigated. The scarcity of interstitial water DOC data could be due to the difficulties encountered in collecting undisturbed, uncontaminated samples and, until recently, a lack of understanding of the importance of interstitial water DOC to the carbon budget of aquatic systems. The composition and quantity of interstitial water DOC in the sediments of marine systems are influenced by the redox conditions in the sediments and particularly by the existence of sulfate reduction zones. In freshwater environments, factors such as physical morphology, trophic state, stratification, oxygen content and the nature and composition of the surrounding watershed influence the composition, preservation and interconversions of organic matter in the sediments and sediment interstitial water.

1. Sediment interstitial dissolved organic carbon

Low molecular weight organic materials soluble in the interstitial water are probably produced by *in situ* microbial transformations (Barcelona 1980). This organic material is available for further decomposition and biological and chemical diagenesis. However, according to Lyons et al. (1979) and Barcelona (1980) relatively little is known concerning the nature and role of dissolved organic materials in the interstitial water. Previous research indicated dissolved organic matter may be important in the adsorption of hydrophobic compounds (Hassett and Anderson 1979) and the chelation of metals (e.g. Presley et al. 1972 and Lindberg and Harriss 1974). The relationship of DOC to carbon cycling, trace metal chelation, organic compound adsorption, however, depends on the concentration and character of the dissolved organic compounds. In Lake Erie sediment interstitial water, the concentration and character of DOC depends on factors such as deposition of particulate organic matter, overlying water productivity and lake circulation patterns.

The harbor stations (HH-4, HH-258 and CH) were affected by different depositional processes than the basin stations. Hamilton Harbour is periodically flushed by Lake Ontario waters (Polak and Haffner 1978), and both Cleveland and Hamilton Harbors are also dredged to maintain ship channels. Dredging and shipping activity will tend to destroy normal depositional features. Also, the harbor stations receive a higher amount of culturally derived wastes than the basin stations because of the urbanization and industrialization of the Hamilton-Burlington and Cleveland areas. The sediments of both harbors are considered very polluted. Chemical oxygen demand (COD), a common measure of the level of anthropogenic contamination, has been measured in both harbors. The COD of Hamilton Harbour surface (top 7 cm) sediment averaged 140 mg/g while Cleveland Harbor surface sediments average 96 mg/g (OME 1977 and R. Plumb, pers. comm.). As a comparison, Plumb (pers. comm.) reported an average COD concentration of 64 mg/g for an open lake reference station in Lake Erie.

Perhaps as a consequence of the high amount of organic materials the harbors receive compared to the open lake stations, the concentration of DOC in the sediment interstitial water of the harbors is higher than the basin stations. In Hamilton Harbour, the color of the sediments was black, indicative of reducing conditions and high organic content (Brown et al. 1972 and Krom and Sholkovitz 1977). Additionally, with the exception of the sand layers at stations HH-4 and HH-258, the concentration of DOC increased with depth. Studies in marine environments attribute increasing DOC to anoxic, reducing conditions in the sediments (Brown et al. 1972 and Krom and Sholkovitz 1977).

DOC also increased with depth in the Cleveland Harbor station cores and was higher in concentration than the open lake stations. Cleveland Harbor, however, is dredged frequently (EPA 1974), and the station location was near the breakwall in an area of heavy shipping activity. As a result, the sediments in the area of the station were probably continuously disturbed. Despite the high amount of sediment carbon in Cleveland Harbor sediments relative to the open lake stations

(5.3% vs. 3.5% for central basin station A-1), DOC did not appear to be accumulating with depth as was observed in Hamilton Harbour.

High concentrations of 13.3% iron, 1000 ppm lead, and 4000 ppm zinc were present in the sediments of Hamilton Harbour (Mudroch and Zeman 1975). Cleveland Harbor sediments also contain high concentrations of heavy metals, for example, 5.1% iron, 160 ppm lead and 570 ppm zinc (Plumb, pers. comm.). Presley et al. (1972) and Nissenbaum and Swaine (1976) suggested that most of the iron and zinc found in the interstitial water of reducing sediments will complex with DOC. Adams and Darby (1980) suggested the greatest release of sediment bound metals occurs during the disturbance of normal sedimentary conditions, including a substantial portion of water soluble organic-metal complexes from the interstitial water of the sediments. Ultrafiltration of the interstitial water dissolved organic matter of Hamilton Harbour station HH-258 revealed some of the organic compounds were in the 1,000-20,000 molecular weight range, the molecular weight range associated with the fulvic acids (Rashid 1974). According to a study by Lindberg and Harriss (1974), lower molecular weight dissolved organic matter (500-20,000 MW) is more important to the chelation of metal compounds. Therefore, it appears the combination of reducing conditions, high metal concentrations and sediment disturbance in the harbor areas could represent a mode of transport of heavy metals from interstitial to overlying waters.

The concentration and composition of dissolved organic matter in the sediment interstitial water of the open lake stations would be influenced by many factors. Lake circulation patterns are responsible for the difference in the concentration of DOC in the interstitial water of station 83 and A-1 in the central basin. Station 83 is in an area of higher overlying water energy as a result of the flow of Detroit River water into the central basin (Hartley 1968 and Thomas et al. 1976). As a result, station 83 has a lower mean annual accumulation rate of sediment than station A-1 (Kemp et al. 1976) despite similar overlying water productivity. In a 1970 survey of the lake, the location of both stations was in a region of high biomass compared to the rest of the lake (Munawar and Burns 1976). As shown in an earlier section of this report, the lower sediment accumulation rate at station 83 resulted in lower mean concentrations of numerous sedimentary parameters as compared to any other station in this study.

The dissolved organic carbon and sediment total carbon of the eastern basin station (EB) is influenced by erosion of shore materials. The eastern basin station is located near the deepest portion of the lake where the sediment accumulation rate, 13 mm yr^{-1}, is the highest in Lake Erie (Kemp et al. 1976). The majority of the deposited material originates from the bluffs on the northern shore of the central basin (Thomas et al. 1976), and overlying water productivity is lower in comparison to the other basins (Munawar and Burns 1976). The rapidly accumulating sediments might decrease the amount of microbial activity in the deeper sediments resulting in preservation and burial of dissolved organic compounds. Barcelona (1980) suggested the presence of high concentrations of DOC in rapidly accumulating sediments of the Santa Barbara basin (4 mm yr^{-1}) was due to the incomplete utilization of organic material by bacteria. The DOC and methane maxima in the upper 10 cm of eastern basin station sediments indicate rapid fermentation of volatile acids. The higher sedimentation rate could result in burial of organic materials below 10 cm before decomposition to lower molecular weight material occurs.

The western basin is also influenced by the influx of eroded shore materials, primarily transported by Detroit River water inflow. Thomas et al. (1976) reported the presence of a gradient of organic carbon in the surface sediments extending from the mouth of the Detroit River. Large quantities of organic rich sediments from the upper Great Lakes watersheds enter Lake Erie at this point. The flow of Detroit River water, wind generated currents, and the shallowness of the western basin result in resuspension and reworking of the surface sediments. Also an active benthic population to depths as great as 20 cm in the sediments (McCall et al. 1979) result in greater recycling of surface sediments. DOC has a lower mean concentration than the eastern basin (15 mg/L vs. 20 mg/L) suggesting the possibility that decomposition reactions are actively converting DOC to labile carbon species. In fact, the greatest loss of carbon gases (mainly as CO_2) occurring in the western basin (Table 23) indicated rapid turnover of organic materials. The differences in CH_4, DOC, and CO_2 concentrations between the western and eastern basins suggest that resuspension and reworking of surficial deposits in the western basin is influential in the carbon cycle of these sediments.

2. Relationships between DOC and other chemical parameters related to carbon cycling

Various authors have suggested pathways of organic carbon diagenesis in sedimentary environments. For example, Krom and Sholkovitz (1977) used carbon and hydrogen isotopes to confirm the pathway of humification of organic matter in anoxic marine sediments. This model was modified by Krom and Westrich (1980) to include all dissolved organic matter (humic acids and low molecular weight material) in anoxic marine sediments. Martens and Goldhaber (1978) suggested the production of soluble organic matter in the White Oak River estuary was related to the extent of bacterial activity and not necessarily to the amount of particulate organic material deposited. Kemp and Wong (1974) utilized gel permeation chromatography size fractionation to infer the same pathway of humification occurred in the freshwater sediments of Lakes Ontario and Erie.

Data for the eight stations in this study showed that the mean concentration of DOC was 0.02 to 0.07% ($\bar{x}$ = 0.05%, 0.02 SD) of the mean concentration of sediment total carbon. The range was so small, however, that the extent and type of bacterial activity may be similar. Despite the amount of organic matter present at any of the stations, only a small percentage would be available for rapid decomposition. Readily available (labile) organic matter was probably recycled quickly in the surface sediments. Although DOC production by decomposition of particulate organic matter probably decreased with depth in the sediments, utilization of DOC also might be less with depth in the sediments due to declining bacterial activity. Bacterial activity has been reported to decrease with depth in terrestrial soils because readily available organic substrate becomes depleted (Brock 1974). DOC concentrations increased significantly with depth in all cores with the exception of three stations (EB, 83, and HH-258). Both Brown et al. (1972) and Krom and Sholkovitz (1977) also reported increases in interstitial water DOC in cores collected from anoxic marine sediments. In the eastern basin the constant DOC concentration with depth was probably due to rapid sedimentation and burial of available substrate before complete utilization.

Utilization of DOC by bacteria results in the formation of other carbon compounds, particularly carbon dioxide or methane. Normally, methane production is confined to strict anaerobic conditions (Rudd and Taylor 1980). However, Bernard et al. (1978) indicated that methanogenesis can occur in organic rich, reducing microenvironments. In Lake Erie, the redox potential of the sediments was only slightly reducing or oxidizing as measured by platinum electrodes (Kemp et al. 1976). But methanogenesis can still occur because of the presence of these reducing microenvironments. A strong linear correlation existed between the mean concentrations of DOC and CH_4 in the sediments of the basin stations (Table 31 and Figure 34a). This was not evident for DOC and ΣCO_2 (Figure 35a). The coefficient of correlation was changed by the addition of Hamilton Harbour data (Table 32 and Figs. 34b, 35b); perhaps the DOC of the harbor stations contained a higher quantity of non-labile organic matter which was not utilizable by bacteria (e.g. oils and greases, etc.). Examination of the correlation of CH_4 to DOC in Figure 34b would indicate that the methane concentration in Hamilton Harbour sediments should be at least three times greater than actually measured. This was not, however, as strongly evident for Cleveland Harbor sediments which exhibited a reasonably similar linear correlation between CH_4 and DOC as was observed for open lake environments. Reasons for the lower methane production in Hamilton Harbour as compared to Cleveland Harbor or open lake sediments is unknown - perhaps it is related to the higher levels of pollutants, as metals and organic compounds, in this highly industrialized environment.

The pathways of biogeochemical cycling of carbon in the sediments are numerous and complicated by many factors. It is obvious from the variability in the data presented in this study that quantitative modeling of the cycle of organic carbon in the sediments would be difficult. On a qualitative basis, the cycling of carbon from deposition to loss by CH_4 and CO_2 diffusion appears to follow natural pathways (Figure 36). Linear correlation analysis shows a relationship exists between carbon deposited on the sediments and the concentration of sediment total carbon of the surface sediments (Table 31). A strong relationship also existed between sediment total carbon and DOC in the interstitial water, indicating DOC in the interstitial water was probably an in situ decomposition product of the organic matter in the sediments. The very strong relationship between methane and DOC indicated that dissolved organic material in the interstitial water was the substrate of choice for fermentative bacteria (e.g. methanogens). Also, a correlation was not found between methane and any of the particulate carbon sources in the sediments (sediment total carbon, volatile solids, or total loaded carbon), which supports the contention that organic material dissolved in the interstitial water was the prime substrate for methanogens. Therefore, it appears that DOC represents a link in the carbon cycle of Lake Erie sediments. If, as indicated by previous authors (e.g. Rudd and Hamilton 1979 and Fallon 1980), the loss of dissolved methane from the sediments represents a source of carbon to the overlying water, then an understanding of the carbon cycle in the sediments is important in understanding the carbon cycle of the entire lake.

3. Composition of the sediment interstitial dissolved organic matter

Only two stations were occupied to obtain samples for characterization of the sediment interstitial water dissolved organic matter. These were station C-11 in the central basin of Lake Erie and HH-258 in the center of Hamilton Harbour. As described earlier, the cores were sub-divided into 0-25 cm and 25 to about 50 cm depth segments for laboratory processing. The character of the dissolved organic matter was evaluated either by ultra-filtration for size analysis of the organic compounds, by methylene chloride extraction of the interstitial water (adjusted to pH 12 and then pH 2) for GC/MS analysis, and by purge and trap techniques combined with GC/MS to evaluate the volatile organic compounds.

The nature of the source material influences the character of the dissolved organic matter in the interstitial water. The characterization of Lake Erie station C-11 and Hamilton Harbour station HH-258 dissolved organic matter by ultrafiltration revealed substantial differences in their molecular weight composition. Station C-11 sediments in the middle of the central basin receive organic carbon primarily from sedimentation of dead planktonic material from overlying waters. This is apparently rapidly recycled in the surface sediments by bacteria. However, under oxic or suboxic conditions in the central basin surface sediments, DOC does not accumulate. Instead, decomposition and utilization by bacteria maintain relatively constant levels. Kemp and Wong (1974) proposed that decomposing cellular material is transformed into higher molecular weight organic material which is resistant to bacterial degradation. Therefore, as the ultrafiltration data suggests in Table 18, higher molecular weight material dominate the interstitial water DOC. Lower molecular weight organic compounds are either rapidly utilized by bacteria, forming methane, carbon dioxide and cellular material, or are transformed to higher molecular weight humic material via a pathway through the fulvic acids (Krom and Sholkovitz 1977).

In contrast, the sediments at Hamilton Harbour station HH-258 received higher quantities of industrial wastes (OME 1977). Under the anoxic conditions of Hamilton Harbour hypolimnetic waters and sediments, long chain aliphatic and aromatic hydrocarbon materials generated by industry will not be easily degraded by bacteria (Brock 1974). Therefore, although dissolved organic carbon was higher in the sediment interstitial water of Hamilton Harbour, the concentration of labile low molecular weight material was not necessarily in greater amounts. This was probably the reason for the lower methane production seen in Figure 34b as compared to the other sampling sites. As shown later, the character of the interstitial organic matter as identified by GC/MS would indicate the unlikelihood of rapid bacterial utilization.

Ultrafiltration of Hamilton Harbour HH-258 interstitial water dissolved organic material also yielded a shift in the 25-50 cm segment of the core to higher molecular weight ranges (Table 18) as compared to the upper section of the same sediments. Yet, this type of data provides only a qualitative assessment of the dissolved organic matter composition. Other authors, however, have noted similar shifts to higher molecular weight materials (e.g. Kemp and Wong 1974 and Krom and Sholkovitz 1977). Utilizing a gel filtration technique, Kemp and Wong (op. cit.) reported a predominance of lower molecular weight material (500-700 MW) in the interstitial water of the western basin of Lake Erie with a shift to slightly higher molecular weight ranges (>1000 MW) in the deeper sediments.

The level of purgeable organic compounds in each of the interstitial water samples was very low (Tables 13 and 14; Figures 14, 17 and 18). The only exceptions were a few halogenated methanes which probably represented laboratory contaminants. There were no purgeable priority pollutants, except those shown in Table 14, which were in excess of detection or about one ppb (approximately 1 μg/L). Hexane (Figure 15) and ethylbenzene were identified in both Lake Erie and Hamilton Harbour samples. Other volatile compounds found in Hamilton Harbour sediments were xylene, indan or methylstyrene (Figure 19), and C_3- and C_4-benzenes (Figure 16). Mass spectra at several time intervals during the elution of the unresolved hump in Figure 18 revealed aromatics, alkenes and cycloalkanes but no alkanes.

Substantial numbers of base neutral (B/N) components were observed in the extractable fractions of interstitial water samples from Hamilton Harbour sediments (Tables 15 and 16; Figures 20 and 21). These compounds also showed considerable diversity and included alkanes, aromatics, PNA's (polynuclear aromatics), and probably some heterocyclic compounds. The levels of PNA's found ranged from the detection limit of about 1 μg/L to 13 μg/L; primarily, 1-4 μg/L. The alkanes and some of the apparent heterocyclic components were estimated to be approximately a factor of 10 higher in concentration than the PNA's (values ranging as high as 30 μg/L). The series of compounds marked (X) in Table 16, eluting at 16.9, 18.0 and 18.6, 19.1 and 19.5 have mass spectra compatible with dialkylthiophene or alkylamino-carbazole species. The high degree of similarity among the mass spectra strongly suggest a series of homologs eluting roughly one minute apart, with isomeric forms of the two later homologs eluting at slightly different times. Examination of the general background of the unresolved hump early in the chromatogram, e.g., at 17.9 min (Figure 22), suggests that the mixture of compounds is very largely aliphatic and alicyclic or alkenyl in nature. Later portions, e.g., at 28.7 min (Figure 23), show a generally larger mixture of compound types, as would be expected. Some specific compounds were identified at low μg/L levels: acenaphthene, anthracene/phenanthrene, chrysene/benzo(a) anthracene, methylnaphthalene, and pyrene. There were no high molecular weight PNA's or chlorinated compounds. However, the presence of low molecular weight PNA's, aromatic and heterocyclic organic compounds dissolved in the interstitial water, particularly in the surface sediments, suggests that the sediments of Hamilton Harbour are potentially dangerous to the surrounding environment. Any disturbance of bottom sediments could easily release these components to the overlying water column.

Similar extractions of samples obtained from the central basin of Lake Erie were much lower in B/N organic compounds. For the open lake station, the concentration of B/N compounds was greater in the bottom 25-50 cm than in the top 0-25 cm portion of the core interstitial water. There were some saturated hydrocarbons, at the 1 to 4 μg/L level, in the interstitial water of these open lake sediments. Judging from elution times these were in the range of C_{28} to C_{36}.

Few, if any, substances were found in acid fraction extracts of the sediment interstitial water (Table 17 and Figures 24 and 25). The analytical procedure favors identification of phenols, so the concentrations of extractable phenols in the samples must be no more than a few μg/L in the original interstitial water.

Specifically, phenolic priority pollutants were not detectable (≥1 μg/L). Carboxylic acids and especially dicarboxylic acids are probably discriminated against in this procedure and would not be readily observed. Only four compounds were identified in these extracts: p-cresol, phthalate (might be a contaminant), dioctyl adipate, and bis-(2-ethylhexyl)-phthalate. Because the last two compounds were identified in only one sample from Lake Erie and not in Hamilton Harbour, these data would need to be confirmed.

CONCLUSIONS

Benthic gas collection devices were deployed numerous times in the central basin of Lake Erie during the summer and fall of 1979. From these observations it was concluded that gas bubbles were not being released in substantial quantities as reported by Howard et al. (1971). Calculations of *in situ* gas pressures within the sediments indicated that bubble ebullition would not occur at any of the open lake stations. However, losses of gases by diffusion was likely because of larger concentrations near the sediment-water interface and the presence of concave gas profiles which generally increased with depth. Indirect flux estimates suggested a substantial loss of methane, nitrogen and total carbon dioxide gases from the sediments to overlying waters. These fluxes ranged from 0.07 to 4.6 mmole $m^{-2}day^{-1}$ for methane, from 1.5 to 8.7 mmole $m^{-2}day^{-1}$ for total CO_2, and from 0.2 to 1.8 mmole $m^{-2}day^{-1}$ for N_2 gas. Calculated diffusive losses from Hamilton Harbour sediments were compared to earlier gas ebullition studies conducted by Snodgrass (1977); these comparisons indicated 10 times greater flux of gas bubbles as compared to diffusion during the same time of year for N_2 gas yet similar transport calculations for methane gas (5.4 mmole m^{-2} day^{-1} for bubble ebullition versus 6.3-7.5 mmole m^{-2} day^{-1} for indirect diffusive flux).

The diffusive loss of methane could represent as much as 30% of the sediment oxygen demand for the central basin of Lake Erie. In addition, it was calculated that the flux of CO_2 across the sediment-water interface could account for about 10% of the hypolimnetic CO_2 budget determined by Burns and Ross (1972) for the central basin. The calculated diffusive loss of CO_2 was always greater than methane for the open lake stations. The upward flux of carbon gases (as CO_2 and CH_4) represented 7-45% of the carbon influx to the sediments as calculated by Kemp et al. (1976), thus representing an important amount of the carbon budget for Lake Erie.

Nitrogen gas was supersaturated in the sediment interstitial water as compared to calculated solubilities for overlying water temperatures.

Concentrations averaged 1.5 times saturation (n = 23) for sediments in the central basin. Values as high as 3.5 times saturation were determined for harbor surficial sediments. These unusually high concentrations have not been previously reported for natural sedimentary environments; difficulties in measuring N_2 is probably the major reason for the lack of such information. Indirect diffusive flux calculations for N_2 gas was 13-44% of the particulate N sedimentation rate determined by Kemp et al. (1976) for the three open lake stations. One calculation indicated a greater N_2 loss than N-sedimentation for a central basin location. The production of denitrified N_2 gas in the interstitial water near the sediment-water interface obviously represents a major pathway for nitrogen loss from the lake.

The decomposition of sedimented particulate matter results in the accumulation of dissolved organic compounds in the sediment interstitial water. The low molecular weight organic compounds formed by decomposition are probably rapidly recycled in the upper surface sediments as methane, carbon dioxide and other gases. These close biochemical relationships were substantiated by significant linear correlations between DOC and methane gas in the sediments of the open lake stations. This was not the case for Hamilton Harbour sediments suggesting the lack of bacterial metabolism to carbon gases. As bacterial metabolism decreases with depth in the sediments, DOC undergoes condensation reactions to form higher molecular weight components. This was observed for one core from Hamilton Harbour and in both surface and deeper sediments collected from the central basin of Lake Erie.

The concentration of DOC in the interstitial water of the open lake basin station sediments depends on a variety of factors such as overlying water productivity and circulation, the nature of the sediment source material and the sedimentation rate. For example, stations 83 in Lake Erie's central basin had the lowest concentrations of interstitial water DOC because of greater surface water currents and lower sedimentation rates. The eastern basin station was located in an area of high sediment accumulation. This station had the highest concentration of DOC of any of the open lake locations because rapid burial of organic material is suggested to lower bacterial activity thus allowing for its accumulation with depth. Stations A-1 and C-11 located in the depositional area (focusing center) of the central basin is influenced primarily by sedimentation of material from the overlying water. Rapid recycling occurs in the surface sediments; DOC did not accumulate and concentrations were relatively low. The western basin station receives source material from the Detroit River. Rapid sediment turnover by organisms and greater overlying water turbulence in this shallow basin have a major impact on the sediments; as a result DOC also did not accumulate in the interstitial water.

The character of organic material dissolved in the sediment interstitial water was determined by GC/MS for single cores from Lake Erie's central basin and Hamilton Harbour. Measurements of purgeable organic compounds and methylene chloride extractables from base/neutral and acidified interstitial water indicated numerous compounds of anthropogenic origin in Hamilton Harbour sediment interstitial water. These were identified as heterocyclic and aromatic in nature with numerous alkanes, polynuclear aromatics and unresolved or unidentified compounds in the base/neutral extractable fraction. In addition, methyl styrene or indan, hexane, ethylbenzene, xylene and C_3- and C_4-benzenes as well as aromatics, alkenes and cycloalkanes were observed in the purgeable fraction of Hamilton Harbour sediment interstitial water. As a comparison, only two of the purgeable compounds were seen in Lake Erie sediments which also contained high molecular weight aliphatic hydrocarbons in the base/neutral fraction. With the exception of a possible contaminant and the presence of two compounds of unknown origin, p-cresol was observed in the interstitial water from both sedimentary environments.

Organic compounds dissolved in sediment interstitial water are easily exchanged with overlying waters through a variety of advective and disruptive processes such as dredging. The contaminants observed in Hamilton Harbour sediments could represent a potentially hazardous situation for free-swimming organisms and benthic populations. These compounds could also interact with other organic and inorganic contaminants forming an even more hazardous environment. Further studies need to address the biogeochemical cycling of these contaminants within the sediment, interstitial water, overlying water and biotic compartments.

In conclusion, this study has shown that sediment gas production and loss across the sediment-water interface can represent a significant proportion of the budget for carbon and nitrogen in surficial freshwater environments. These gases need to be examined when assessing oxygen and C and N cycles in lake ecosystems. The composition of dissolved organic carbon (DOC) precusor material in the sediments was shown to have a close relationship to gas production. Sediment DOC was of greater concentration, and contained organic compounds of a deleterious nature, in the harbor sediments; this was not the case for the open lake environment. The partitioning of these organic compounds between sediment particles and dissolved phases needs to be evaluated. Mobilization to interstitial water and transport either by sediment disruption, irrigation or perhaps as surfactant organic film material coated to gas bubbles could represent possible pathways from the depositional environment back to overlying waters.

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Table 1. Data for SOD Cruise number 1 with Ohio State University, June 1979, to the central basin of Lake Erie. Resultant wind speed and direction are for Cleveland. Vessel: R/V Hydra

Date	Location	Water Depth	Sampling Activities	Weather Conditions
June 16	A-1	23.5 m	Black chamber was placed at 0800 hrs Chamber could not be diver secured One core collected near chamber for gas analysis	Mean air temp. - 73.0°F Weather Type - hazy Wind direction - 20° Wind speed - 6.0 mph Precipitation - 0
June 17	A-1	23.5 m	Black chamber turned over and sank in mud due to ship's rotation One core collected near chamber for carbon analysis	Mean air temp. - 73.0°F Weather type - hazy Wind direction - 18° Wind speed - 1.5 mph Precipitation - trace
June 18	A-3	23.5 m	Black chamber was placed at 1900 hrs	Mean air temp. - 57.0°F Weather type - clear Wind direction - 36° Wind speed - 6 mph Precipitation - trace
June 19	A-3	23.5 m	1.0 mL of gas collected from chamber at 1600 hrs. Sample was lost during processing. Returned chamber again to bottom.	Mean air temp. - 62°F Weather type - clear Wind direction - 06° Wind speed - 7.0 mph Precipitation - 0
June 20	A-3	23.5 m	1.0 mL of gas collected from chamber at 1000 hrs.	Mean air temp. - 72.0°F Weather type - thunderstorms Wind direction - 16 Wind speed - 11.0 mph Precipitation - 2.11

Table 2. Data for cruise 1 with Case Western Reserve University, July 1979, to the Central Basin of Lake Erie. Resultant wind direction and speed are for Cleveland. Vessel: R/V Hydra.

Date	Location	Water Depth	Sampling Activities	Weather Conditions
July 8	83	16.6 m	Black SOD chamber and gas funnel collector were deployed at 1700 hrs. Water was collected from chamber for carbon analysis	Mean air temp. - 71°F Weather type - hazy Wind direction - 09° Wind speed - 1.6 mph Precipitation - 0
July 9	A-1	23.5 m	Two cores were collected for gas and carbon analysis at 1600 hrs.	Mean air temp. - 69°F Weather type - fog, haze Wind direction - 17° Wind speed - 10.9 mph Precipitation - 0.58
July 10	83	16.6 m	Sample was collected from the chamber at 1200 hrs. Gas was not present. Two cores were collected near the chamber for carbon analysis One core was collected 200 m away from the chamber for gas analysis.	Mean air temp. - 74°F Weather type - fog, haze Wind direction - 17° Wind speed - 4.7 mph Precipitation - trace

Table 3. Data for cruise numbers 2 and 3 with Case Western Reserve University, August and September 1979, to the Central Basin of Lake Erie. Resultant wind direction and speed are for Cleveland. Vessel: R/V Hydra.

Date	Location	Water Depth	Sampling Activities	Weather Conditions
Aug. 8	A-1	23.5 m	Black SOD chamber and gas funnel collector were placed at 1340 hrs. Cores were collected on both sides of the chamber for gas analysis One core was collected for carbon analysis	Mean air temp. - 78°F Weather type - clear Wind direction - 29° Wind speed - 4.8 mph Precipitation - trace
Aug. 9	Cleveland Harbor	9.6 m	Two cores were collected for carbon analysis One core was collected for gas analysis	(See Table 7)
Aug. 9	A-1	23.5 m	Samples were collected from the chamber at 1430 hrs. Gas was not present. Gas funnel collector was retrieved at 1430 hrs. Gas was not present. Gas funnel collector was redeployed.	Mean air temp. - 96°F Weather type - clear Wind direction - 14° Wind speed - 2.7 mph Precipitation - trace
Sep. 5	A-1	23.5 m	Gas funnel collector was placed at 1230 hrs to be collected in October.	Mean air temp. - 77°F Weather type - haze Wind direction - 06 Widn speed - 6.1 mph Precipitation - 0
Sept. 6	A-1	23.5 m	One core was collected for gas analysis One core was collected for carbon analysis	Mean air temp. - 76°F Weather type - haze Wind direction - 27.0° Wind speed - 9.4 mph Precipitation - trace

Table 4. Data for cruises with the R/V GS-1 from the Ohio Geological Survey to the Western Basin of Lake Erie and the R/V Roger R. Simons with NOAA and EPA to the Eastern Basin of Lake Erie, 1980. Scientific party chief on GS-1: Nate Fuller.

Date	Location	Water Depth	Sampling Activities	Weather Observations
June 3	Eastern Basin* (EB)	65 m	Used Benthos corer Collected cores 2 and 4 for dissolved gases and cores 1 and 3 for dissolved organic carbon (DOC) Core 5 for physical description	Foggy and damp, lake calm, air temp 13°C
Aug 6	Western Basin (WB)	10.8 m	Collected cores 1 and 2 for dissolved gases, and core 3 for DOC; DOC also measured on subsample of core 2. Core 4 for physical description Sediment at 5 cm 21.5°C, water temp 25°C Visibility at bottom 20 cm	Light wind out of SW Cloudy, hazy and warm

*Near NOAA station 28 in the Eastern Basin off Long Point

Table 5. Data for cruise with Canada Centre for Inland Waters, August 1980, to the Central Basin of Lake Erie. Vessels: CSS Advent and CSS Limnos. Scientific party chief: Farrell Boyce.

Date	Location	Water Depth	Sampling Activities	Weather Observations
Aug 15	C-11	24 m	Cores 1 and 2 collected together (for gases) Core 3 (for gases) and physical core collected 0.5 km away Core 4 for DOC analyses Overlying water 11.4°C, core temp. 13°C	Partially cloudy, 20 knot wind from NNW choppy, 4 ft. swells
Aug 18	C-11	24 m	Six cores collected for microcosm study Cores sectioned 25-50 cm for interstitial water organic compounds and DOC size analysis (depth sometimes greater than 50 cm) Shipek grab samples for surface and for interstitial water organic compounds and DOC size analysis	Did not record weather information

Table 6. Data for cruises to Hamilton Harbour. Sampling was conducted from a private vessel.

Date	Location*	Water Depth	Sampling Activities	Weather Observations
7 July 79	Station 4	18.0 m	Collected core for dissolved organic carbon (DOC)	Not recorded
	Station 258	18.4	Same as above	
24 May 80	Station 4		Collected cores 1 and 2 for gases, core 4 for DOC, core 3 discarded (sand at 17 cm)	Slightly overcast, calm water conditions, warm Air temp 21-26°C
	Station 258		Core 5 for gases, core 1 for DOC Water temp 9.5-10°C	
17 Aug 80	Station 258		Collected cores 1,2 and 3 for gases, core 2 also used for DOC and volatile solids Multiple cores collected for interstitial water organic compounds and DOC size analysis Water temp 20°C, mud temp 12.5°C	Warm, sunny with light breezes, small waves

*HH-4 located at 43°17' N. lat., 79°48' W. long.; HH-258 located at 43°17' N. lat., 79°50' W. long.

Table 7. Data for cruises to Cleveland Harbor. Sampling was conducted with R/V Hydra in 1979 and a private vessel in 1980.

Date	Location	Sampling Activities	Weather Observations
9 Aug 79	Center of harbor	Collected one core for testing GC system (gases) Cores 2 and 3 for dissolved organic carbon (DOC) Had problems recovering Benthos corer	Not recorded
31 July 80	Near breakwater marker no. 28 10 m from breakwall	Diver collected cores Core 1 for gases, core 2 for DOC Water temp 22°C	Overcast, southerly wind

Table 8. Coring locations, dates and sample processing activities.

Station Number	Station Location Lat.N.	Long.W.	Water Depth (m)	Dates	Analyses
Lake Erie Central Basin					
A-1	41°50'	81°51'	23.5	6/79	water content, DOC[*]
				7/79	water content
				8/79	water content, CH_4, DOC
				9/79	water content, CH_4, peeper
				10/79	water content
83	41°42.5'	82°19.2'	16.6	11/78	volatile solids
				7/79	water content
				10/79	water content, CH_4, DOC
C-11	41°50.2'	81°51.2'	24.0	8/80	water content volatile solids DOC, DIC, DTC[**] CH_4, N_2, ΣCO_2 DOC size analysis GC/MS samples
A-3	42°10'	81°20'	23.5	6/79	water content, DOC[*]
Lake Erie Western Basin					
WB	41°48'	82°58'	10.8	8/80	water content volatile solids DOC, DIC, DTC[**] CH_4, N_2, ΣCO_2
Lake Erie Eastern Basin					
EB[***], [+]	42°33'	79°48'	65	6/80	water content volatile solids DOC, DIC, DTC[**] CH_4, N_2, ΣCO_2
Lake Erie Islands Area					
IA[+],[++]	41°41'	82°51'	9[+++]	10/79	water content volatile solids DOC

[*] Acid not added to interstitial water sample before DOC analyses

[**] Interstitial dissolved organic carbon, inorganic carbon and total carbon (organic + inorganic)

[***] NOAA station 28

[+] Collected with a Benthos gravity corer

[++] 0.5 miles NE of Rattlesnake Island

[+++] Taken from Canadian Hydrographic Service chart L/C 2100 Lake Erie

Table 8. (Continued)

Station Number	Station Location	Water Depth (m)	Dates	Analyses
Cleveland Harbor				
CH	harbor center	unknown	8/79	water content, DOC, CH_4
	near break-water marker number 28	8	7/80	water content volatile solids DOC, DIC, DTC CH_4, N_2, ΣCO_2
Hamilton Harbour*				
HH-4	near SE arm and causeway	18	7/79	DOC
			5/80	water content volatile solids DOC, CH_4, N_2
HH-258	middle of harbor	18.4	7/79	DOC
			5/80	water content volatile solids DOC, CH_4, N_2
			8/80	water content volatile solids DOC, DIC, DTC CH_4, N_2, ΣCO_2 DOC size analysis GC/MS samples

*Sediment sampling stations from OME (1977)

Table 9. Summary of SOD chamber gas collection experiments during 1979.

Date/Time Deployed Location	Data/Time Collected	Total Time Deployed (Hours)	Amount of Gas Collected	Resultant Wind Direction (Cleveland Data)	Mean Wind Speed (Cleveland Data) (mph)
June 16 0800 hrs A-1	Chamber turned over and sank in mud due to ship's motion		–	20°	7.5
June 18 1900 hrs A-3	June 19 1600 hrs	21	1 mL	06°	8.3
June 19 1600 hrs A-3	June 20 1000 hrs	18	1 mL	16°	11.5
July 8 1700 hrs 83	July 10 1200 hrs	43	–	15°	18.0
Aug 8 1340 hrs A-1	Aug 9 1430 hrs	27	–	22°	9.6

Table 10. Detection limits for the flame ionization detector (FID) and thermal conductivity detector (TCD) using a modified Carle model 311M gas chromatograph (see text).

	Minimum Detectable Quantity (μL)		Detectable Concentration* (mL/L)	
Gas	FID	TCD	FID	TCD
Ar	-	1.03	-	1.54
O_2	-	0.97	-	-
N_2	-	0.64	-	0.95
CO_2	did not test	1.66	-	2.44
CH_4	0.017	0.68	0.027	1.00

* mL/L = mL per L of sediment interstitial water; calculations assumed 30 mL syringe headspace and 20 mL sediments with 50% water content

Table 11. Concentration ranges for sediment interstitial water dissolved gases in the three basins of Lake Erie, Cleveland Harbor and Hamilton Harbour.

Location	Methane (mL/L)	Nitrogen (mL/L)	Total CO_2 (mL/L)
Lake Erie			
Western Basin (WB)	5.72-51.1	11.9-25.6	118.3-298.5
Central Basin			
Station 83	1.05-9.73	-	-
Station A-1	5.70-51.0	-	-
	1.80-74.6*	-	-
Station C-11	3.18-22.7	14.4-37.0	50.1-61.7
Eastern Basin (EB)	59.9-81.6	18.1-25.2	89.1-129.6
Cleveland Harbor	36.1-135.7	8.9-58.3	190.4-253.7
Hamilton Harbour			
Station 4			
May	7.24**-68.7	14.5-74.9***	-
Station 258			
May	16.2-57.8	9.55-28.7	-
August	64.4-155.8	15.2-32.3	92.2-356.2

*For peeper samples

**Measurement from sand layer in core

***Unusually high measurement at station 4 (this might reflect high organic loading from nearby wastewater effluent); next highest value was 43.4 mL/L

Table 12a. Sediment interstitial water dissolved organic carbon data for Lake Erie, Cleveland Harbor and Hamilton Harbour. Concentrations are given in mg carbon per liter of interstitial water.

Station	Core Designation*	Core Length Analyzed (cm)	Number of Samples	Mean DOC (Std. Dev.) (mg/L)	Range DOC (mg/L)
Western Basin	WB08802	51.5	11	17.8(3.7)	12.0 - 23.0
	WB08803	57	21	15.1(4.2)	10.0 - 23.0
Islands Area	IA10792	60	24	8.3(3.9)	2.3 - 16.3
Central Basin 83	8310792	50	15	5.8(3.4)	2.0 - 14.0
Central Basin A-1	A106792**	61	32	43.7(6.1)	28.9 - 55.4
A-1	A108792	75	17	10.8(3.2)	5.3 - 15.0
C-11	A108804	65	13	15.3(3.3)	12.0 - 23.0
Eastern Basin	EB06801	55	11	19.2(7.9)	8.1 - 32.0
	EB06803	67	21	21.7(4.8)	15.3 - 31.7
Cleveland Harbor	CH08792	70	38	30.5(8.5)	11.0 - 48.0
	CH08793	43	20	25.4(8.1)	16.0 - 43.0
	CH07802	71	10	32.8(5.3)	26.0 - 40.0
Hamilton Harbour 258	H207792	68	37	39.6(15.5)	21.0 - 79.4
	H205801	71	20	37.5(6.7)	21.3 - 48.0
	H208802	60.5	11	32.8(5.3)	24.0 - 53.0
Hamilton Harbour 4	H407792	67	32	91.3(19.9)	32.0 - 257.0
	H405801	12***	12	36.0(9.97)	26.0 - 58.5

*Core designation: station, month, year, core number

**Unacidified interstitial water

***Sand layer identified at 12cm depth in sediments

Table 12b. Interstitial water dissolved total carbon (DTC), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) for selected cores from Lake Erie, Cleveland Harbor and Hamilton Harbour. Concentrations are given in mg carbon per liter of interstitial water.

Station	Core Designation	Length of Core Analyzed (cm)	No. of Samples	Mean Concentration DTC (std. dev.)	Range	Mean Concentration DOC (std.dev.)	Range	Mean Concentration DIC (std.dev.)	Range
Western Basin	WB08802	51.5	11	42.9(8.70)	30.0-53.0	17.8(3.7)	12.0-23.0	25.1(6.63)	13.0-34.0
Eastern Basin	EB06803	57.5	21	59.3(5.42)	52.5-73.5	21.7(4.8)	15.3-31.7	37.5(7.39)	22.2-50.0
Central Basin C-11	A108804	51.5	13	21.9(6.47)	13.0-33.0	15.3(3.3)	12.0-23.0	6.83(5.56)	1.0-18.0
Cleveland Harbor	CH07802	51.0	11	60.8(12.3)	46.0-82.0	32.8(5.3)	26.0-40.0	25.9(13.5)	9.0-48.0
Hamilton Harbour 258	H208802	49.5	11	80.2(15.5)	54.0-99.0	32.8(5.3)	24.0-53.0	40.3(7.16)	30.0-53.0

Table 13. Purgeable organic compounds (μg/L) determined in sediment interstitial water from Lake Erie and Hamilton Harbour. Concentrations were corrected for background.

Minutes*	Component	Hamilton Harbour Station 258 FRN 11935	Lake Erie Station C-11 11936
6.4	Dichlorodifluoromethane	--	78**
10	Dichloromethane	163	60
15.1	Trichloromethane (Chloroform)	--	18
21.3	Benzene	3	--
22.8	Hexane (T) (m/e 57,41,56,86)	≃30***	≃30***
27.4	Toluene	2	1
30.1	Ethylbenzene	4	1
31.2	Silicone	+	+
33.4	Unknown (m/e 91,106,57,134) ++	2	--

* Approximate retention time

** Probable contaminant from leak-checking the GC/MS system

*** Standard not present for quantitation

\+ Present in all samples; possibly due to chromatographic system

++ Probably trialkylbenzene

(T) = Tentative identification; not confirmed with a standard
Internal standards, bromochloromethane and 1,4-dichlorobutane, were present at 400 μg/L concentrations.

Table 14. Purgeable organic compounds (µg/L) determined in sediment interstitial water from Lake Erie and Hamilton Harbour. Concentrations were corrected for background.

			Lake Erie Station C-11		Hamilton Harbour Station 258	
			(Surface)	(Bottom)	(Surface)	(Bottom)**
Minutes*	Component	FRN	12370	12371	12372	12372
10.2	methylene chloride		33	11	ND	ND
15.1	chloroform		$14.6x10^2$	$7.1x10^2$	2.8	14
21.2	benzene***		0.9	ND	0.8	1.0
27.3	toluene***		1.0	1.7	ND	ND
30.0	ethylbenzene		ND	ND	ND	0.9
32.9	xylene+ (1)		ND	ND	ND	~1
33.2	xylene+ (1)		ND	ND	~1	~2
35.5	indan or methylstyrene+(2)		ND	ND	~4	~33
36.1	C_3 - benzene+ (3)		ND	ND	ND	~2
40 plus	C_4 - benzene+ (4)		ND	ND	ND	?

*Approximate retention time

**Surface = 0- 25 cm sediment section; Bottom = 25 -50 cm or deeper sediment section

***Possibly a contaminant of the analytical system; background level was approximately ½ of the value before correction

+Tentative identification and quantification in absence of authentic standard; quantitation based on major ion, assuming same relative response as for the average of the major ion responses in toluene and ethylbenzene

(1) Major masses: 91, 106
(2) Major masses: 117, 118, 115
(3) Major masses: 105, 120, 50
(4) Major masses: 119, 134

ND = Not detected where detection limit in general was 1-5 µg/L

Table 15. Relative amounts of alkanes present in Lake Erie Station C-11 interstitial water for the 25-50 cm sediment depth

Retention Time (Min.)	Area	Relative Amount	Estimated Amount, μg/L*
28.0	45	0.11	0.5
28.9	202	0.48	2
29.7	352	0.83	4
30.6	422	1.00	5
31.4	335	0.79	4
32.5	339	0.80	4

* The estimated concentration in the original sediment interstitial water

Table 16. Analysis of base-neutral mass spectral data from the HH-258 station chromatogram (see Figures 20 and 21). Mass spectra of unknown compounds are given in Appendix B.

Retention Time (Min.)			
Major Peaks*	Minor Peaks**	Compound (major masses in parentheses)	Concentration µg/L in original water***
	12.3	Methylnaphthalene$^{@@@}$	1.6^{+}
15.2		Alkane (57,71,85)	8^{++}
	15.6	Acenaphthene	3.7
15.9		Alkane (71,57,85)	18^{++}
16.4		Unknown (97,84,69)	
16.9		Unknown (X) (181,166,165,196)	12^{+++}
17.2		Alkane (71,57,85)	16^{++}
18.0		Unknown (X) (195,165,180)	16^{+++}
18.4		Alkane (71,85,57)	6^{++}
18.6		Unknown (X) (195,180,210)	6^{+++}
18.9		Unknown (143,91,142)	6^{+++}
19.1		Unknown (X) (209,224,179)	
19.5		Unknown (X) (209,224,71)	
20.2		Anthracene/phenanthrene$^{@}$	13
20.6		Unknown (71,85,57)	6^{++}
21.1		Alkane (71,57,85)	8^{++}

* Peaks easily observable by inspection of chromatogram

** Very small peaks or components not apparent as a separate peak

*** Concentrations not followed by a footnote were calculated relative to the Supelco B/N standards.

\+ Concentration of alkylated species were calculated relative to response of nonalkylated parent compound in the Supelco standards

++ Concentration estimated based on area of m/e 71 in the unknown relative to m/e 164 in the biphenyl-d_{10} internal standard

+++ Concentration estimated based on area of major mass in the unknown relative to m/e 164 on the biphenyl-d_{10} internal standard

@ Not resolved by chromatography or mass spectra; either or both may be present

@@ Mass spectrum too weak for positive identification, but retention time in GC identical to standard compound

@@@ Tentative identification based on mass spectra; not confirmed with authentic sample

(X) See text for discussion of this series of peaks

Table 16. (Continued)

Retention Time (Min.) Major Peaks*	Minor Peaks**	Compound (major masses in parentheses)	Concentration µg/L in original water***
	21.5	Methyl-anthracene/phenanthrene[@,@@@]	3^+
	22.0		
22.2		Alkane (71,57,85)	14^{++}
	23.0	C_2 - anthracene/phenanthrene[@,@@@]	1^+
23.1		Alkane (71,85,57)	15^{++}
	23.9	Fluoranthene	2.6
24.0		Unknown (71,83,69)	
24.2		Alkane (71,57,85)	14^{++}
	24.7	Pyrene	2.2
25.3		Alkane (57,71,85)	12^{++}
26.2		Alkane plus? (71,57,85)	9^{++}
27.1		Alkane plus? (71,57,85)	9^{++}
28.1		Alkane plus? (71,57,85)	6^{++}
	28.3	Chrysene/benzo(a)anthracene[@,@@]	0.9
28.3		Unknown (104,91,184)	
28.9		Unknown (71,57,85)	6^{++}
29.5		Unknown (195,196,220)	5^{+++}
29.9		Unknown (57,71,85)	5^{++}
30.6		Alkane (57,71,85)	5^{++}
31.5		Unknown (191,97,95)	

[*] Peaks easily observable by inspection of chromatogram

[**] Very small peaks or components not apparent as a separate peak

[***] Concentrations not followed by a footnote were calcualted relative to the Supelco B/N standards

[+] Concentration of alkylated species were calculated relative to response of nonalkylated parent compound in the Supelco standards

[++] Concentration estimated based on area of m/e 71 in the unknown relative to m/e 164 in the biphenyl-d_{10} internal standard

[@] Not resolved by chromatography or mass spectra; either or both may be present

[@@] Mass spectrum too weak for positive identification, but retention time in GC identical to standard compound

[@@@] Tentative identification based on mass spectra; not confirmed with authentic sample

(X) See text for discussion of this series of peaks

Table 17. Organic substances determined in the acid extractable (phenolic) fractions of sediment interstitial water from Lake Erie and Hamilton harbour. Concentrations (μg/L) listed below were estimated for original interstitial water from injected extracts.

		Lake Erie C-11			Hamilton Harbour 258		
		(top)	(top)	(bottom)	(bottom)	(blank)	(bottom)
(min)*	Identity**	FRN 12043	12044	12045	12046	12047	12048
10.2	p-cresol	1-5	≤ 1	a	a	N.D.	≤ 1
12.5	***	≤1	a	a	a	a	a
13.7	***	1-5	1-2	0.5-1	≤ 1	≤ 1	1-2
17.1	phthalate^{+}	1-5	1-3	0.5-2	1-5	a	10-25
18.9	dioctyl adipate	N.D.	N.D.	10-25	N.D.	N.D.	N.D.
21.3	bis(2-ethylhexyl) phthalate	N.D.	N.D.	7-15	N.D.	N.D.	N.D.

* Approximate retention time

** Identity based on mass spectra. This was not confirmed by authentic standards

*** Mass spectra too weak for identification

$^{+}$Found also in the Supelco standard at the 1-5 μg/L level; undoubtedly an artifact at that level

N.D. = not detected

a = mass spectra too weak for accurate identification

Table 18. Dissolved organic carbon fractionation of sediment interstitial water by ultrafiltration. Values listed in parentheses below each station are percentages of total DOC in the eluate.

	Dissolved organic carbon (mg/L)	
Surface 0-20 cm sediment section	Lake Erie Station C-11	Hamilton Harbour Station 258
UM2 (1,000 Mol. Wt.)*	0 (0.0)	0 (0.0)
UM 10 (10,000 Mol. Wt.)	0 (0.0)	3.0 (6.1)
UM 20 (20,000 Mol. Wt.)	0 (0.0)	35.0 (70.7)
Retained by UM 20	13 (100.0)	14.5 (29.3)
Total of fractions	13	52.5
DOC before fractionation	13	49.5
Bottom 20-50 cm sediment section		
UM 2 (1,000 Mol. Wt.)*	0 (0.0)	0. (0.0)
UM 10 (10,000 Mol. Wt.)	0 (0.0)	12.5 (19.5)
UM 20 (20,000 Mol. Wt.)	0 (0.0)	34.0 (53.1)
Retained by UM 20	17 (100.0)	30.5 (46.9)
Total of fractions	17	77
DOC before fractionation	17	64

* Molecular weight cutoff of the Diaflo ultrafiltration membrane utilized (Amicon 1980)

Table 19. Sediment percent water and porosity data for Lake Erie, Cleveland Harbor and Hamilton Harbour.

Station	Core Designation	Core Length Analyzed (cm)	No. of Samples	Mean % Water (Std.Dev.)	Range % Water	Mean Porosity (Std. Dev.)	Range Porosity
Western	WB08801	56.5	13	61.4(11.2)	74.77 - 42.00	0.814(0.071)	0.944 - 0.681
Basin	WB08802	51.5	12	64.4(10.7)	87.11 - 45.71	0.792(0.082)	0.881 - 0.644
Islands							
Area	IA10792	59.5	25	49.7(12.1)	75.28 - 34.19	0.702(0.093)	0.884 - 0.565
Central	8307792	47.0	25	62.2(14.3)	98.85 - 42.42	0.796(0.089)	0.995 - 0.648
Basin 83	8310793	45.0	15	46.7(12.1)	72.07 - 32.71	0.677(0.099)	0.866 - 0.549
Central A-1	A107792	99.0	25	80.4(9.31)	98.24 - 67.07	0.909(0.049)	0.993 - 0.836
Basin A-1	A108793	90.5	45	71.9(8.18)	85.40 - 62.29	0.862(0.046)	0.936 - 0.805
A-1	A109793	84.0	24	75.1(7.81)	83.87 - 62.68	0.880(0.044)	0.932 - 0.808
C-11	A108803	51.0	12	73.6(6.59)	83.26 - 65.53	0.876(0.037)	0.925 - 0.826
C-11	A108804	57.0	12	74.4(6.55)	83.66 - 64.95	0.877(0.037)	0.927 - 0.822
Eastern	EB06801	37.5	11	59.9(10.7)	73.75 - 39.92	0.782(0.079)	0.875 - 0.624
Basin	EB06802	50.0	12	60.9(5.06)	69.40 - 54.27	0.794(0.034)	0.850 - 0.748
	EB06803	57.5	22	63.3(6.10)	74.83 - 55.24	0.810(0.040)	0.881 - 0.755
	EB06804	63.0	12	61.4(5.26)	70.39 - 54.08	0.798(0.035)	0.856 - 0.746
Cleveland	CH08792	70.0	35	50.2(5.94)	70.03 - 39.35	0.713(0.046)	0.854 - 0.619
Harbor	CH07801	48.0	12	52.0(3.24)	55.56 - 46.01	0.730(0.026)	0.758 - 0.681
	CH07802	51.0	11	50.5(4.35)	58.51 - 44.16	0.717(0.035)	0.779 - 0.664
Hamilton	H205805	64.0	13	71.7(8.25)	82.71 - 59.74	0.861(0.048)	0.923 - 0.788
Harbour 258	H205806	57.5	23	72.8(10.9)	85.16 - 45.03	0.865(0.069)	0.935 - 0.672
	H208801	80.0	14	66.8(12.1)	81.00 - 38.50	0.832(0.089)	0.914 - 0.610
	H208802	49.5	12	71.3(12.4)	84.00 - 40.03	0.854(0.085)	0.929 - 0.625
Hamilton	H405801	45.0	13	59.7(22.3)	79.71 - 25.67	0.757(0.183)	0.908 - 0.463
Harbour 4	H405802	56.0	12	54.7(23.1)	79.43 - 22.76	0.718(0.193)	0.906 - 0.424
	H405804	13.0	13	61.4(22.2)	79.12 - 22.23	0.767(0.190)	0.904 - 0.417

Table 20. Sediment volatile solids data for Lake Erie, Cleveland Harbor, and Hamilton Harbour. Concentrations are given in percent volatile solids of the sediment expressed on a dry weight basis.

Station	Core Designation	Core length Analyzed (cm)	Number of Samples	Mean (Std.Dev.)	Range
Western Basin	WB08801	38.5	12	7.79(1.49)	4.91 - 9.44
Islands Area	IA10791	52	9	5.05(1.23)	3.45 - 4.78
Central Basin 83	8311781	40	24	2.73(0.80)	1.83 - 4.75
Central Basin C-11	A108803	51	12	9.17(2.21)	6.70 - 12.84
Eastern Basin	EB06802	63	12	6.66(0.89)	5.32 - 8.30
Cleveland Harbor	CH07801	48	11	7.56(0.64)	6.73 - 9.02
Hamilton Harbour 258	H205802 H208802	49.5 64	14 12	13.9(4.14) 13.6(4.72)	9.29 - 20.7 3.77 - 19.8
Hamilton Harbour 4	H405802	56	12	8.81(6.50)	0.87 - 16.6

Table 21. Comparison of sediment pore water methane of Lake Erie's three basins, Cleveland Harbor, and Hamilton Harbour with concentrations for several lakes and other organic rich environments.

Methane Concentration Range (mM)	Comments	Location	Source
0.2-2.3	Concave profile; concentration increase with depth	Western Basin, Lake Erie	Fendinger 1981
0.1-3.3	Concave profile; concentration increase with depth	A-1 and C-11, Central Basin, Lake Erie	Fendinger 1981
0.04-0.4	Little variability with depth	83, Central Basin, Lake Erie	Fendinger 1981
2.7-3.6	Decrease in concentration with depth	Eastern Basin, Lake Erie	Fendinger 1981
1.6-6.1	Variable with depth	Cleveland Harbor	Fendinger 1981
0.3-8.1	Variable with depth	Hamilton Harbour	Fendinger 1981
0.0-0.5	Increase with depth	Lake 227	Rudd & Hamilton 1975
0.0-1.5	Concave profile; increase with depth	Lake 227	Hesslein 1976b
0.0-0.6	Concave profile; increase with depth	An arctic lake	Welch et al. 1980
0-1.1	Decrease in concentration with depth	Ace Lake, Alaska	Reeburgh & Heggie 1977
0-0.5	Increase in concentration with depth	White Oak Estuary, North Carolina	Martens & Goldhaber 1978
0-6.1	Increase in concentration with depth	Chesapeake Bay	Reeburgh 1969
0-2.5	Increase in concentration with depth	Cape Lookout Bight, North Carolina	Martens & Klump 1980
0-0.01	Increase in concentration with depth	Georgia Salt Marsh	Atkinson & Hall 1976

Table 22. Mean Fickian first order diffusive fluxes for dissolved methane calculated from sediment interstitial water concentration gradients (see text) for Lake Erie, Cleveland Harbor and Hamilton Harbour.

Location	Methane flux 10^{-6} moles $m^{-2}day^{-1}$	Method/Description	Depth interval for least squares (cm)	Linear least squares fit*
Lake Erie				
Western Basin	240**	One-dimensional numerical model	3-45	n=11
	540	One core, LSF (least squares fit)	3-33	n=9, r=0.94
	700***	Surface to first measurement	(0-3)	n=2
Central Basin 83	20**	One-dimensional numerical model	2-57	n=10
	70	One core, LSF	2-27	n=6, r=0.74
A-1	150**	One-dimensional numerical model	2-97	n=12
	330	Core next to peeper, LSF	2-32	n=5, r=0.99
	300	Three cores at same station, LSF	2-43	n=12, r=0.95
	1800+	Peeper-surface to CH_4 max, LSF	0-5	n=6, r=0.63
C-11	120**	One-dimensional numerical model	3-45	n=9
	140++	One core, LSF	3-21	n=6, r=0.92
	530+++	Two cores next to each other, LSF	1-8	n=5, r=0.80
Eastern Basin	160**	One-dimensional numerical model	4-51	n=10
	930	One core, LSF	4-16	n=5, r=0.58
	4590***	Surface to first measurement	(0-4)	n=2
Cleveland Harbor	480	One core, LSF	2-14	n=4, r=0.97
Hamilton Harbour				
Station 4 - May	3100***	Ave flux, 2 cores, surface to first data	(0-5, 0-9)	n=2, n=2
Station 258 - May	840	One core, LSF	8-23	n=5, r=0.89
Station 258 - Aug	7480	Two cores at same station, LSF	3-18	n=10, r=0.24
	6270***	Ave flux, 2 cores, surface to first data	(0-3, 0-6)	n=2, n=2

* Number of methane, depth data points for linear least squares regression; the least squares equation was used to calculate $\partial C/\partial z$ in equation 2 (see text)

** For entire core profile using equation 5 (see text)

*** Calculated from the surface (Z=0) to the first measurement of methane (Z=3, 4 cm, etc.); methane at Z=0 was considered zero

\+ Calculated from the surface to the near-surface methane maximum at 5 cm

++ For core A108803 data; this core was obtained 0.5 km away from other two cores

+++ For cores A108801 and A108802 (taken next to each other) calculated from 1 cm below sediment-water interface to the near-surface methane maxima at approximately 8 cm

Table 23a. Mean Fickian first order diffusive fluxes for dissolved carbon dioxide gas (total CO_2) calculated from sediment interstitial water concentration gradients (see text) for Lake Erie, Cleveland Harbor and Hamilton Harbour.

Location	ΣCO_2 flux 10^{-6} moles $m^{-2} day^{-1}$	Method/Description	Depth interval for least squares (cm)	Linear least squares fit*
Lake Erie				
Western Basin	8740**	One cm above surface to first measurement	(+1 to 3.5)	n=2
	6880	One core, LSF (least squares fit)	3.5-6.5	n=2
Central Basin Station C-11	1540**	One cm above surface to first measurement	(+1 to 3)	n=2
Eastern Basin	5400**	One cm above surface to first measurement	(+1 to 2)	n=2
	1800**	One core, LSF, to one cm above surface	2-26	n=6, r=0.77
	820	One core, LSF	2-26	n=6, r=0.77
Cleveland Harbor	5620	One core, LSF	6-18	n=5, r=0.29
	9754**	One cm above surface to first measurement (assume 44.8 mL/L for overlying water)	(+1 to 6)	n=2
Hamilton Harbour				
Station 258	14800***	One cm above surface to first measurement	(+1 to 1.5)	n=2
(August)	4480***	One core, LSF, to one cm above surface	1.5-13.5	n=5, r=0.76
	2020	One core, LSF	1.5-13.5	n=5, r=0.76

[*] Number of total carbon dioxide, depth data points for linear least squares regression; the least squares was used to calculate $\partial C/\partial z$ in equation 2 (see text)

[**] A value of 2 mM/L (44.8 mL/L), the volume weighted Lake Erie central basin hypolimnium average, from Burns and Ross (1972) was assigned as the concentration 1 cm (+1 cm) above the sediment-water interface; other fluxes taken to sediment-water interface, Z=0

[***] A value of 2.13 mM/L (47.8 mL/L) was used for Hamilton Harbour overlying water; this was the average of 130 mg HCO_3^-/L from the Ontario Ministry of Environment, Hamilton Harbour Study 1977, vol. 1 (1981), Table 10, p. c-33, station 258.

Table 23b. The calculated diffusive loss of carbon gases (methane and total carbon dioxide) across the sediment-water interface in Lake Erie as a percentage of present day sedimentation of organic carbon. Values are listed in units of mmole $m^{-2}day^{-1}$.

Location	Organic Carbon Sedimentation*	CH_4-C Gas Loss**	ΣCO_2-C Gas loss	Percent of C budget (%)
Western Basin	38	0.2-0.5	6.9-8.7	19-24
Central Basin Station C-11	23	0.1-0.5 (1.8***)	1.5	7-9 (15***)
Eastern Basin	14	0.2-0.9	0.8-5.4	7-45

[*] C sedimentation rates were taken from Kemp et al. 1976

[**] Flux calculations (Table 22) were not used where methane at Z=0 was considered zero

[***] Calculated flux at station A-1 using peeper data (see Table 22)

Table 24. Gas ebullition and bubble composition from various freshwater and marine environments.

Ebullition Rate (ml m^{-2} day^{-1})	Comments & Gas Composition	Source
10-97	Evasion from two small ponds in Michigan	Baker-Blocker 1977
CH_4 - 245 N_2 - 78	Hamilton Harbour	Chau et al. 1977
	45-75% CH_4, 24-50% N_2; Lake Mendota, Wisconsin	Chen et al. 1972
2,592	95% CH_4, 3% N_2, 2% CO_2; Islands Area, Lake Erie	Howard et al. 1971
	25% N_2, 55% CH_4, 12% H_2, 7% CO_2; silt from Russian Lake	Kuznetsov 1968
	88% CH_4, 11% N_2; Gas collected over bubble tubes in Cape Lookout Bight, North Carolina	Martens 1976
377 ml m^{-2} per low tide	86% CH_4; Cape Lookout Bight, North Carolina	Martens and Klump 1980
46	88-92% CH_4, 1% H_2, 1% CO_2, remainder N_2; Pluss Lake	Ohle 1978
640	92-94% CH_4, 1% H_2, 1-2% CO_2, rest N_2; Hemmelsdorf Lake	Ohle 1978
855	Wintergreen Lake, Michigan	Strayer and Tiedje 1978
158	46% CH_4, 15% CO_2, 39% N_2; Western Basin, Lake Erie	Ward & Frea 1979
1440-2640	63-88% CH_4, 3-5% CO_2, balance composed of N_2; Cleveland Harbor	Ward & Frea 1979

Table 25a. Mean Fickian first order diffusive fluxes for dissolved nitrogen gas calculated from sediment interstitial water concentration gradients (see text) for Lake Erie, Cleveland Harbor and Hamilton Harbour.

Location	Nitrogen flux 10^{-6} moles $m^{-2} day^{-1}$	Method/Description	Depth interval for least squares (cm)	Linear least squares fit*
Lake Erie Western Basin	170	One cm above surface to first measurement	(+1 to 2.9)	n=2
Central Basin Station C-11	420	One core, LSF, to one cm above surface	3-18	n=5, r=0.76
	550**	Same core, LSF, to surface (Z = 0)	3-18	n=5, r=0.76
		Two cores, side by side	1-5	n=3, r=0.99
	1180	To one cm above surface, LSF	(+1 to 5)	n=2
	1790	One of these cores, +1 cm to first measurement	(+1 to 1)	n=2
	1230	Same core, +1 to second measurement	(+1 to 4)	n=2
	1230	Other core, +1 to first measurement	(+1 to 5)	n=2
Eastern Basin	590	One cm above surface to first measurement	(+1 to 4)	n=2
Cleveland Harbor	5250	One cm above surface to first measurement	(+1 to 2)	n=2
Hamilton Harbour Station 4 - May	450	One core, LSF, to one cm above surface	5-20	n=4, r=0.76
	200	Same core, +1 to first measurement	(+1 to 5)	n=2
	1640**	Same core, LSF, flux between 10 and 4 cm	5-20	n=4, r=0.76
	880	Nearby core, +1 to first measurement	(+1 to 9)	n=2
Station 258 - May	330	One core, LSF, to one cm above surface	8-14	n=3, r=0.89
	780**	Same core, LSF, flux between 14 and 7 cm	8-14	n=3, r=0.89
Station 258 - August	230	One cm above surface to first measurement	(+1 to 6)	n=2

* Number of nitrogen, depth data points for linear least squares regression; the least squares was used to calculate $\partial C/\partial z$ in equation 2 (see text)

** With the exception of these calculations all other fluxes were determined using a value of 16.6 mL/L (nitrogen gas saturation at 4°C; Murray et al. 1969), which was assigned as the concentration 1 cm (+1 cm) above the sediment-water interface

Table 25b. The calculated diffusive loss of nitrogen gas across the sediment-water interface in Lake Erie as a percentage of present day sedimentation of organic nitrogen. Values are listed in units of mmole $m^{-2}day^{-1}$.

Location	Nitrogen Sedimentation*	N loss as N_2 gas	Percent of N budget (%)
Western Basin	2.6	0.34	13
Central Basin Station C-11	1.9	0.84-3.6	44-188
Eastern Basin	5.2	1.2	23

*N sedimentation rates were taken from Kemp et al. 1976

Table 26. The significance of denitrification in the annual nitrogen budgets of several lakes (Tirén 1976).

Lake	% of Annual Loading	References
Mendota, U.S.A.	11	Brezonik and Lee 1968
Malaren, Sweden	57	Ahl 1973
Narrviken, Sweden	41-61	Ahlgren 1973
Six shallow Danish lakes	0-54	Anderson 1974
Hald, Denmark	23	Larson 1975
Glenstrup, Denmark	61	Larson 1975
Ramsjan, Sweden	60	Ryding and Forsberg 1976

Table 27. Effective diffusion coefficients (D_i') used for indirect flux calculations at 8°C. Calculated from Wollast and Garrels (1972), Li and Gregory (1972) and Lerman (1979). Coefficients are adjusted for a porosity to tortuosity squared (ϕ/θ^2) = 0.75 ratio. Units are 10^{-6} cm^2 sec^{-1}.

Chemical Constituent	Diffusion Coefficient
Fe^{2+}	3.53
NH_4^+	10.15
Mn^{2+}	3.16
CH_4	7.95

Table 28. Sediment interstitial water data for station A-1 in the central basin of Lake Erie (from Adams, Matisoff and Snodgrass 1982).

PEEPER DATA

Depth (cm)	CH_4 (mM)	NH_4^+ (µM)	Fe^{2+} (µM)
10*		55	
5		79	
2		91	
0	0.36	110	58.7
1	0.54	119	48.0
2	0.51	118	52.8
3	0.13	115	38.3
4	0.79	122	
5	1.05		52.1
6	0.31		54.0
7	0.08	130	52.0
8	0.11		55.9
9	0.38		63.1
10	0.42	157	
12	0.10		62.2
14	0.58		
16	0.38		
18	0.48	289	
20	0.89		58.5

SEDIMENT CORE DATA

Depth Interval (cm)	CH_4 (µM)			NH_4^+ (µM)	Fe^{2+} (µM)
	Aug. 79 Core 1	Aug. 79 Core 2	Oct 79**		
OW*				5.4	
0–2				145	127
1–3			0.31		
2–4	0.25			145	156
4–6				207	197
6–8				145	226
7–9	0.25	0.50			
8–10				187	189
10–13				232	190
11–13			0.76		
16–18			0.99		
17–21				235	195
21–23			1.36		
22–24	0.89				
29–33				250	228
31–33			1.68		
37–39	1.47	1.75			
42–44		1.77			

*Overlying water data and depth above the sediment surface; 0 = sediment-water interface

**Core collected next to the peeper

Table 29. Mean Fickian first order diffusive fluxes calculated from sediment interstitial water concentration gradients. Units are 10^{-6} moles m^{-2} day^{-1} (from Adams, Matisoff and Snodgrass 1982).

	Station A-1		Station 83 (Core Data Only)			
Parameter	Peeper	Core	5-78	6-78	7-78	8-78
Fe^{2+}	179	387	55	0	2	38
NH_4^+	49	1228	403	649	719	602
Mn^{2+}	-	-	-	-	58	49
CH_4	1881	328* (295)	-	-	-	72**

*For core collected in October 1979 next to the peeper; methane flux calculated from composite data for 3 cores collected at the same station in August and October is given in parenthesis

**Sampling date of October 1979

Table 30. Oxygen consumption calculations for station A-1 in the central basin of Lake Erie, September 1979. Using an SOD of 9.4 millimoles m^{-2} day^{-1}, the percentage of oxygen utilization is given in parenthesis. Units are 10^{-6} moles m^{-2} day^{-1} (from Adams, Matisoff and Snodgrass 1982).

Parameter	Peeper	Core	Reductant: oxygen ratio
Fe^{2+}	45 (0.5)	97 (1.0)	1:0.25
NH_4^+	98 (1.0)	2456 (26)	1:2
Mn^{2+}	–	54* (0.6)	1:0.5
CH_4	2822 (30)	492 (5.2)	1:1.5

*For Station 83 (see text)

Table 31. Correlation coefficient matrix for selected parameters for stations in the three major basins of Lake Erie. The surface 5 cm total loaded carbon (Kemp et al. 1976) was included with the other parameters. ^{r}test values were taken from Texas Learning Center (1977).

	DOC	CH_4	STC	Volatile Solids	Total Loaded C	% H_2O	Porosity
DOC	--	0.93^{*}	0.81^{**}	0.67^{+}	0.23	0.64^{+}	0.68^{+}
CH_4		--	0.58	0.53	0.18	0.51	0.57
STC			--	0.91^{*}	0.67^{++}	0.80	0.82
Volatile Solids				--	0.66^{++}	0.96^{*}	0.96^{*}
Total Loaded C					--	0.82^{***}	0.80^{***}
% H_2O						--	0.99

*99% degree of certainty

**Between 95-99% degree of certainty

***Between 90-95% degree of certainty

$^{+}$Between 80-90% degree of certainty

$^{++}$80% degree of certainty

STC = Sediment total carbon

In most cases statistics were conducted on surface sediments only

Table 32. Correlation coefficient matrix for selected parameters for stations from the three major basins of Lake Erie, Cleveland Harbor and Hamilton Harbour. ^{r}test values were taken from Texas Instr. Learning Center (1977).

	DOC	Volatile Solids	CH_4	STC
DOC	--	0.69^{***}	0.75^{**}	0.74^{**}
Volatile Solids		--	0.77^{**}	0.88^{*}
CH_4			--	0.84^{*}
STC				--

*Between 95-99% degree of certainty

**Between 90-95% degree of certainty

***Between 80-90% degree of certainty

STC = Sediment total carbon

In most cases statistics were conducted on surface sediments only

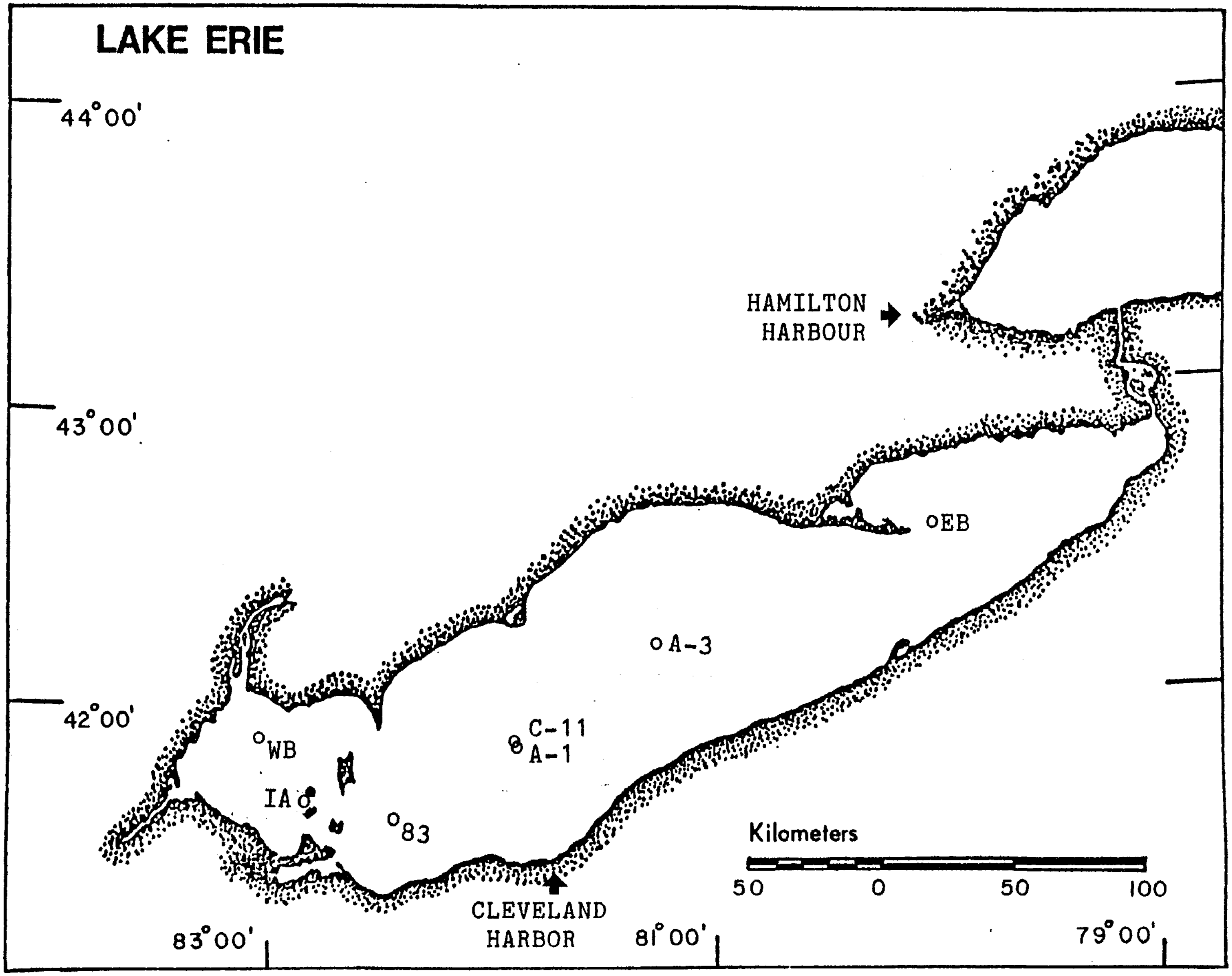


Figure 1. Sampling stations for the three basins of Lake Erie (western = WB, central = 83, A-1, C-11 and A-3, eastern = EB) and the islands area (IA). Locations for Hamilton and Cleveland are also shown.

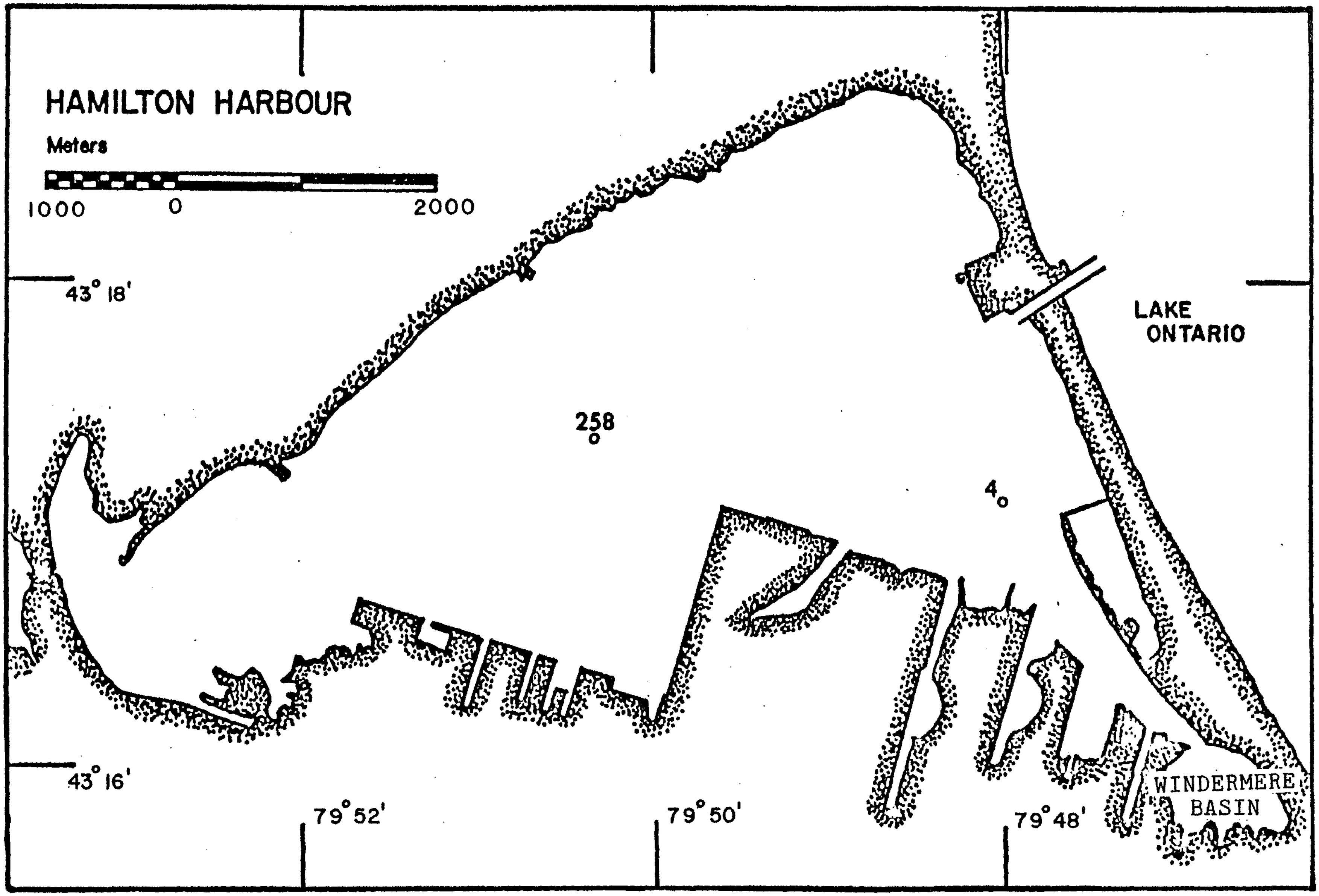


Figure 2. Station locations in Hamilton Harbour at the western end of Lake Ontario. Station 258 is in the center of the harbor while station 4 is located due south of the Burlington Ship Canal and about 2 miles northwest of the Hamilton water Pollution Control Plart in Windermere Basin.

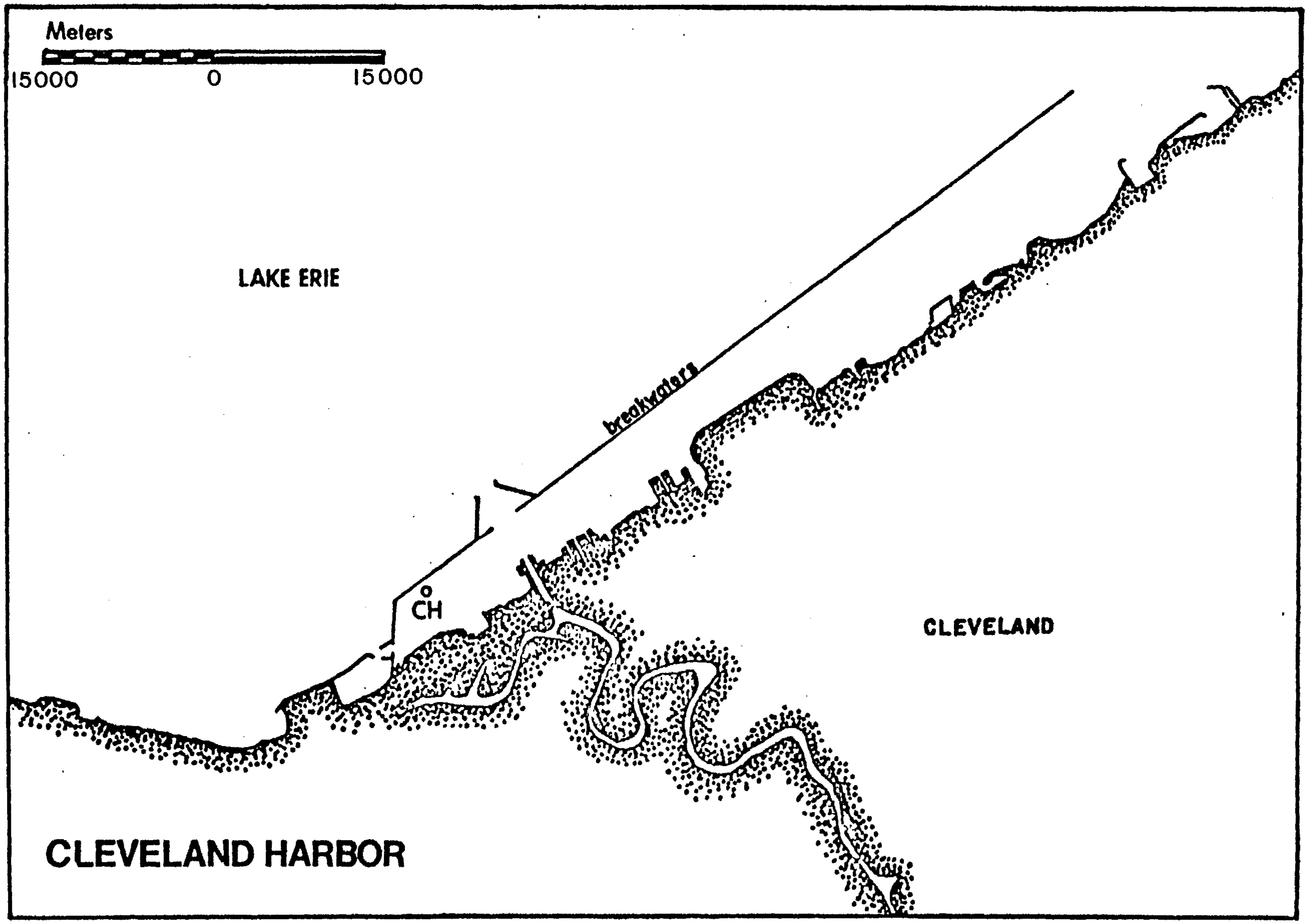


Figure 3. Station location in Cleveland Harbor near the breakwater wall and marker number 28.

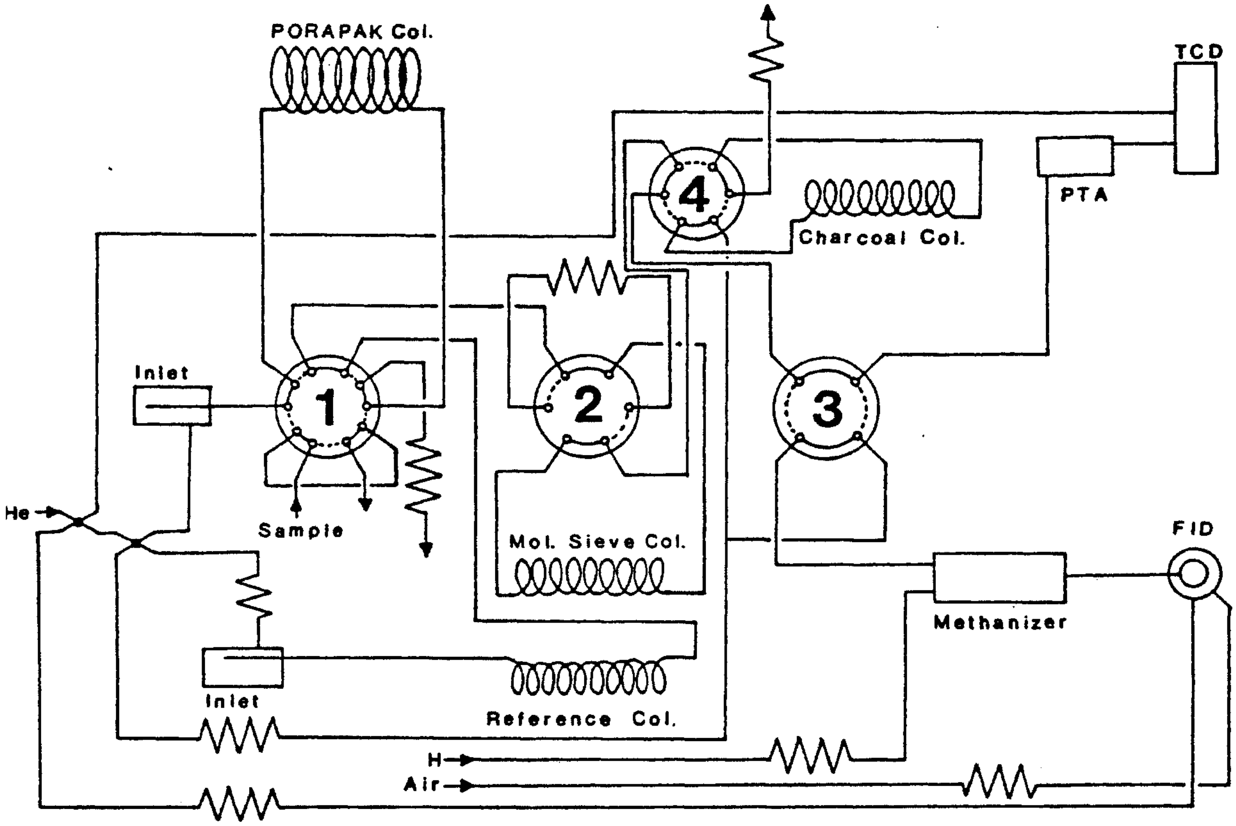


Figure 4. Schematic of the modified Carle 311M gas chromatograph. Clockwise valve positions are represented by dashed lines and counterclockwise positions by solid lines. Flame ionization (FID) and thermoconductivity (TCD) detectors are noted.

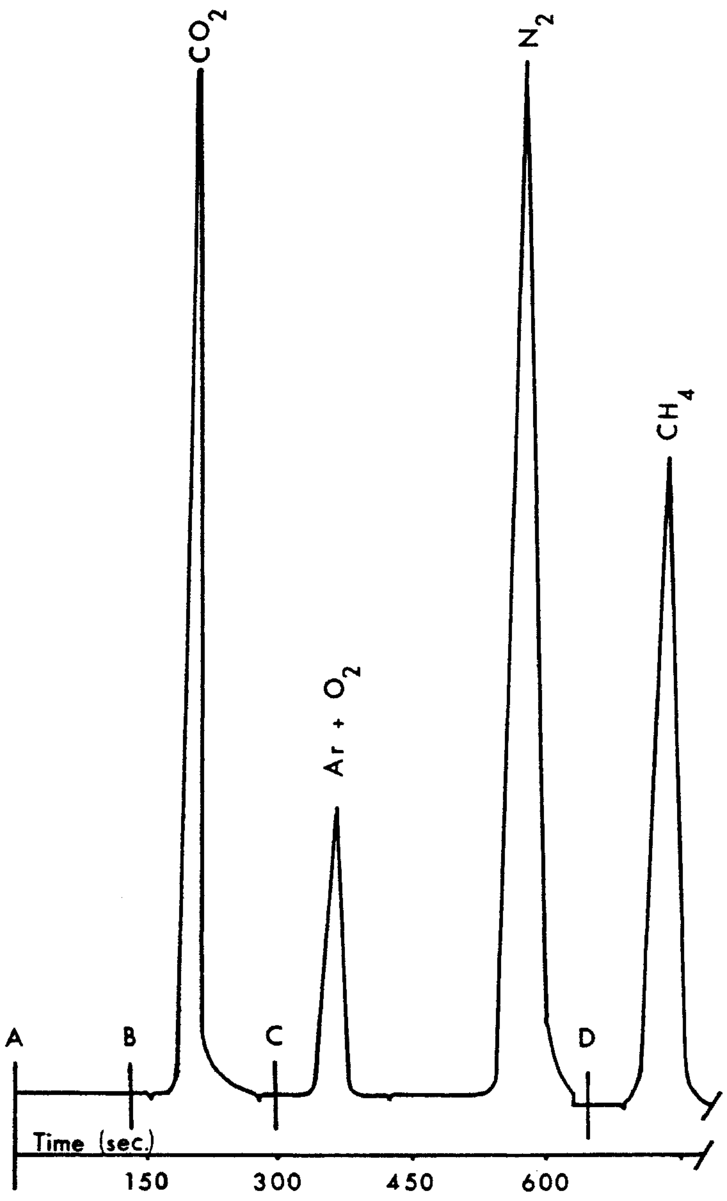


Figure 5. A typical chromatogram for the analysis of $Ar + O_2$, N_2 and CH_4. Equilibrated headspace CO_2 at sediment pH conditions is also measured. Valve switches are shown as A , B, C and D.

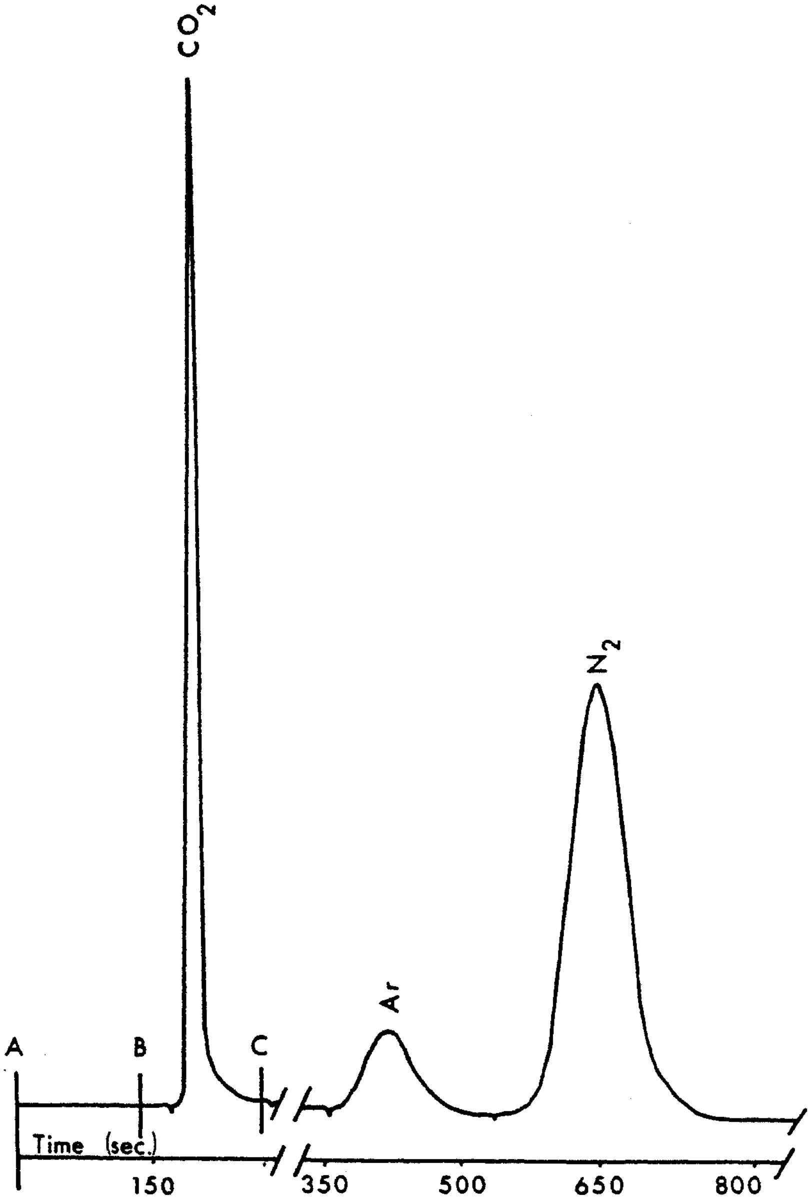


Figure 6. A typical chromatogram with the charcoal column employed to remove headspace oxygen. The difference between Ar and Ar + O_2 (Fig. 5) will provide a measure of headspace oxygen. Valve switches are designated as A, B and C.

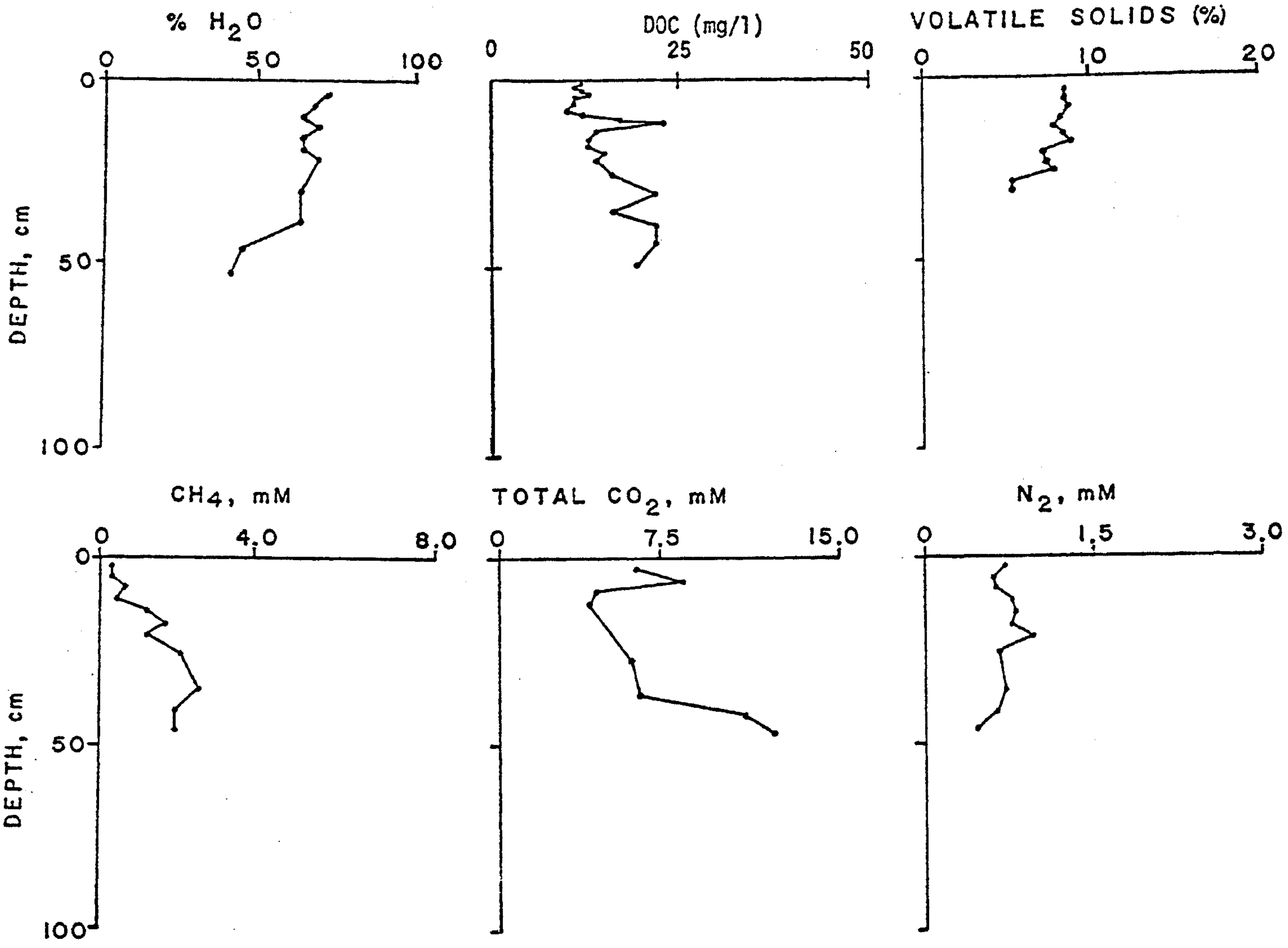


Figure 7. Vertical distributions of sediment interstitial water variables and sediment volatile solids at the western basin station (WB) of Lake Erie.

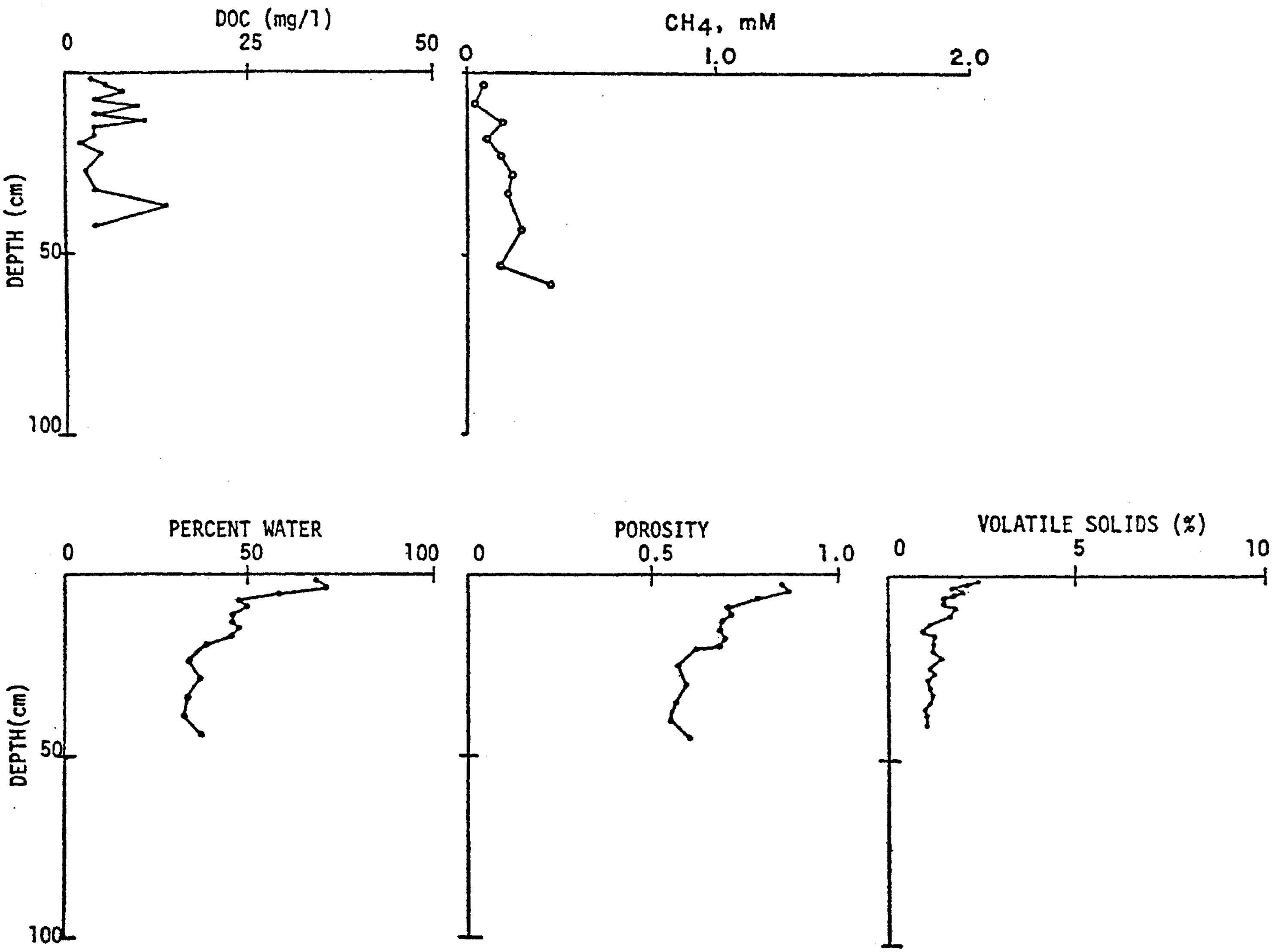


Figure 8. Vertical distributions of sediment interstitial water variables and sediment volatile solids at station 83 in the central basin of Lake Erie. Total CO_2 and N_2 gases were not measured.

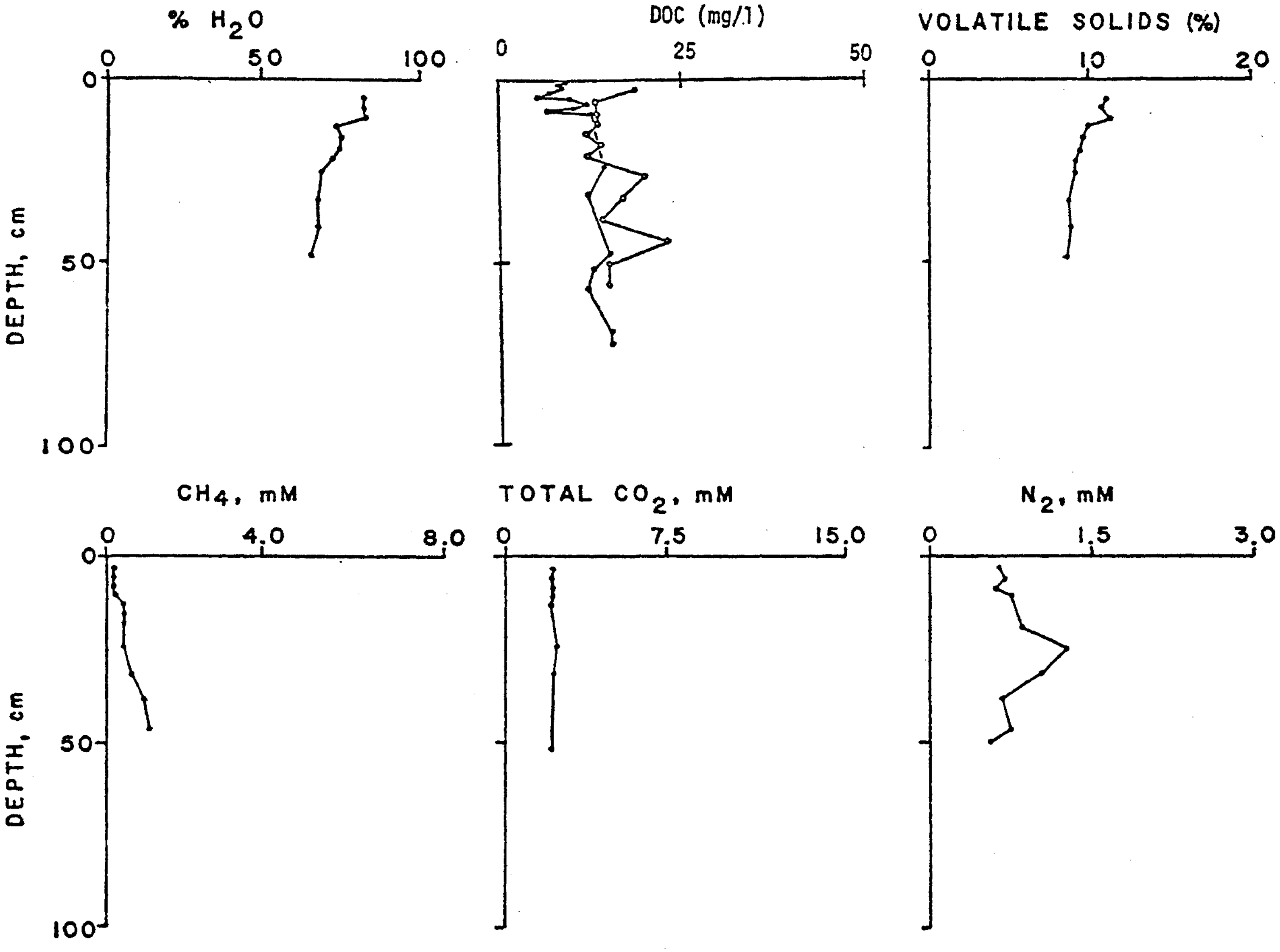


Figure 9. Vertical distributions of sediment interstitial water variables and sediment volatile solids at station C-11 in the central basin of Lake Erie. Dissolved organic carbon from both stations C-11 (o) and A-1 (●) are given.

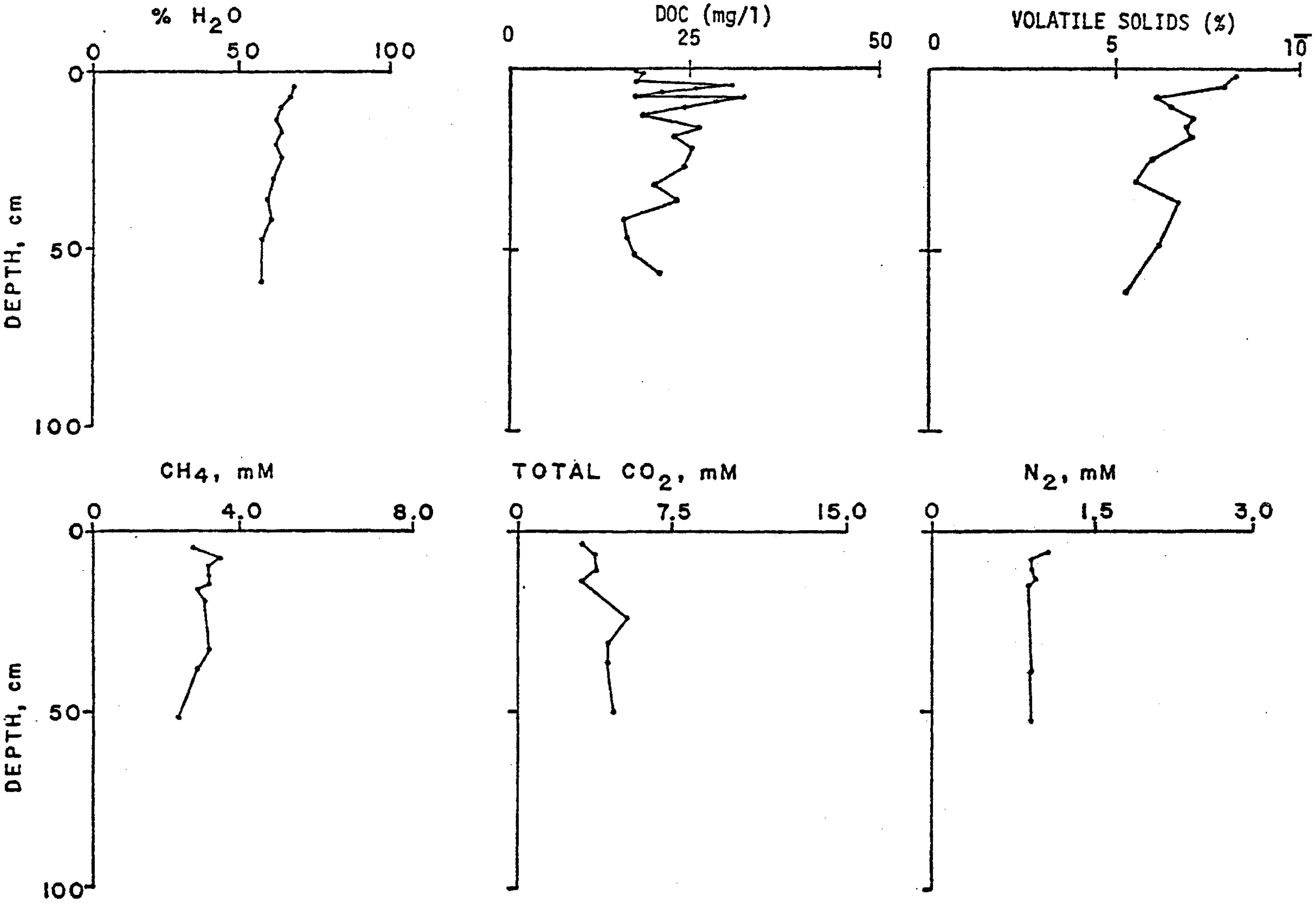


Figure 10. Vertical distributions of sediment interstitial water variables and sediment volatile solids at the eastern basin station (EB) of Lake Erie. This station was the only location sampled with a gravity corer (with exception of IA10792 in the Lake Erie islands area - see Appendices).

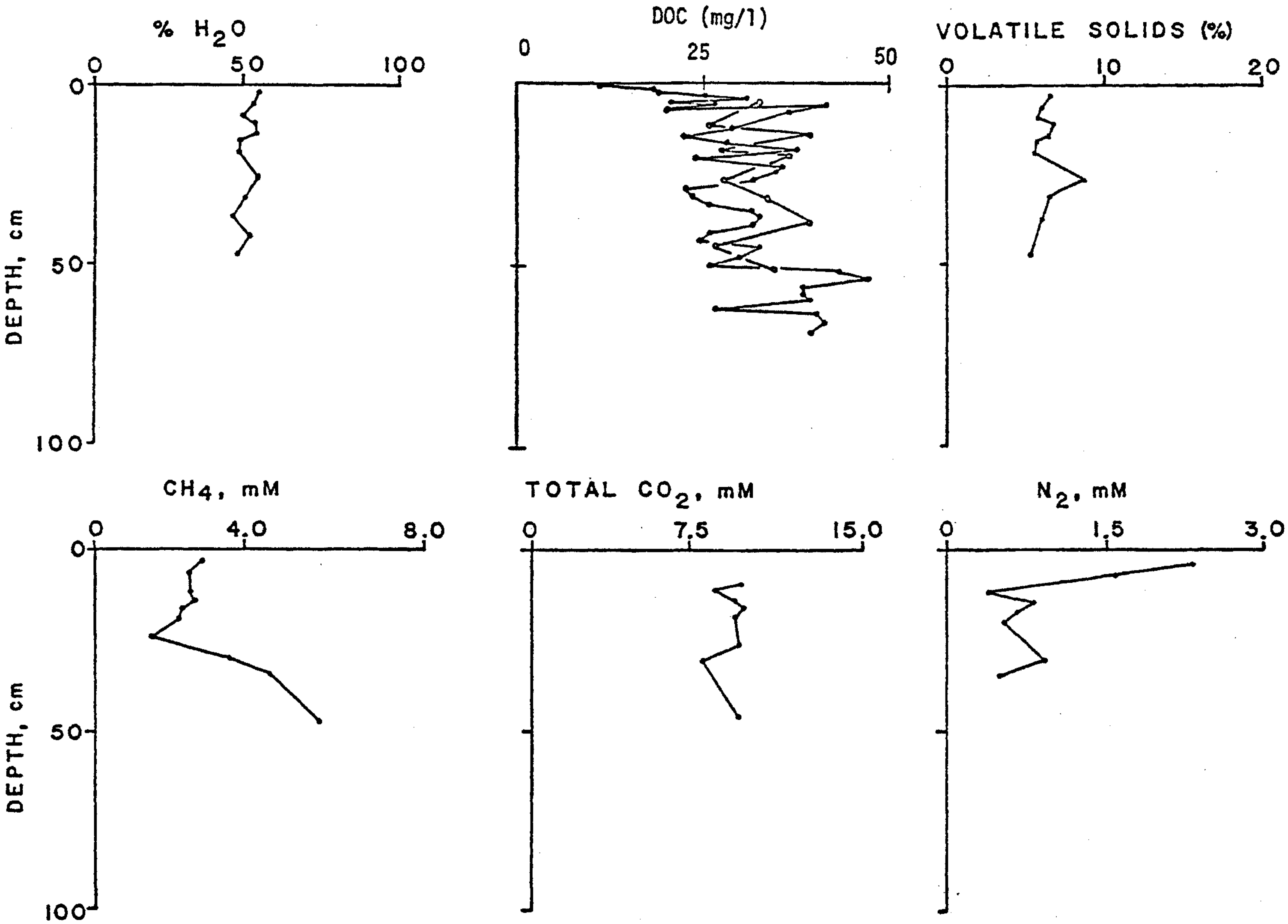


Figure 11. Vertical distributions of sediment interstitial water variables and sediment volatile solids at a station in Cleveland Harbor. Dissolved organic carbon for a 1979 (●) and 1980 (o) core are presented on the same figure.

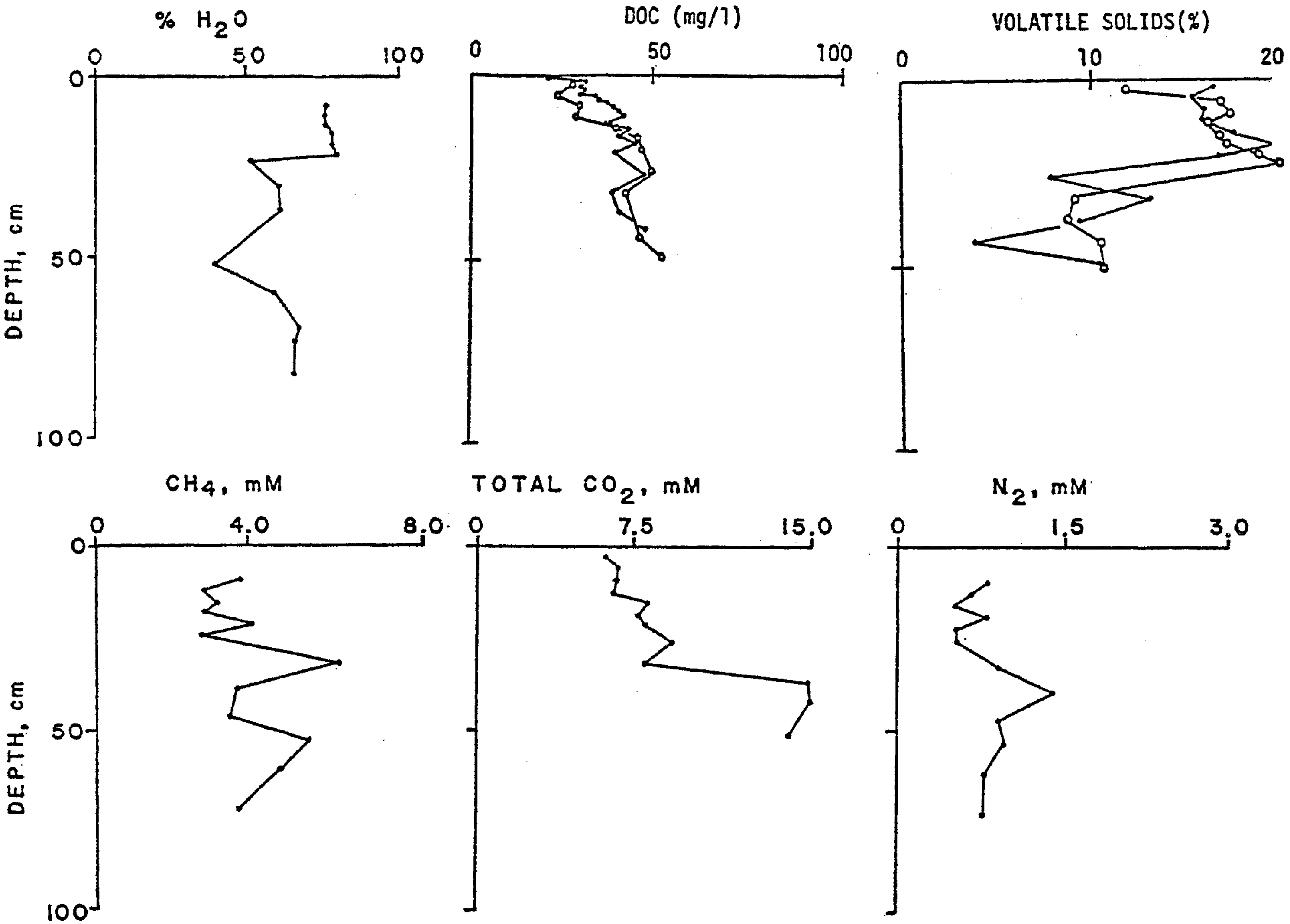


Figure 12. Vertical distributions of sediment interstitial water variables and sediment volatile solids at station 258 in Hamilton Harbour Dissolved organic carbon in cores collected in May (●) and August (o) 1980 are presented along with sediment volatile solids for the same time periods (May = o, August = ●).

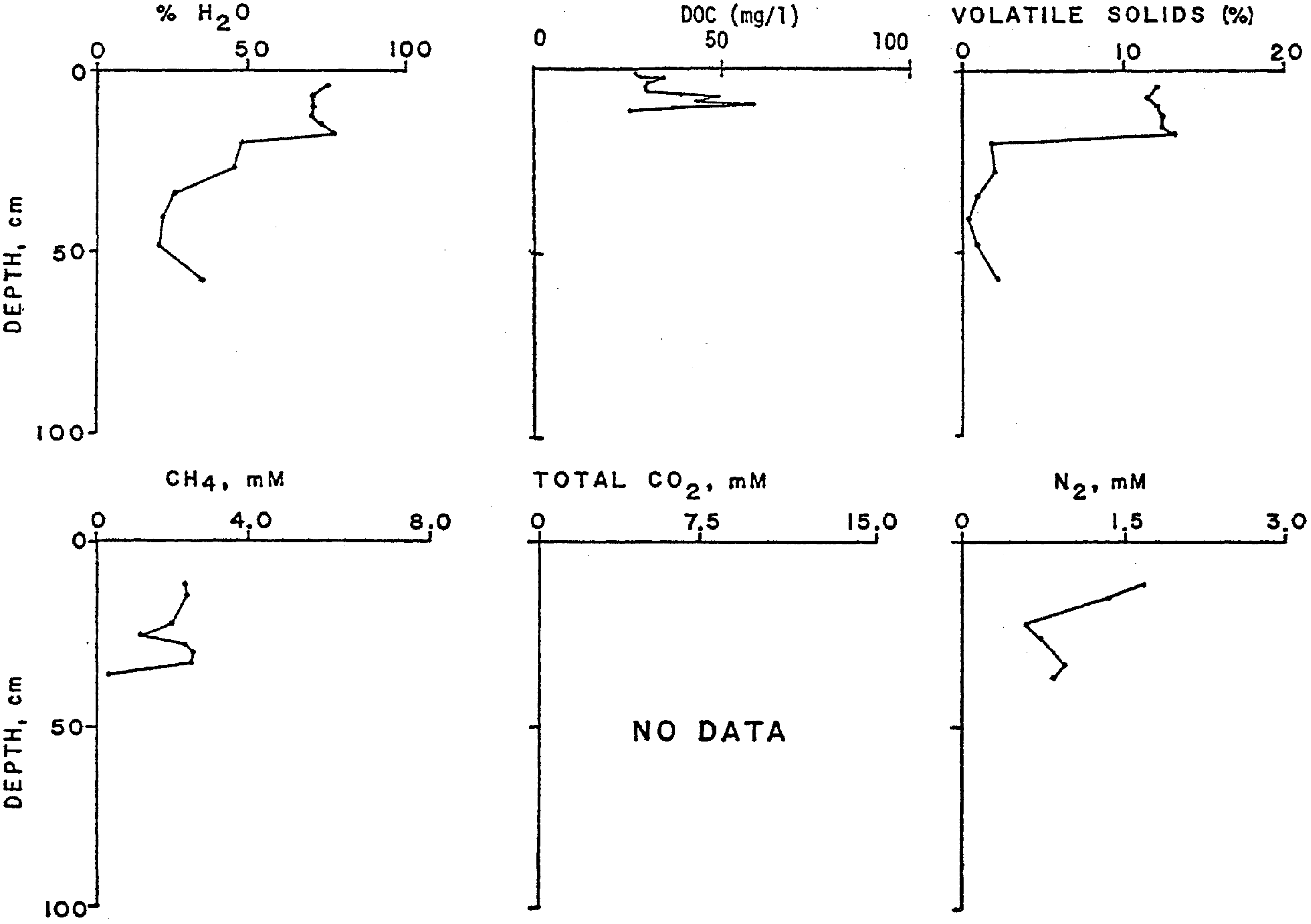


Figure 13. Vertical distributions of sediment interstitial water variables and sediment volatile solids at station 4 in Hamilton Harbour. Variables were measured in different cores collected by SCUBA at the same station; note the depth variability for the occurrence of sand (from 12 cm for DOC core to 30 cm for CH_4 core).

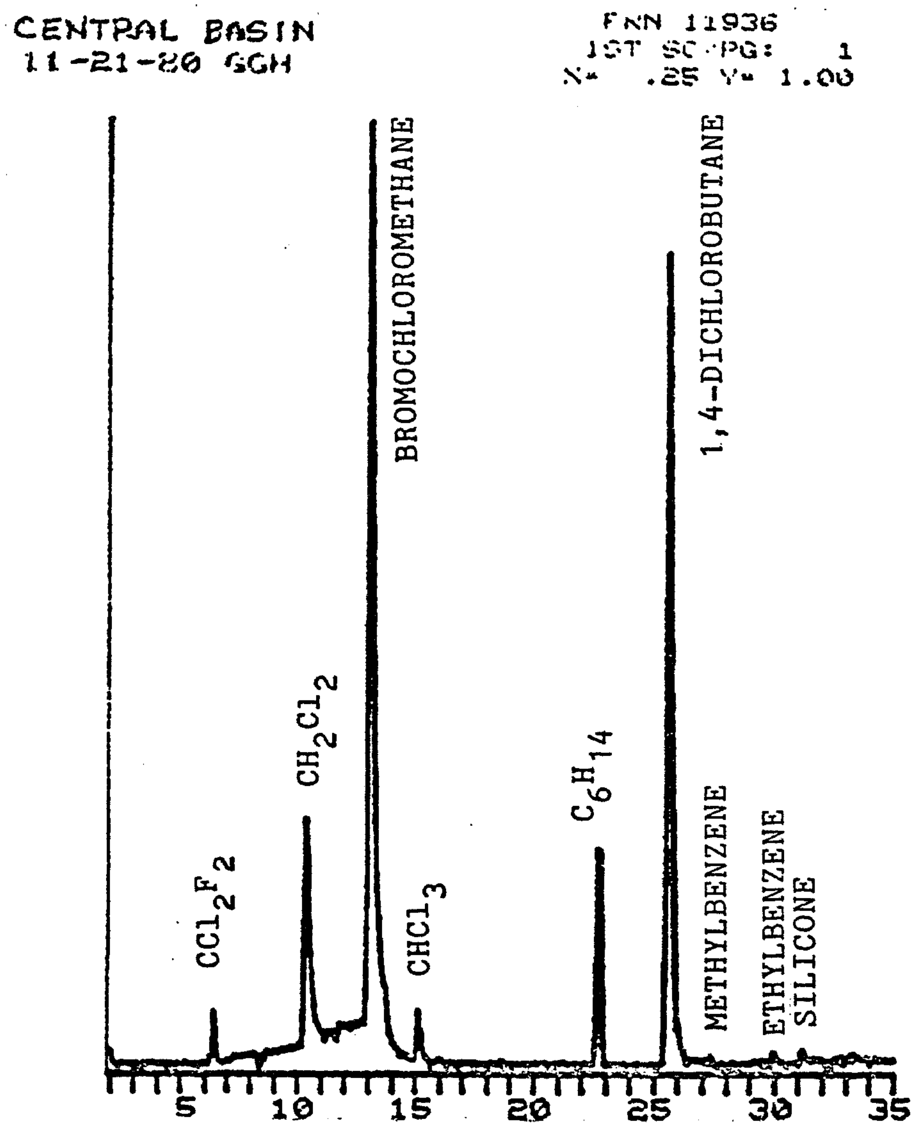
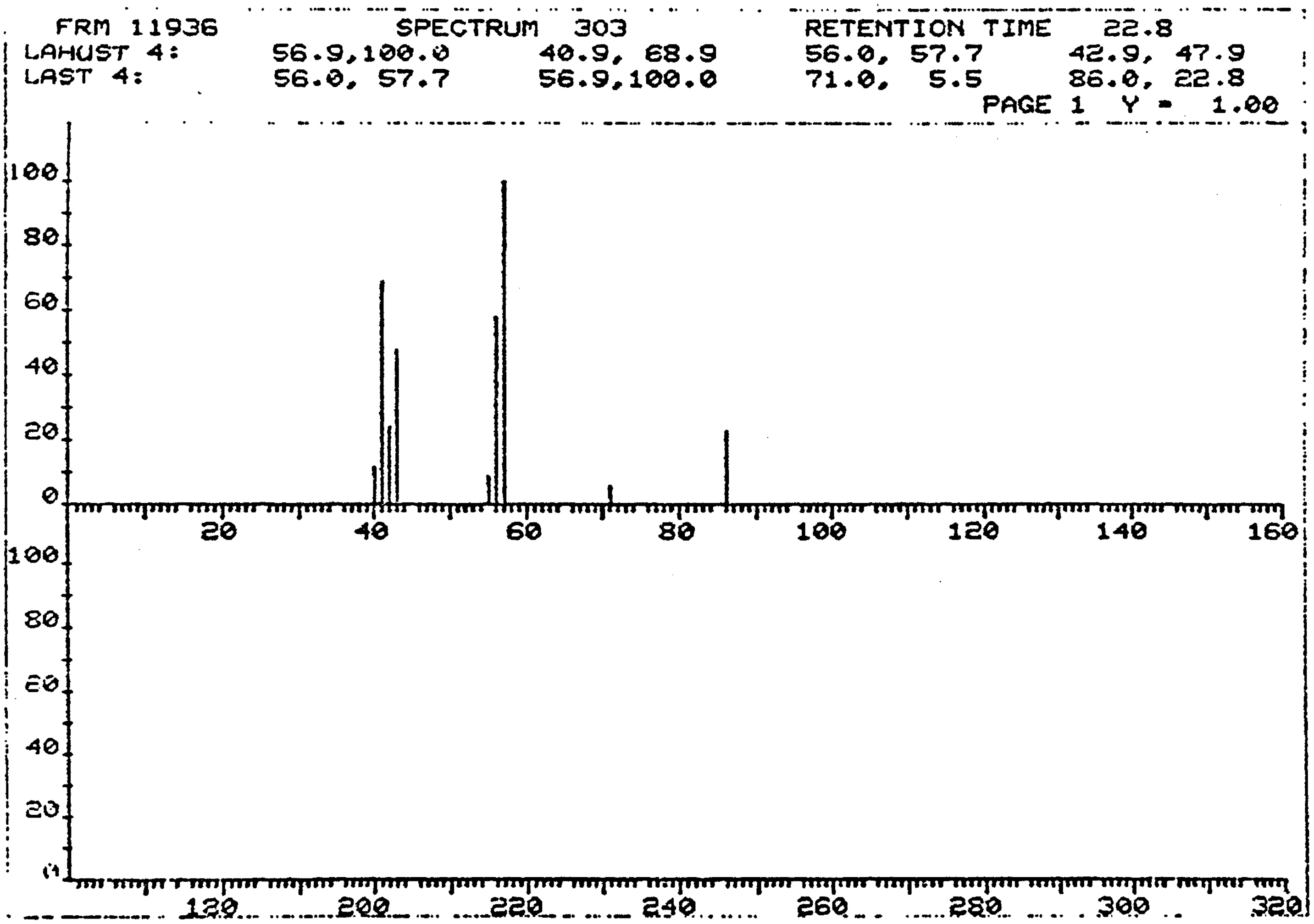
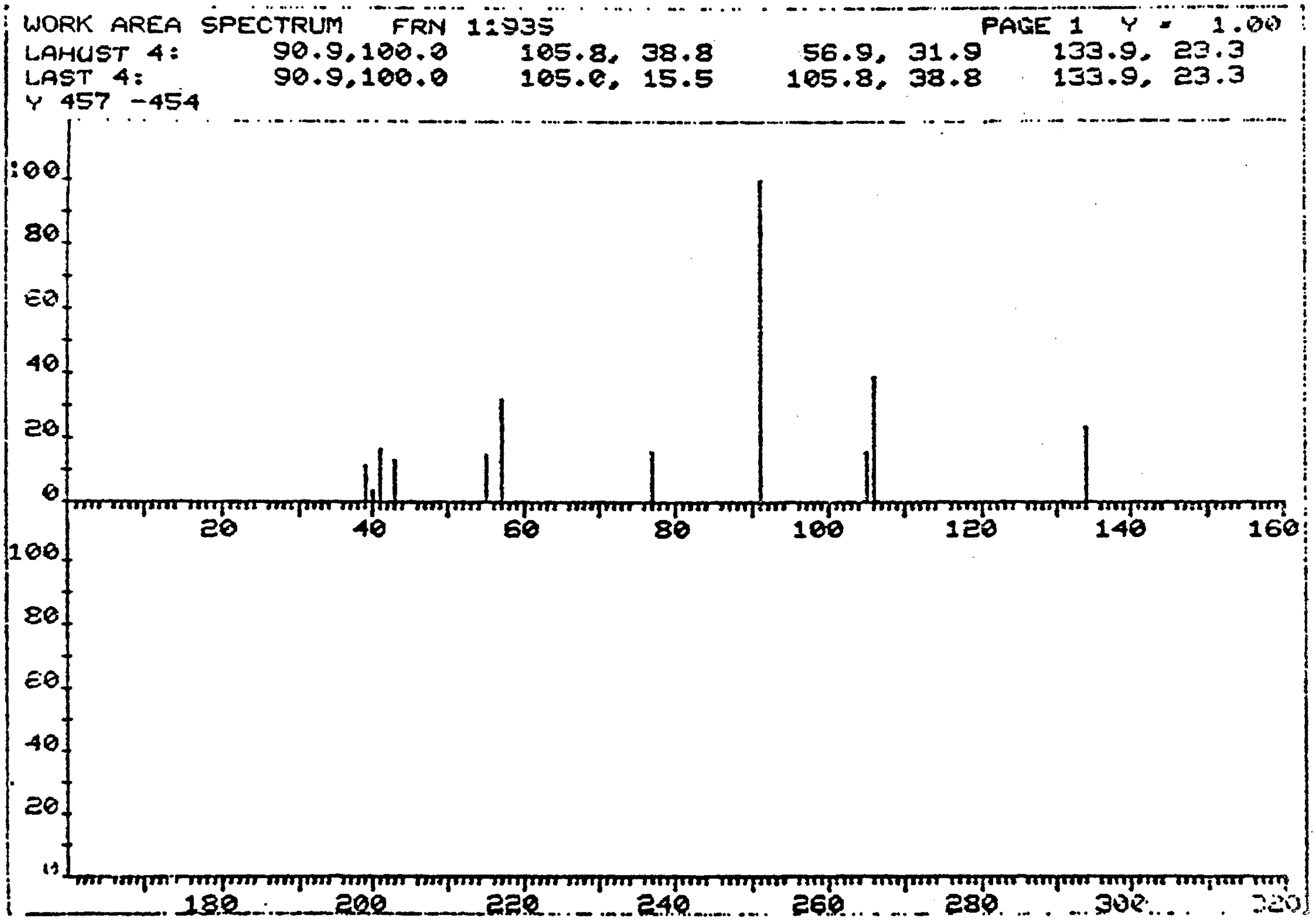


Figure 14. Gas chromatogram of purgeable organic compounds in sediment interstitial water collected from station C-11 in the central basin of Lake Erie. Sediment was accidentally frozen before removal of the interstitial water for analysis.



```
FRM 11936             SPECTRUM  303           RETENTION TIME   22.8
LAHUST 4:    56.9,100.0      40.9, 68.9      56.0, 57.7      42.9, 47.9
LAST 4:      56.0, 57.7      56.9,100.0      71.0,  5.5      86.0, 22.8
                                                        PAGE 1  Y =  1.00
```

Figure 15. Mass spectrum of a purgeable organic compound eluting at 22.8 minutes tentatively identified as hexane. This sample was collected from sediment interstitial water at station C-11 in the central basin of Lake Erie. (Identification number FRN 11936)



```
WORK AREA SPECTRUM   FRN 11935                              PAGE 1  Y =  1.00
LAHUST 4:       90.9,100.0     105.8, 38.8     56.9, 31.9     133.9, 23.3
LAST 4:         90.9,100.0     105.0, 15.5    105.8, 38.8     133.9, 23.3
Y 457 -454
```

Figure 16. Mass spectrum of a purgeable organic compound eluting at 33.4 minutes tentatively identified as a C_3-benzene. This sample was collected from sediment interstitial water at station 258 in Hamilton Harbour. (Identification number FRN 11935)

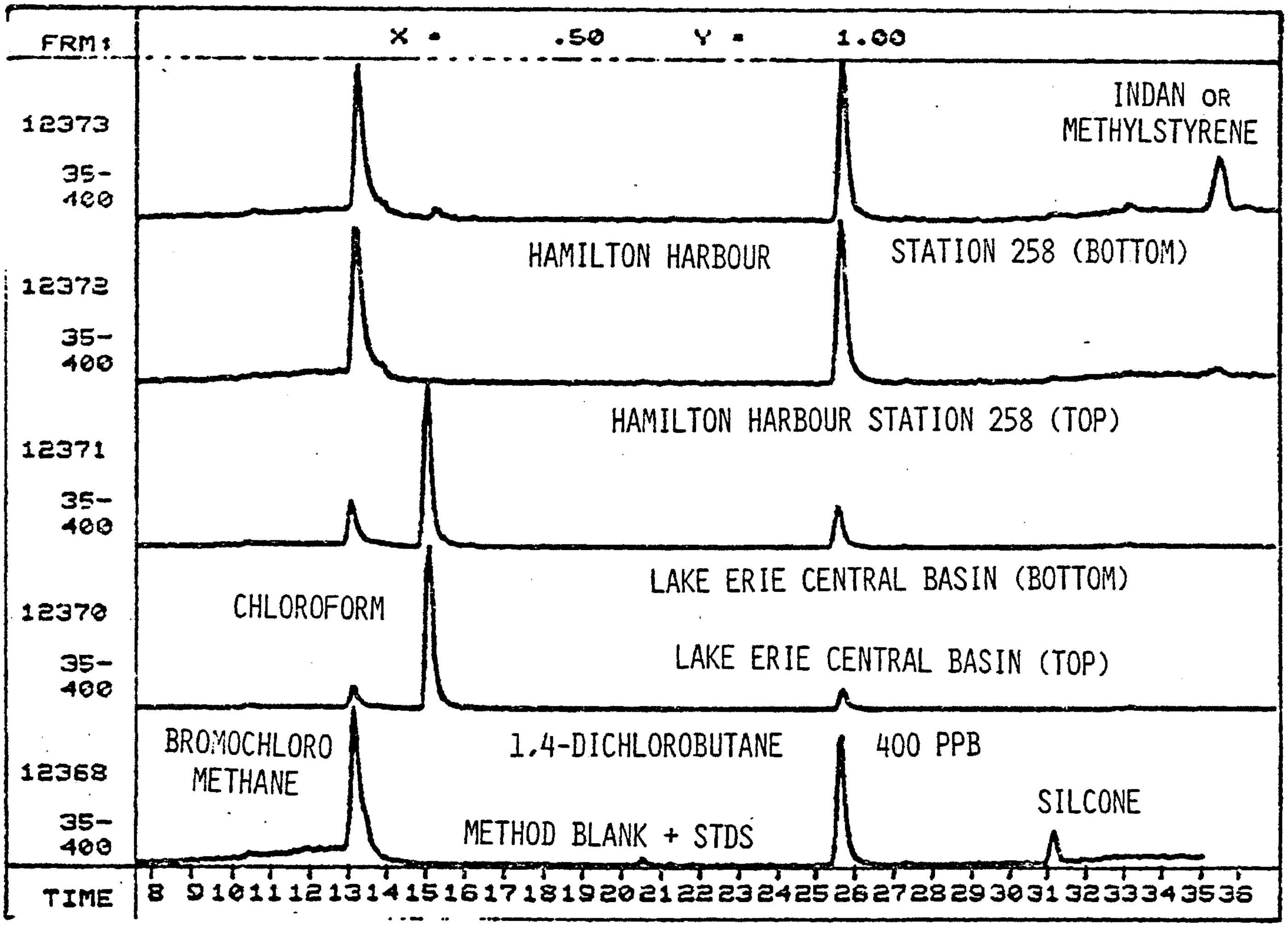


Figure 17. Comparison of chromatograms for the purgeable organic analysis of sediment interstitial water collected from stations C-11 in the central basin of Lake Erie and 258 in Hamilton Harbour. Sediment depth ranges are designated as TOP (0-25 cm) and BOTTOM (25 to about 50 cm). Each chromatogram was normalized to its largest peak. The bottom chromatogram consisted of a method blank (distilled water) containing $BrClCH_2$ (13.1 min) and $Cl(CH_2)_4Cl$ (25.6 min) at 400 µg/L. Identification codes (FRN numbers) are listed in the left margin.

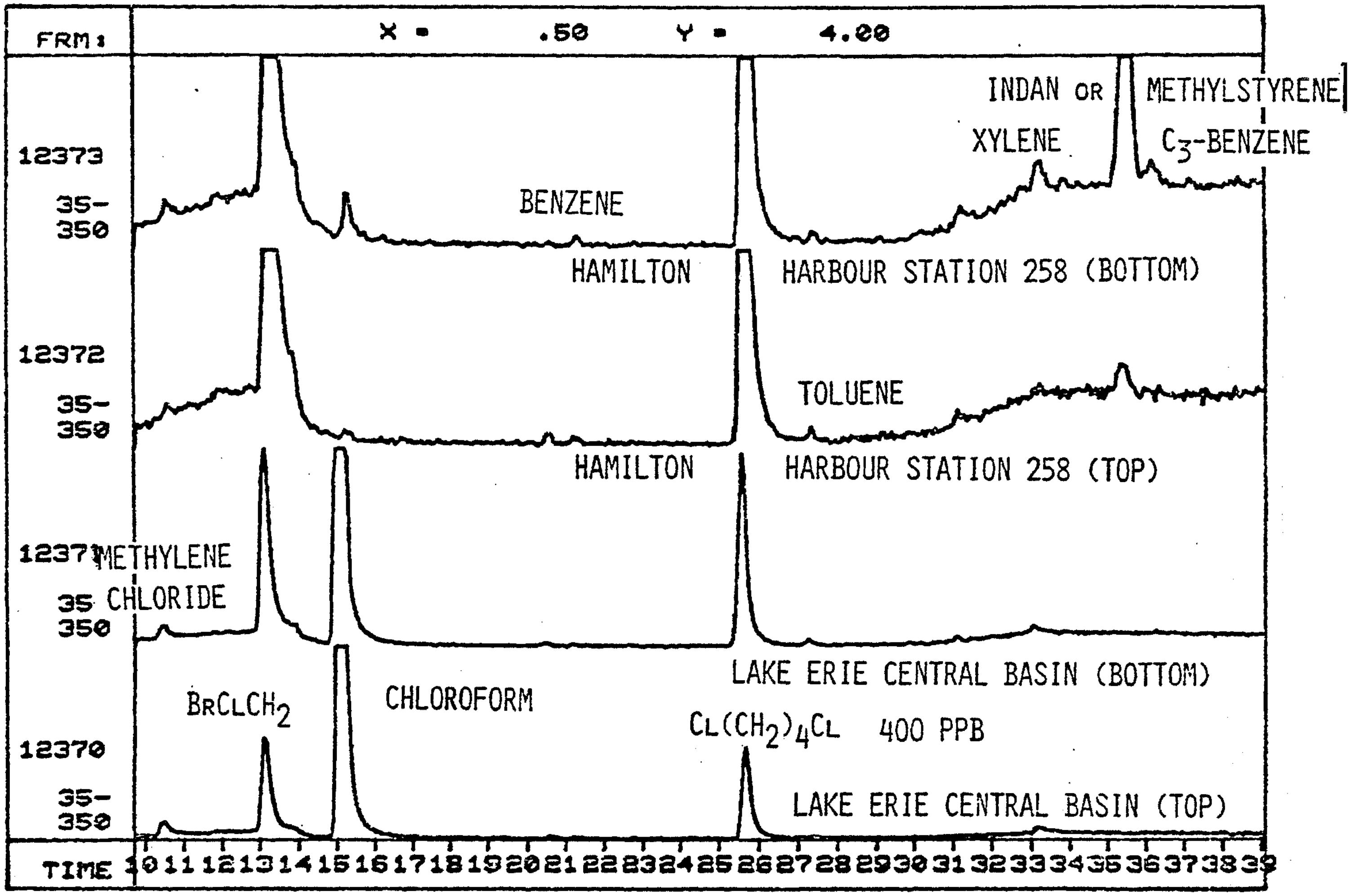
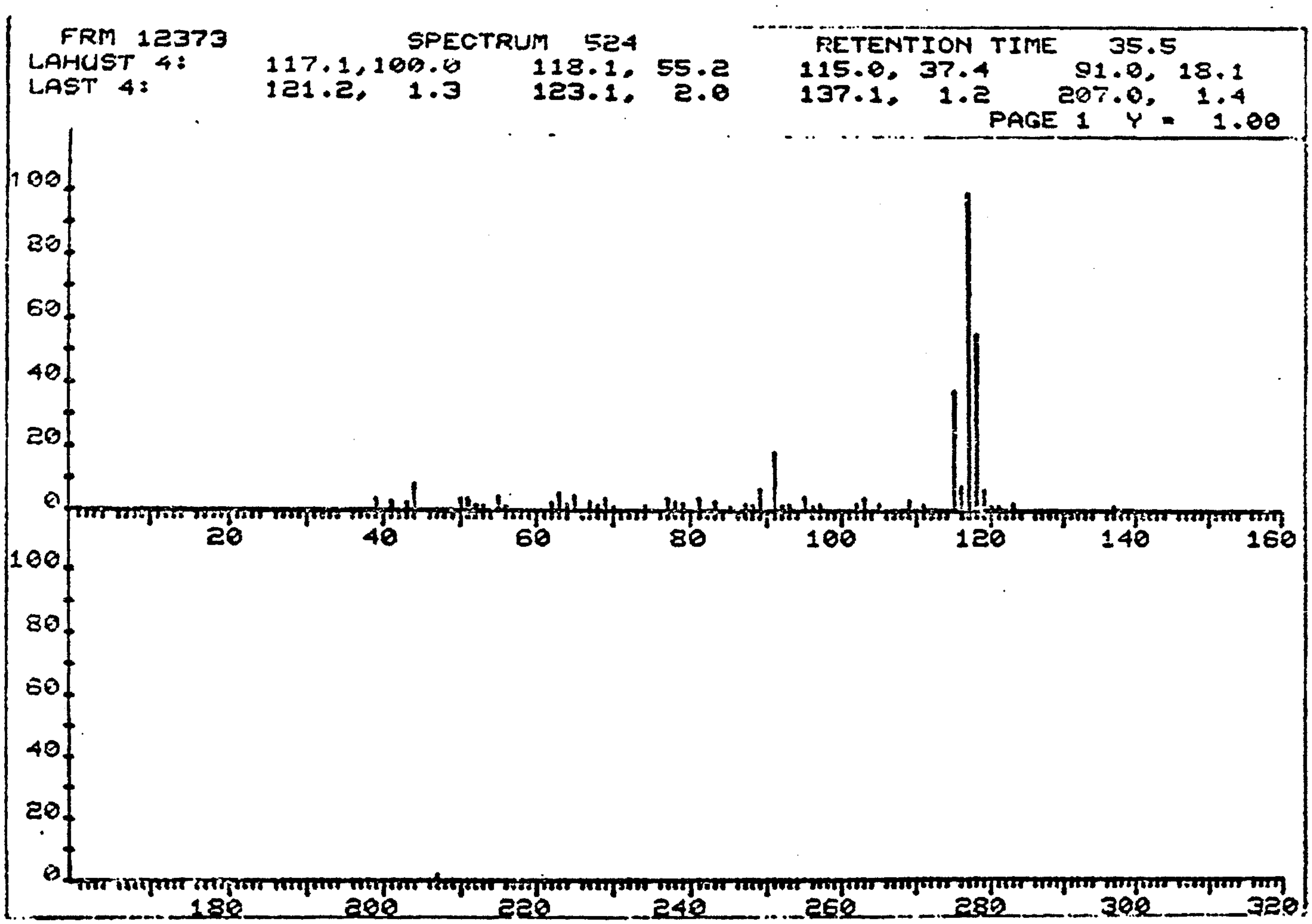


Figure 18. Four times expansion of Figure 17. The method blank was not included.



```
 FRM 12373              SPECTRUM  524            RETENTION TIME   35.5
LAHUST 4:     117.1,100.0    118.1, 55.2    115.0, 37.4      91.0, 18.1
LAST 4:       121.2,  1.3    123.1,  2.0    137.1,  1.2     207.0,  1.4
                                                       PAGE 1  Y =  1.00
```

Figure 19. Mass spectrum of a purgeable organic compound eluting at 35.5 minutes tentatively identified as indan or methylstyrene. This sample was collected from sediment interstitial water at station 258 (bottom) in Hamilton Harbour. (Identification number FRN 12373)

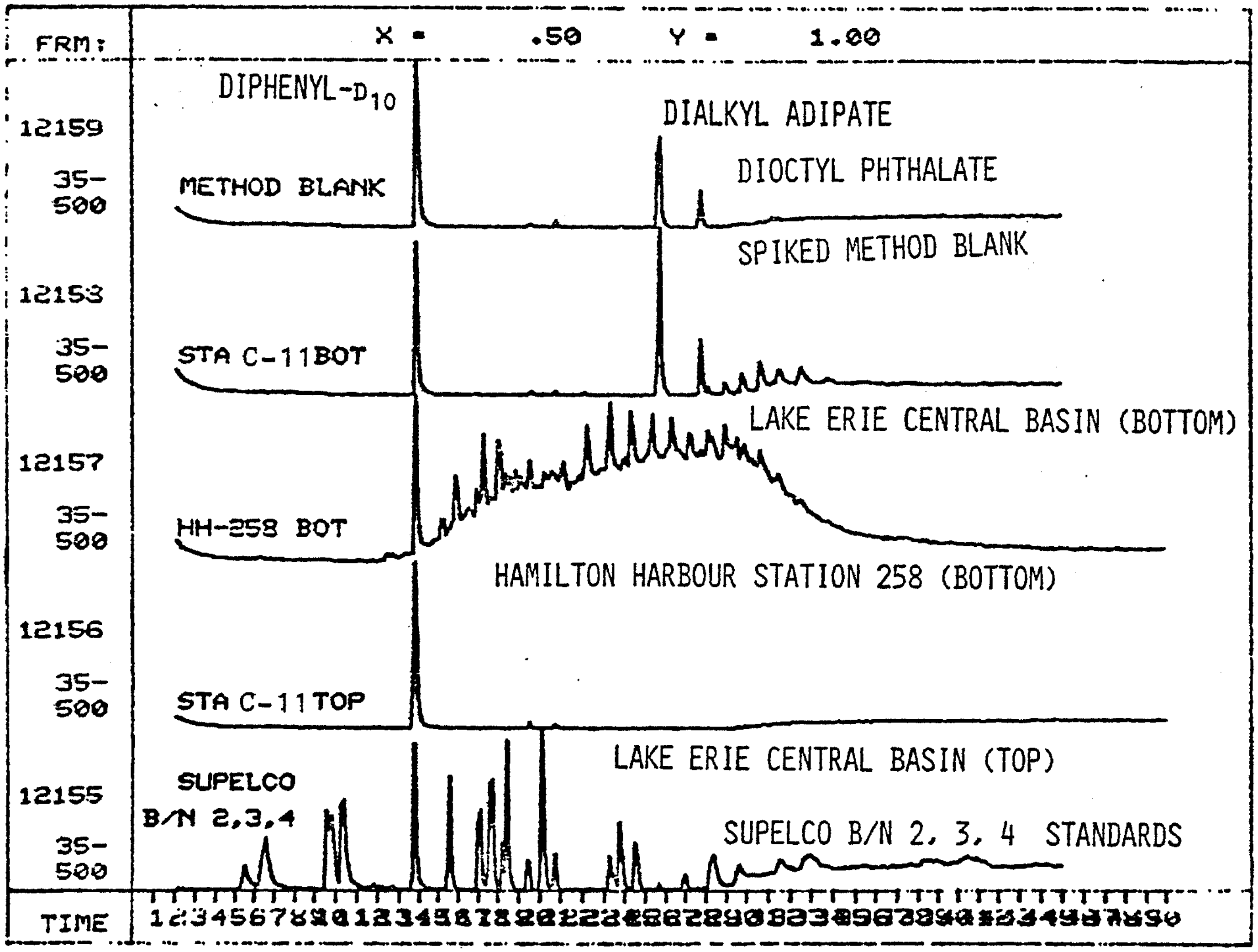


Figure 20. Comparison of chromatograms for the base/neutral methylene chloride extracts of sediment interstitial water collected from stations C-11 in the central basin of Lake Erie and 258 in Hamilton Harbour. Sediment depth ranges are designated as TOP (0-25 cm) and BOTTOM (25 to about 50 cm). Each chromatogram is normalized to its largest peak. Included are a spiked method blank (top fig.) and a Supelco B/N standard mixture. Vertical Y-axes are not comparable because of different concentration volumes and injection volumes: C-11 top x 2.4 = C-11 bottom; HH-258 x 2.0 = C-11 bottom. Identification codes (FRN numbers) are listed in the left margin.

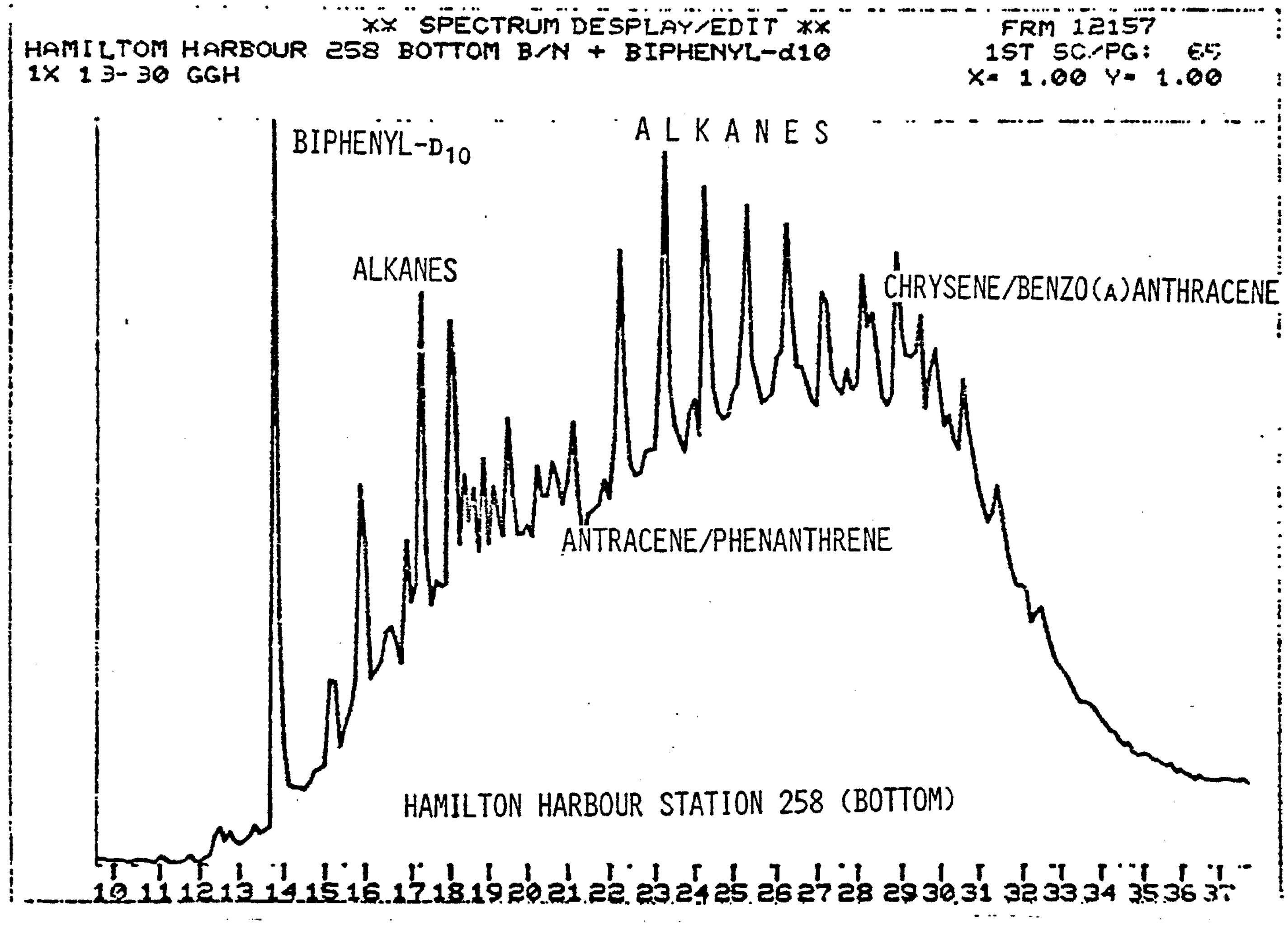


Figure 21. Expanded presentation of the 10-37 minute portion of the Hamilton Harbour base/neutral chromatogram (FRN 12157) seen in Figure 20. Internal standard biphenyl-d_{10} at 14 minutes was 102 µg/L in the original water sample.

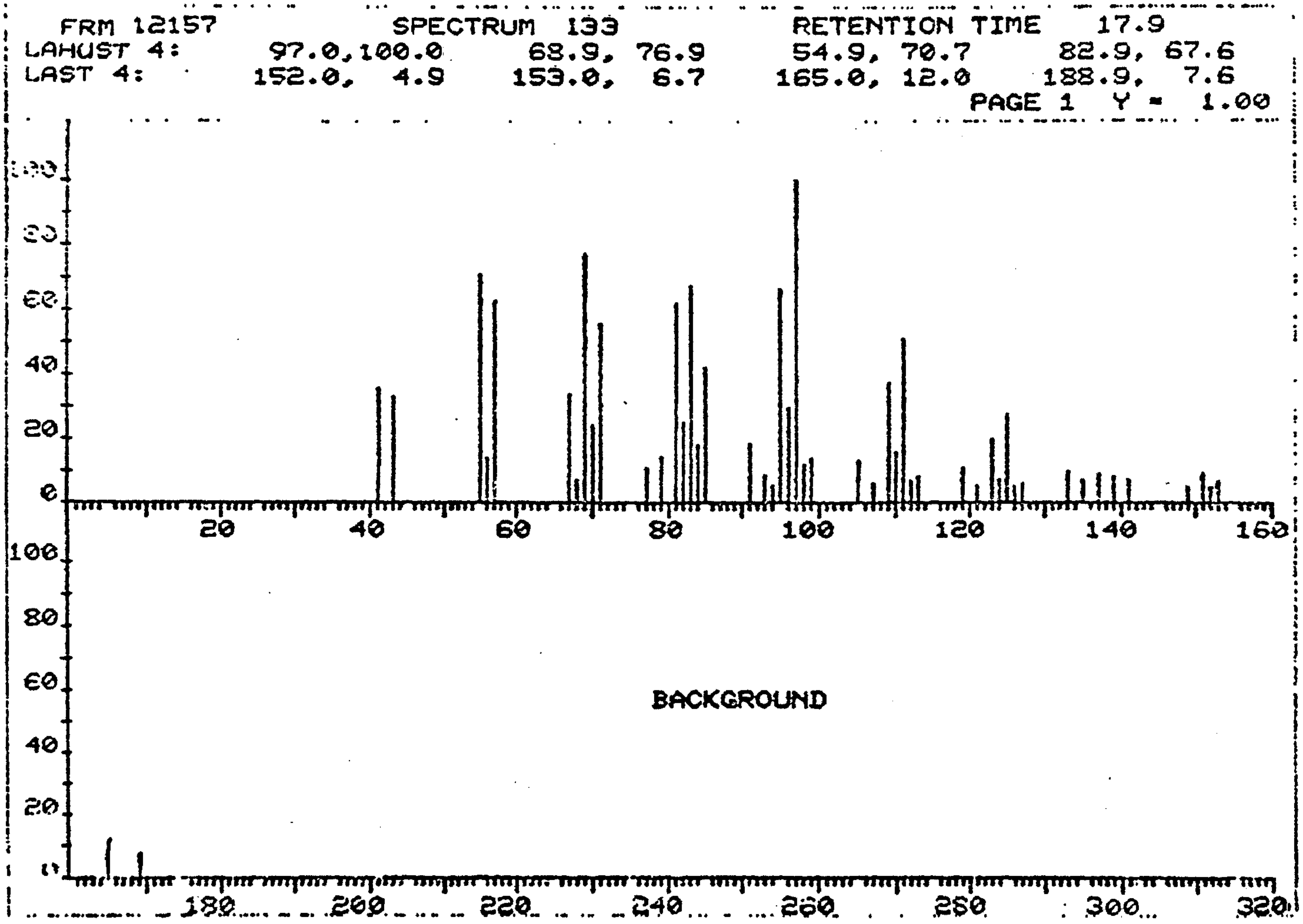


Figure 22. Background mass spectrum at 17.9 minutes of the base/neutral methylene chloride extract from the station 258 Hamilton Harbour chromatogram given in Figure 20 (FRN 12157). This is tentatively identified as a mixture of alkanes and cycloalkanes.

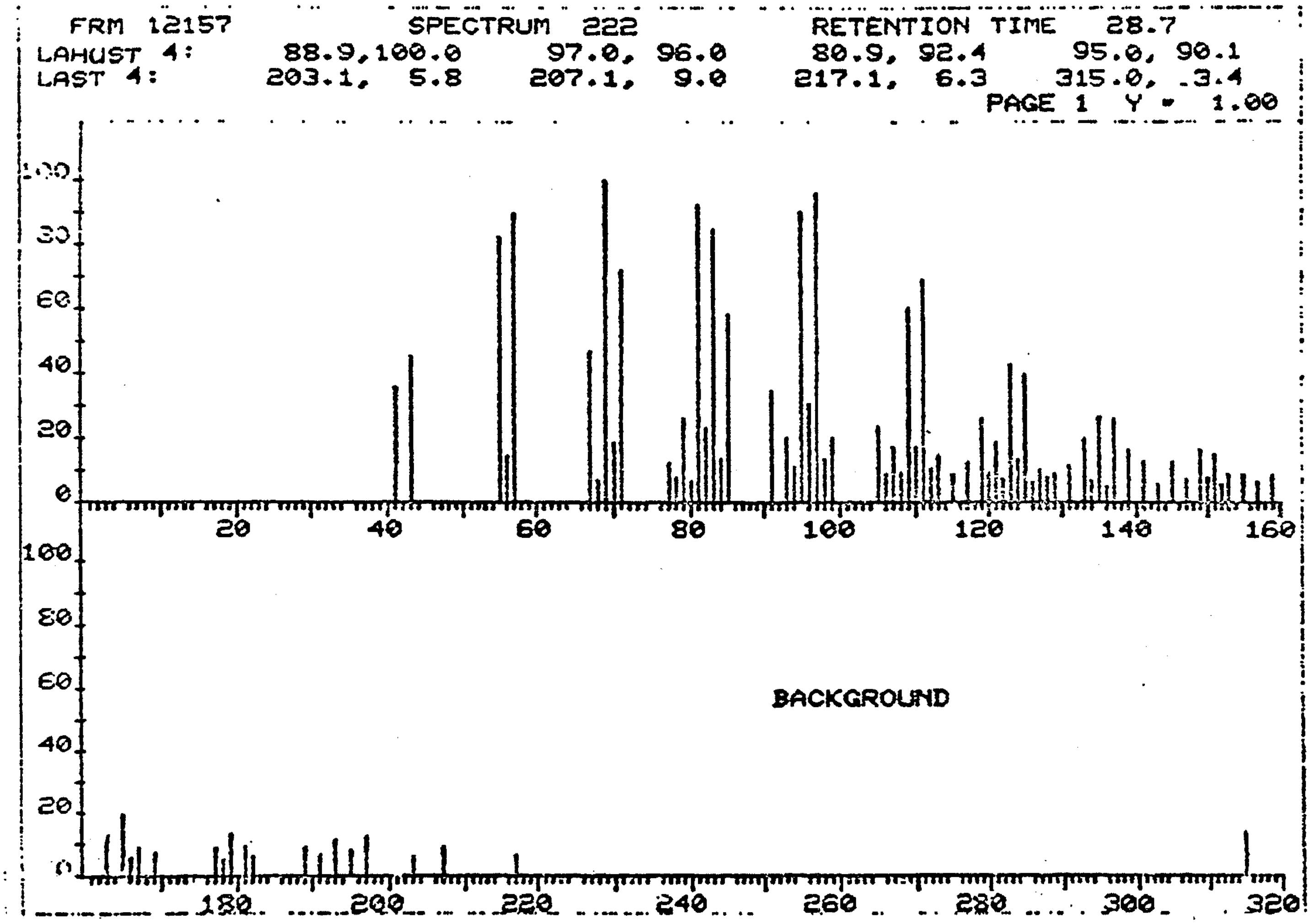


Figure 23. Background mass spectrum at 28.7 minutes of the base/neutral methylene chloride extract from the station 258 Hamilton Harbour chromatogram given in Figure 20 (FRN 12157). This is tentatively identified as alkanes and cycloalkanes or alkenes of higher molecular weight and greater complexity than at 17.9 minutes.

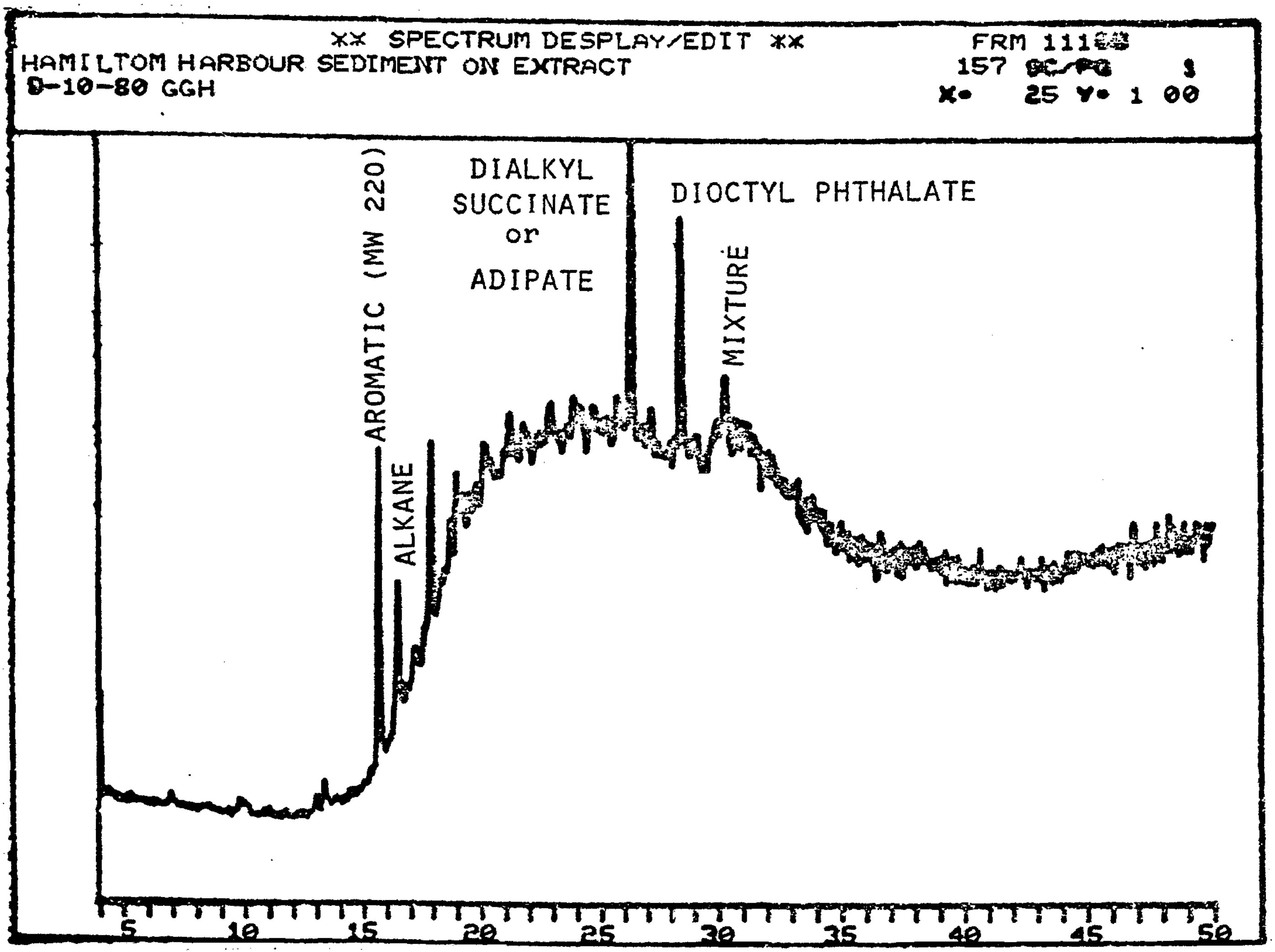


Figure 24. Gas chromatogram of base/neutral methylene chloride extract of sediment interstitial water collected from station 258 in Hamilton Harbour (0-25 cm section). Identification of mass spectra, given above, are available; the remainder were damaged by the tape recorder.

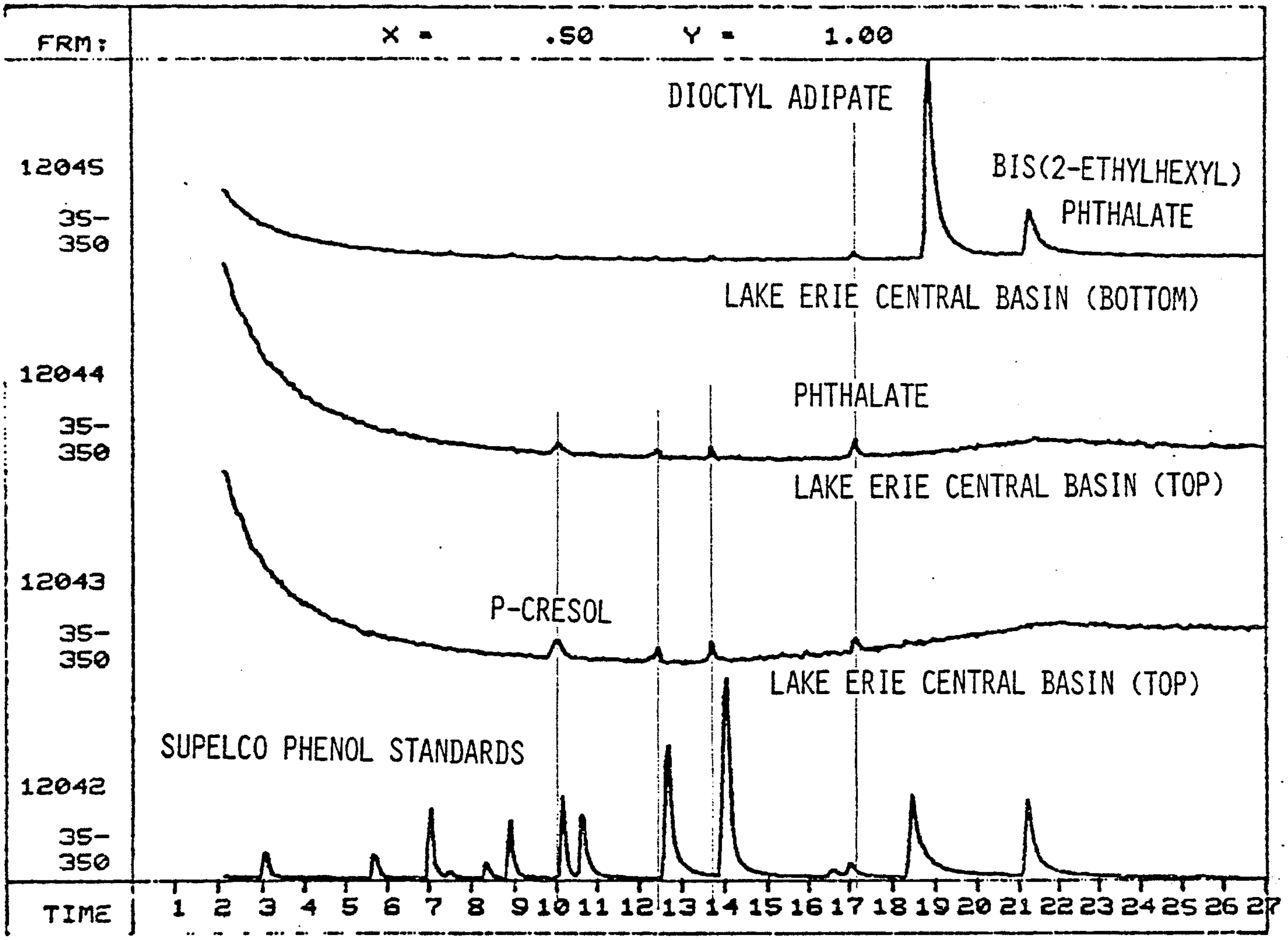


Figure 25a. Comparison of chromatograms for the acid fraction methylene chloride extracts of sediment interstitial water collected from station C-11 in the central basin of Lake Erie. Sediment depth ranges are designated as TOP (0-25 cm) and BOTTOM (25 to about 50 cm). Each chromatogram is normalized to its largest peak. Supelco phenol standards are also provided. Identification codes (FRN numbers) are listed in the left margin.

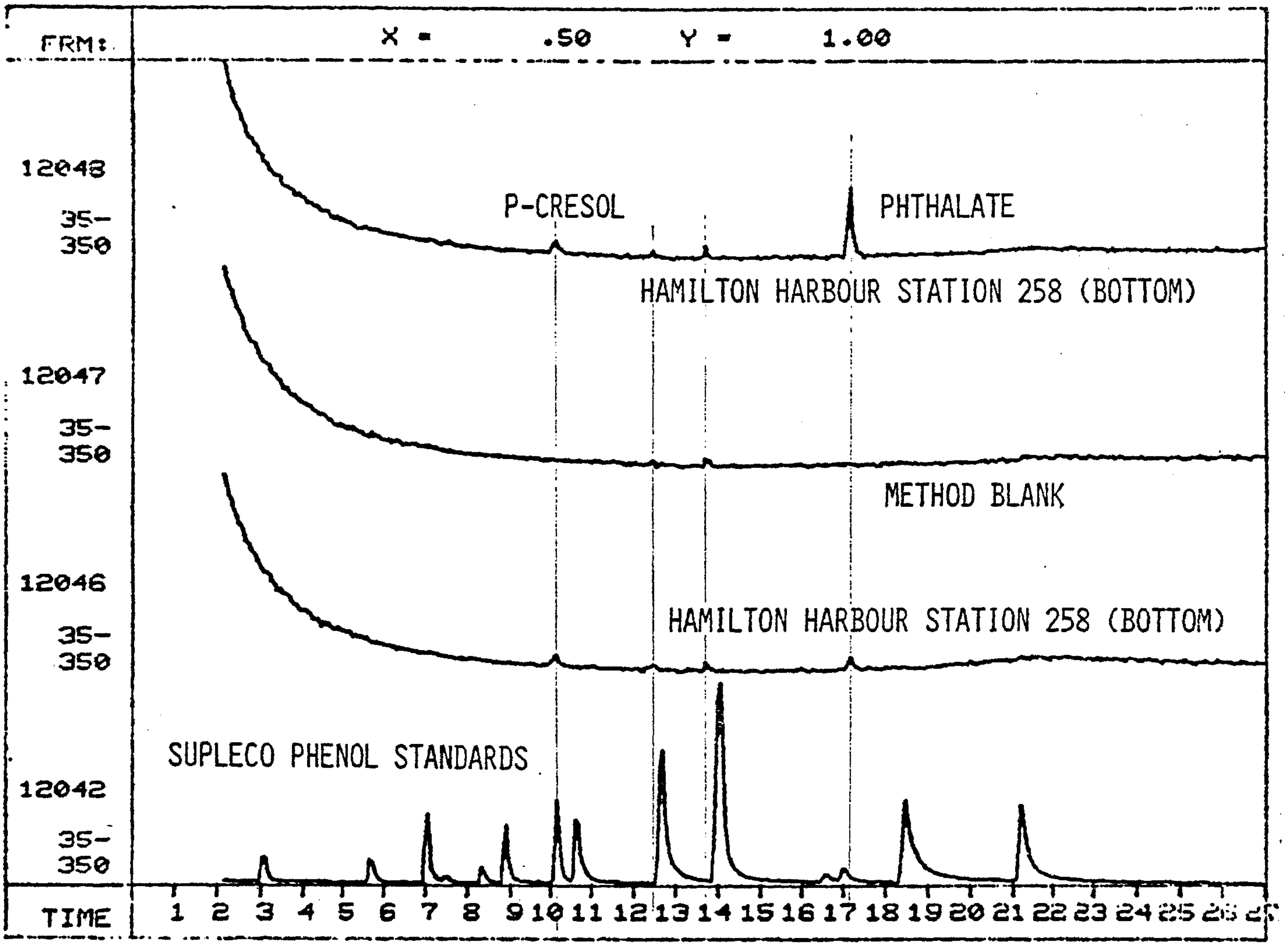


Figure 25b. Comparison of chromatograms for the acid fraction methylene chloride extracts of sediment interstitial water collected from station 258 in Hamilton Harbour. Sediment depth range is designated as BOTTOM (25 to about 50 cm). Each chromatogram is normalized to its largest peak. Supelco phenol standards and the method blank are also provided. Identification codes (FRN numbers) are listed in the left margin.

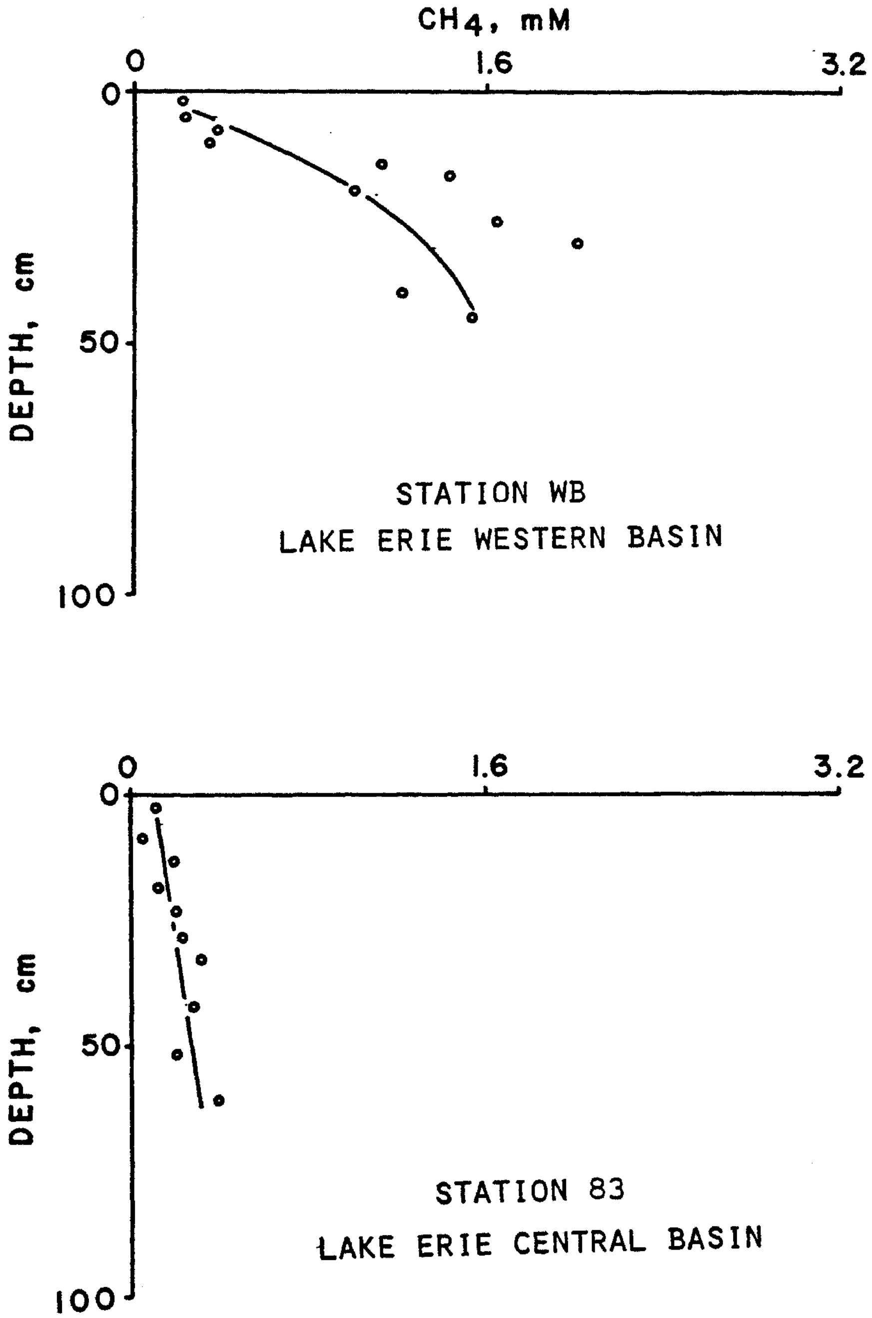


Figure 26. Measured sediment interstitial water methane concentrations (o) at stations WB in the western basin and 83 in the central basin of Lake Erie. The solid line designates the methane profile determined from a one dimensional numerical model (see text).

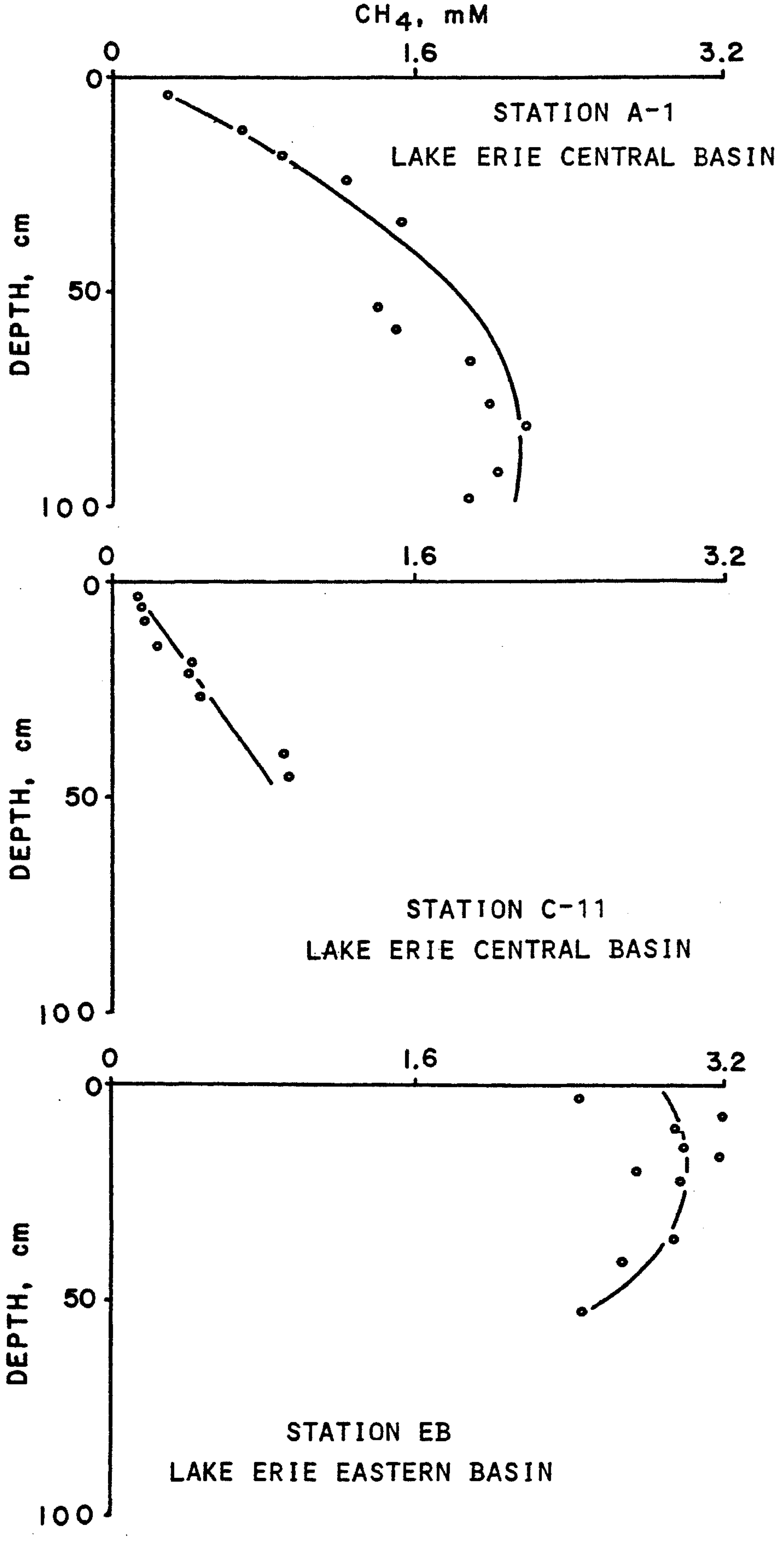


Figure 26. (continued) Data for stations A-1 and C-11 in the central basin and EB in the eastern basin of Lake Erie.

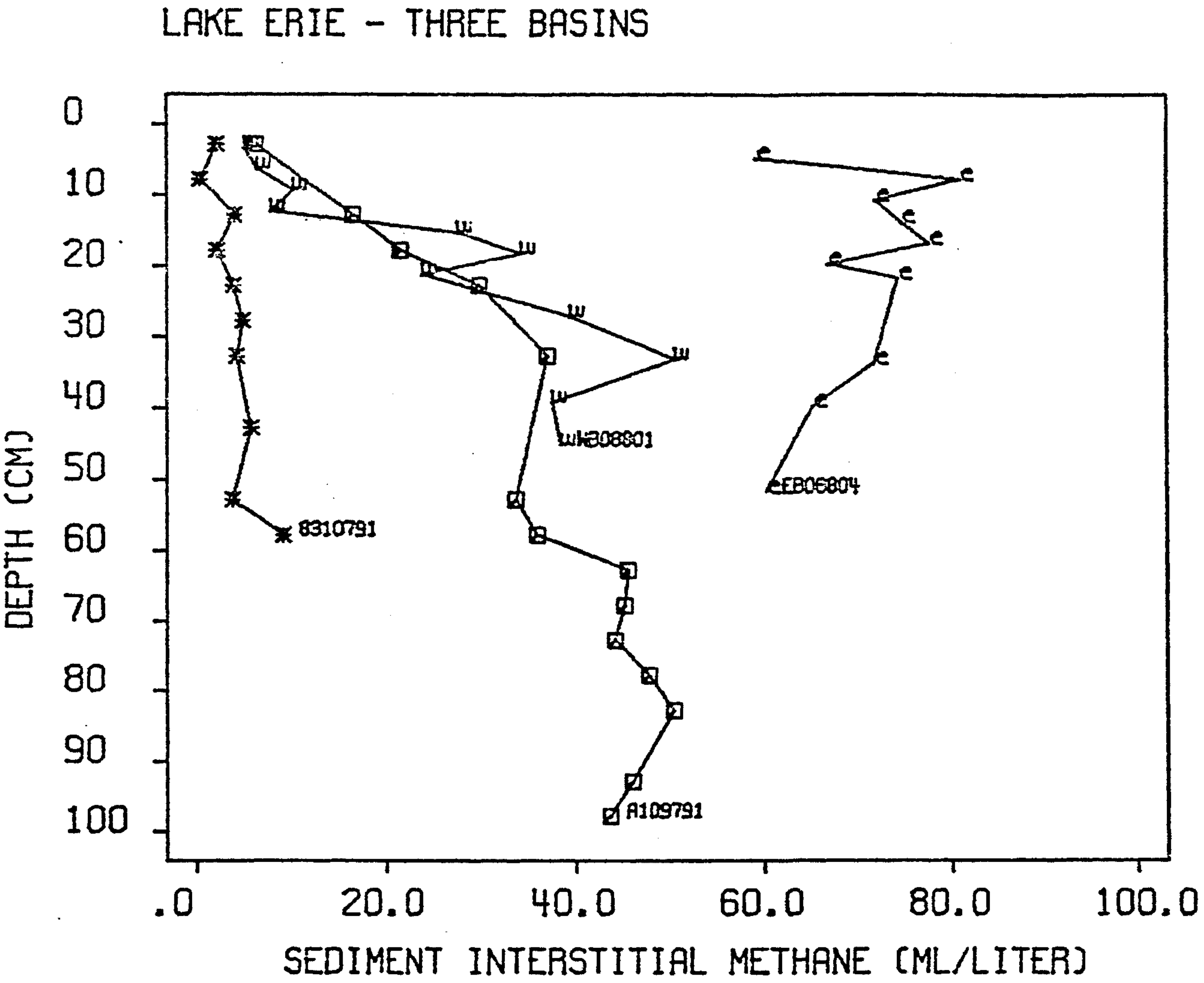


Figure 27. Representative profiles for sediment interstitial water concentrations of dissolved methane in the three basins of Lake Erie. The station codes are WB08801 (w) for the western basin, 8310791 (*) and A109791 (⊠) for the central basin and EB06804 (e) for the eastern basin. Digits 3,4 represent the month, 5,6 are for the year and 7 is for the core number. The eastern basin station was the only location sampled with a gravity corer (with exception of IA10792 in the Lake Erie islands area - see Appendices).

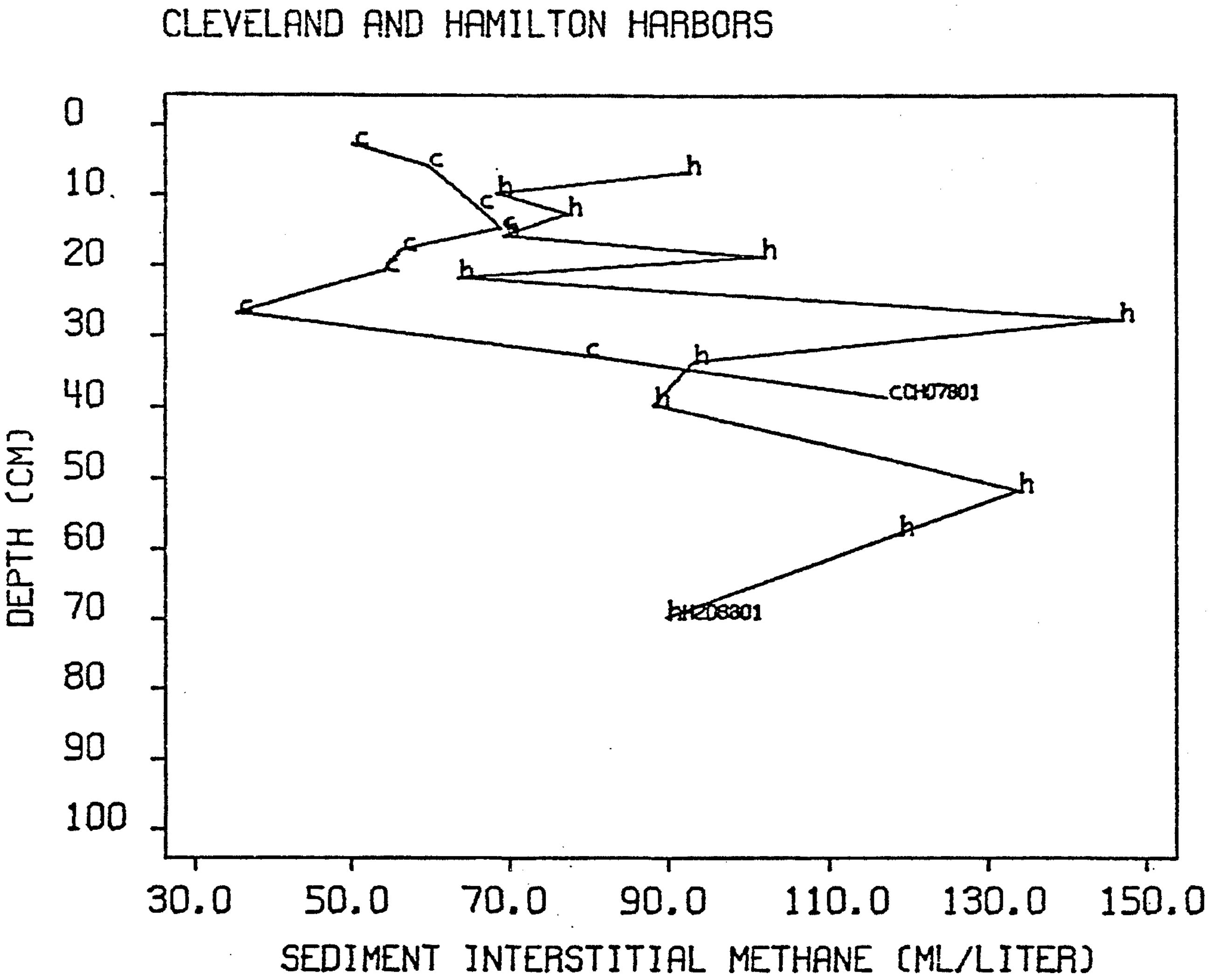


Figure 28. Representative profiles for sediment interstitial water concentrations of dissolved methane in Cleveland and Hamilton harbors. The station codes are CH07801 (c) for Cleveland Harbor and H208801 (h) for Hamilton Harbour. H2 signifies station 258 in Hamilton Harbour. Digits 3,4 represent the month, 5,6 are for the year and digit 7 is for the core number.

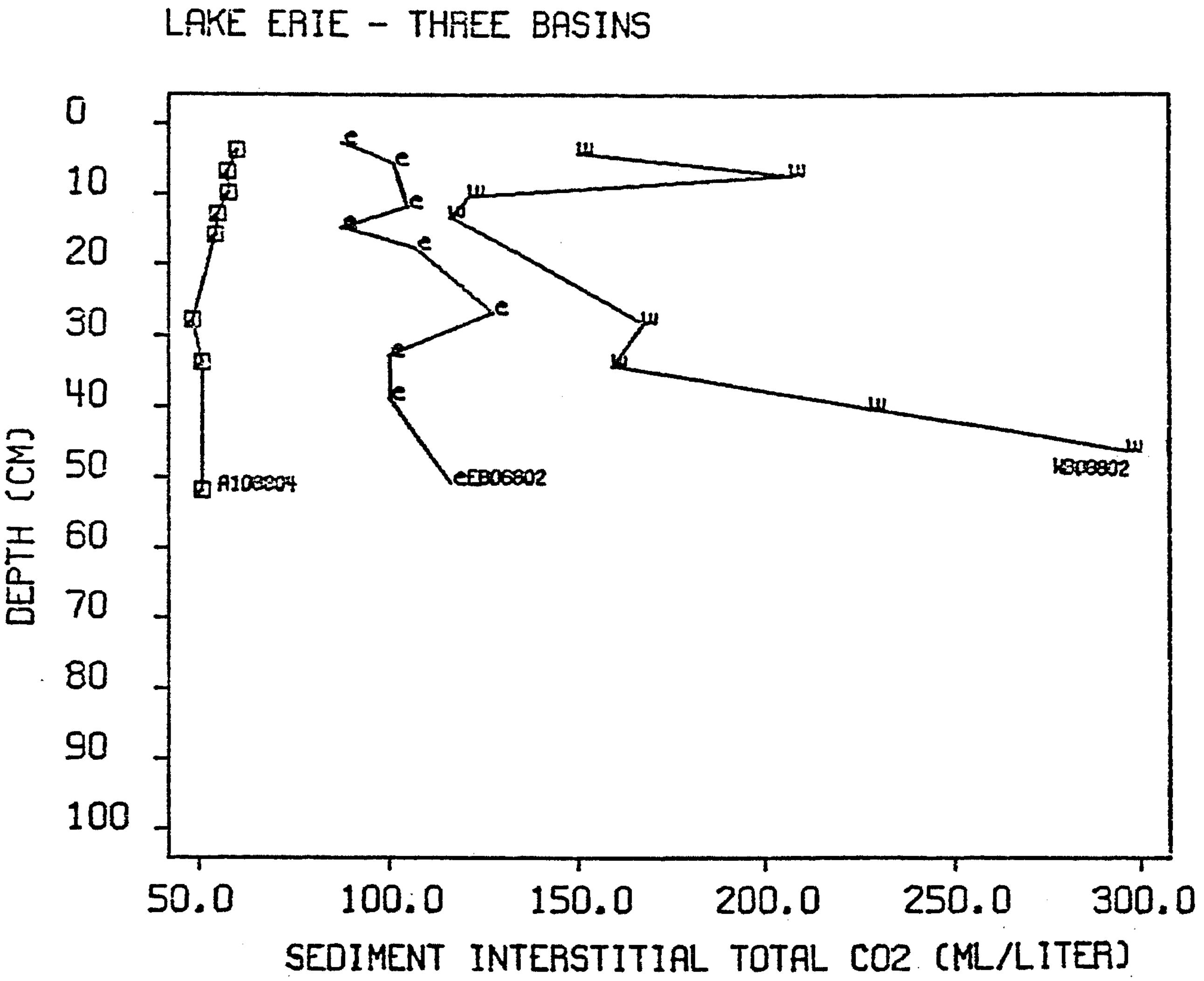


Figure 29. Profiles for sediment interstitial water concentrations of dissolved total carbon dioxide in the three basins of Lake Erie. The station codes are WB08802 (w) for the western basin, A108804 (⊡) for the central basin and EB06802 (e) for the eastern basin. Digits 3,4 represent the month, 5,6 are for the year and digit 7 is for the core number. The increase below 30 cm in the western basin is suspected to coincide with an occurrence of shell fragments. The eastern basin station was the only location sampled with a gravity corer (with exception of IA10792 in the Lake Erie islands area - see Appendices).

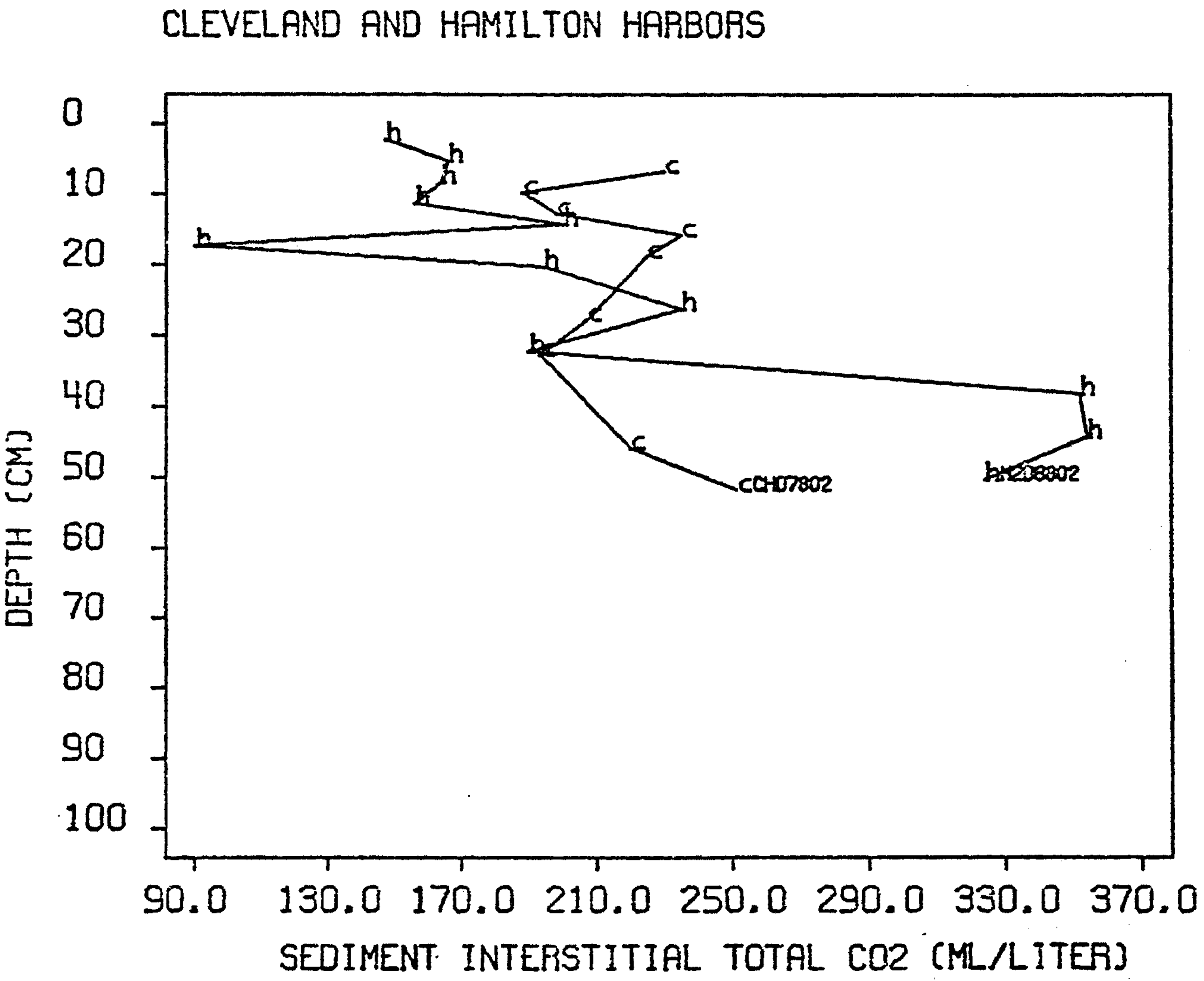


Figure 30. Profiles for sediment interstitial water concentrations of dissolved total carbon dioxide in Cleveland and Hamilton harbors. The station codes are CH07802 (c) for Cleveland Harbor and H208802 (h) for Hamilton Harbour. H2 signifies station 258 in Hamilton Harbour. Digits 3,4 represent the month, 5,6 are for the year and digit 7 is for the core number.

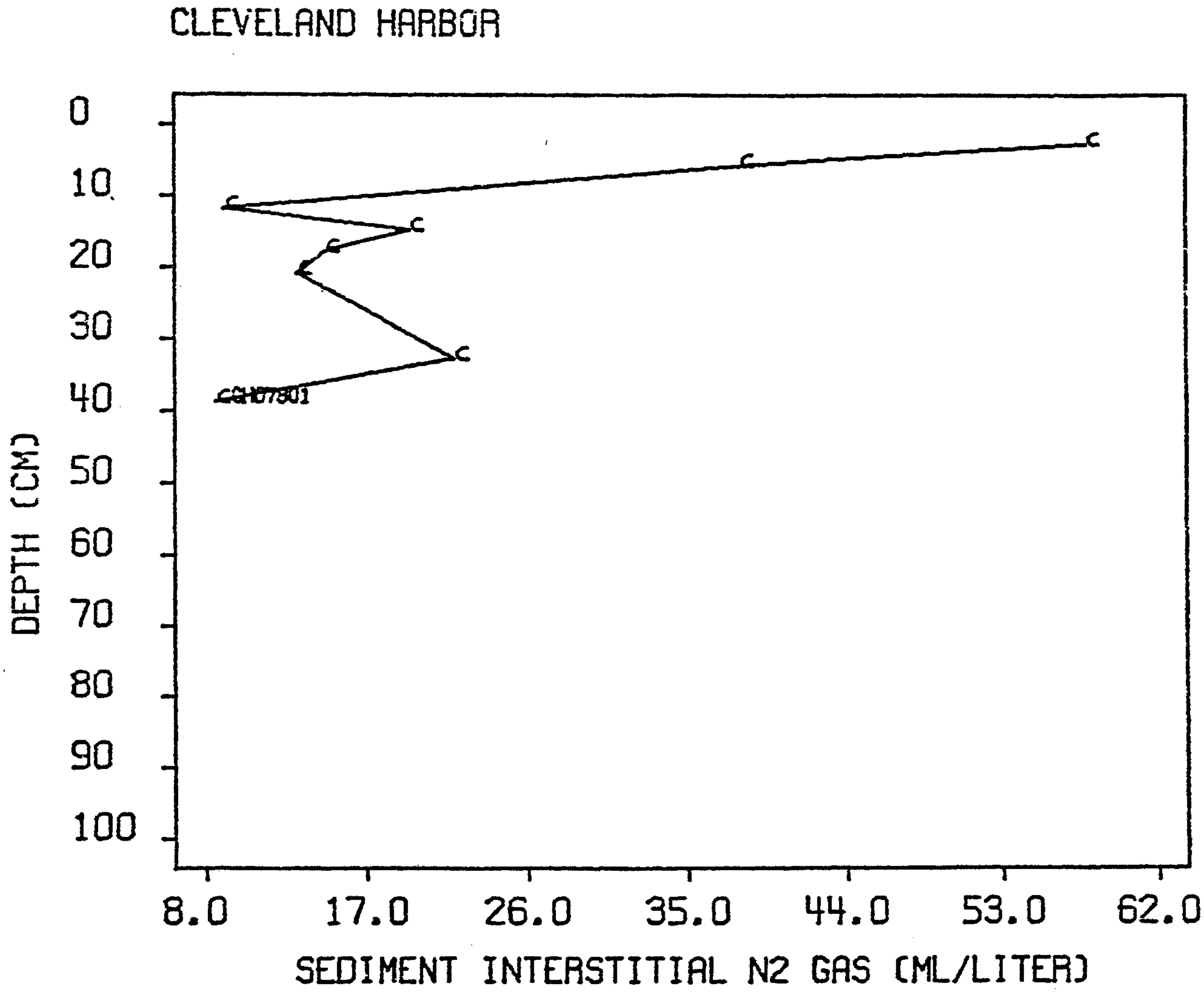


Figure 31a. Profile for sediment interstitial water concentration of dissolved nitrogen gas in Cleveland Harbor. The station code is CH07801 and was occupied in July 1980.

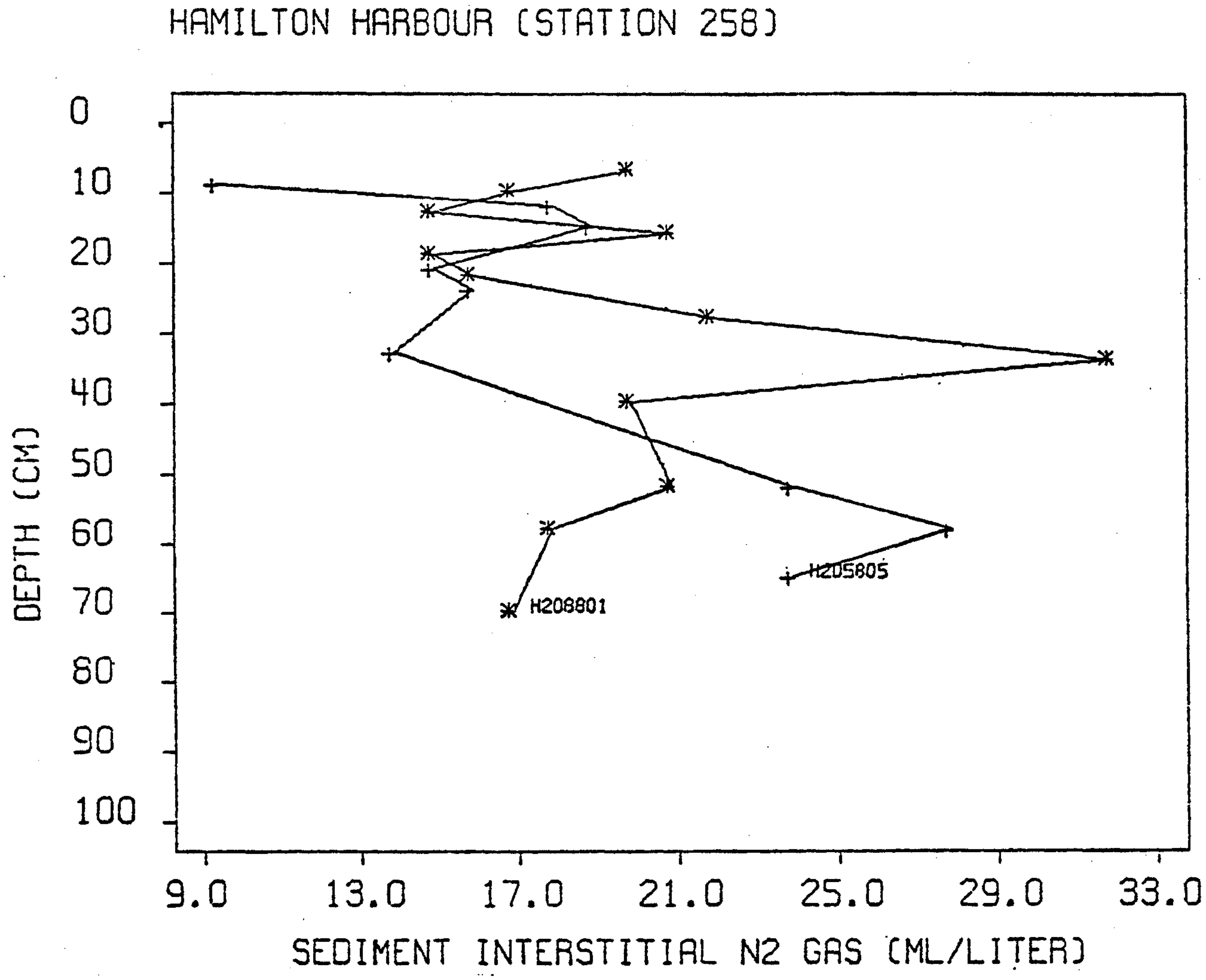


Figure 31b. Profiles for sediment interstitial water concentrations of dissolved nitrogen gas at station 258 in Hamilton Harbour. The cores were collected in May (+, H205805) and August (*, H208801) of 1980.

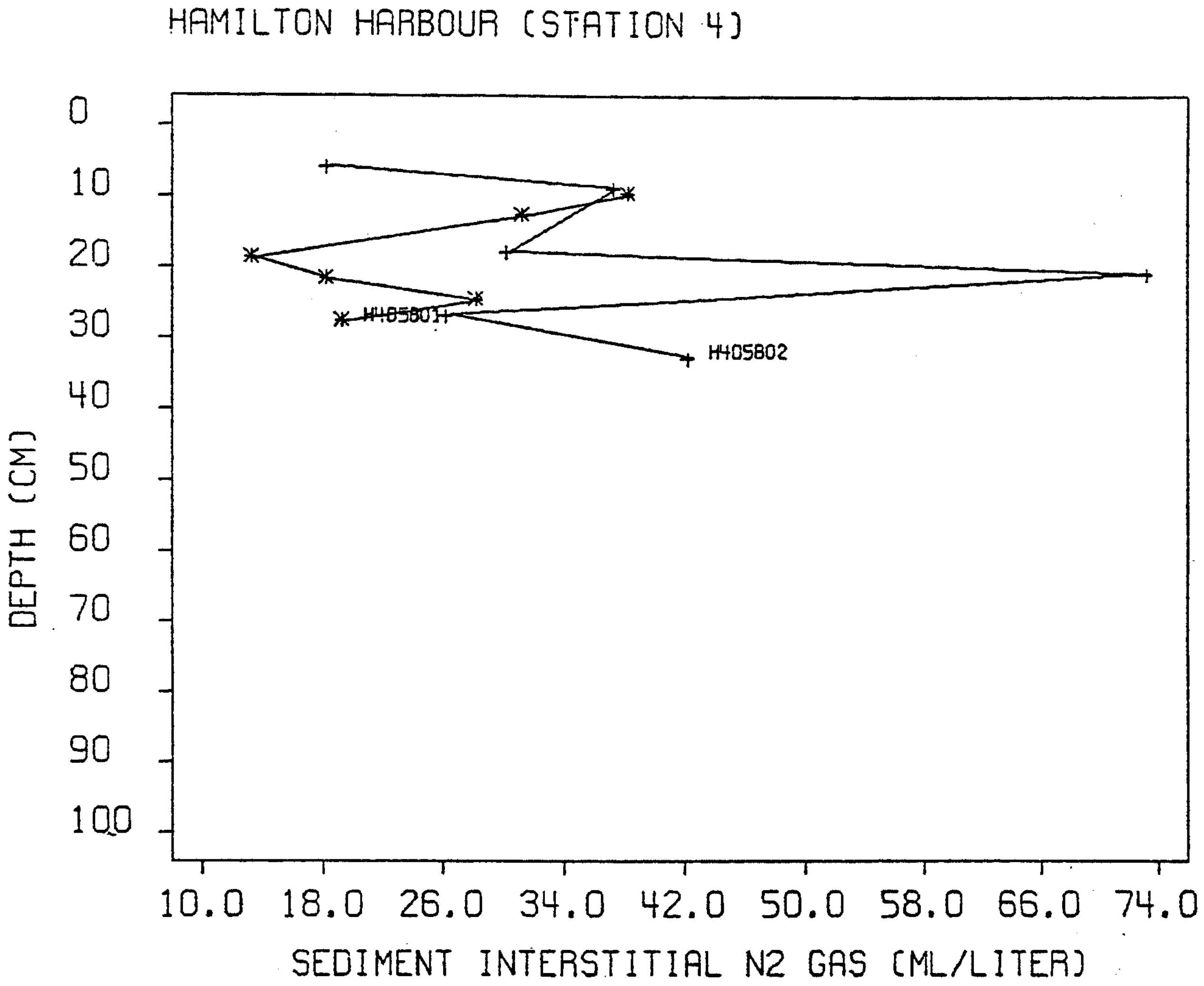


Figure 31c. Profiles for sediment interstitial water concentrations of dissolved nitrogen gas at station 4 in Hamilton Harbour. Both cores were collected in May 1980 within a few meters of each other by means of SCUBA.

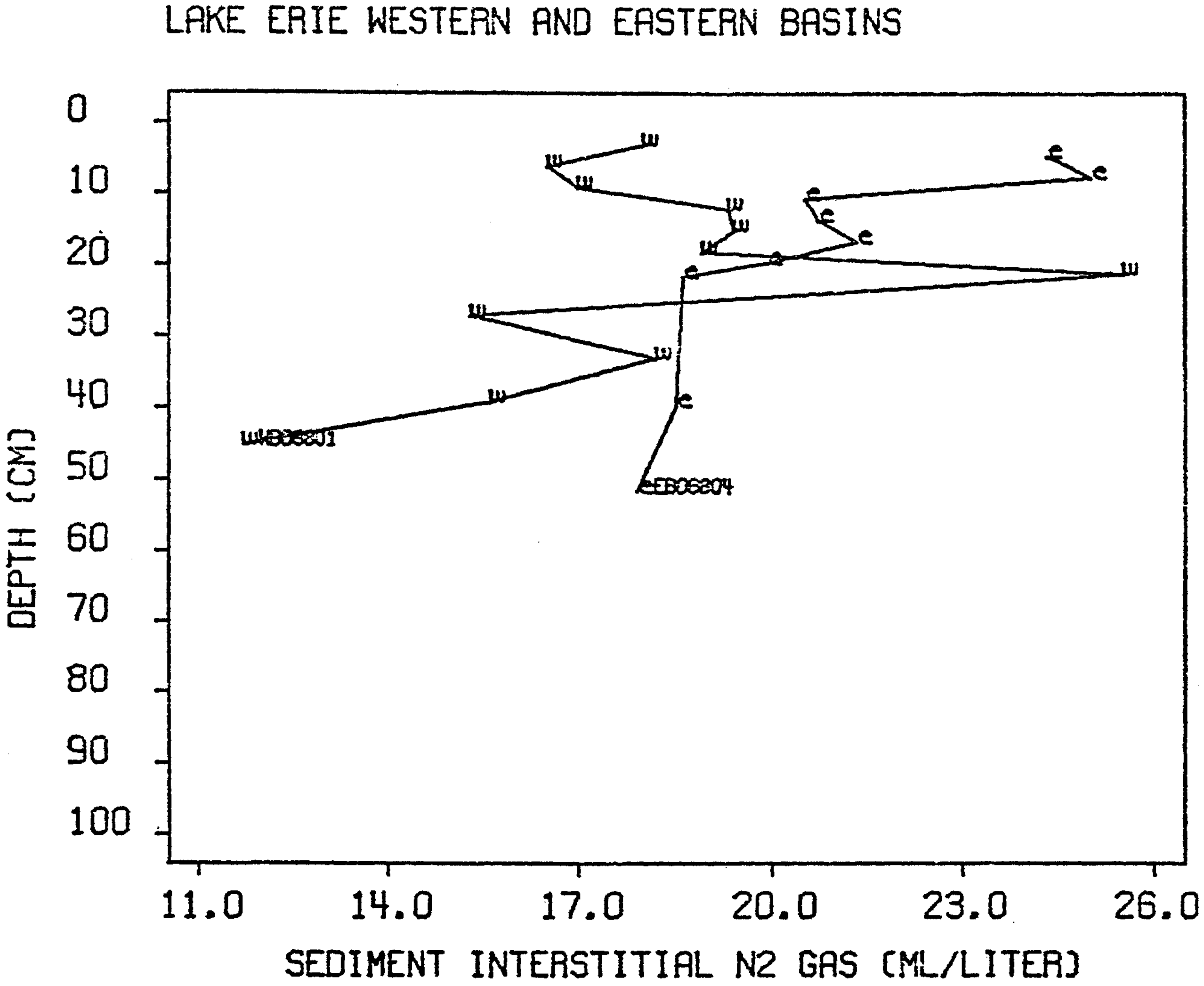


Figure 32a. Profiles for sediment interstitial water concentrations of dissolved nitrogen gas in the western (w, WB08801) and eastern (e, EB06804) basins of Lake Erie. Digits 3,4 represent the month, 5,6 are for the year and digit 7 is for the core number. The eastern basin station was the only location sampled with a gravity corer (with exception of IA10792 in the Lake Erie islands area - see the Appendix).

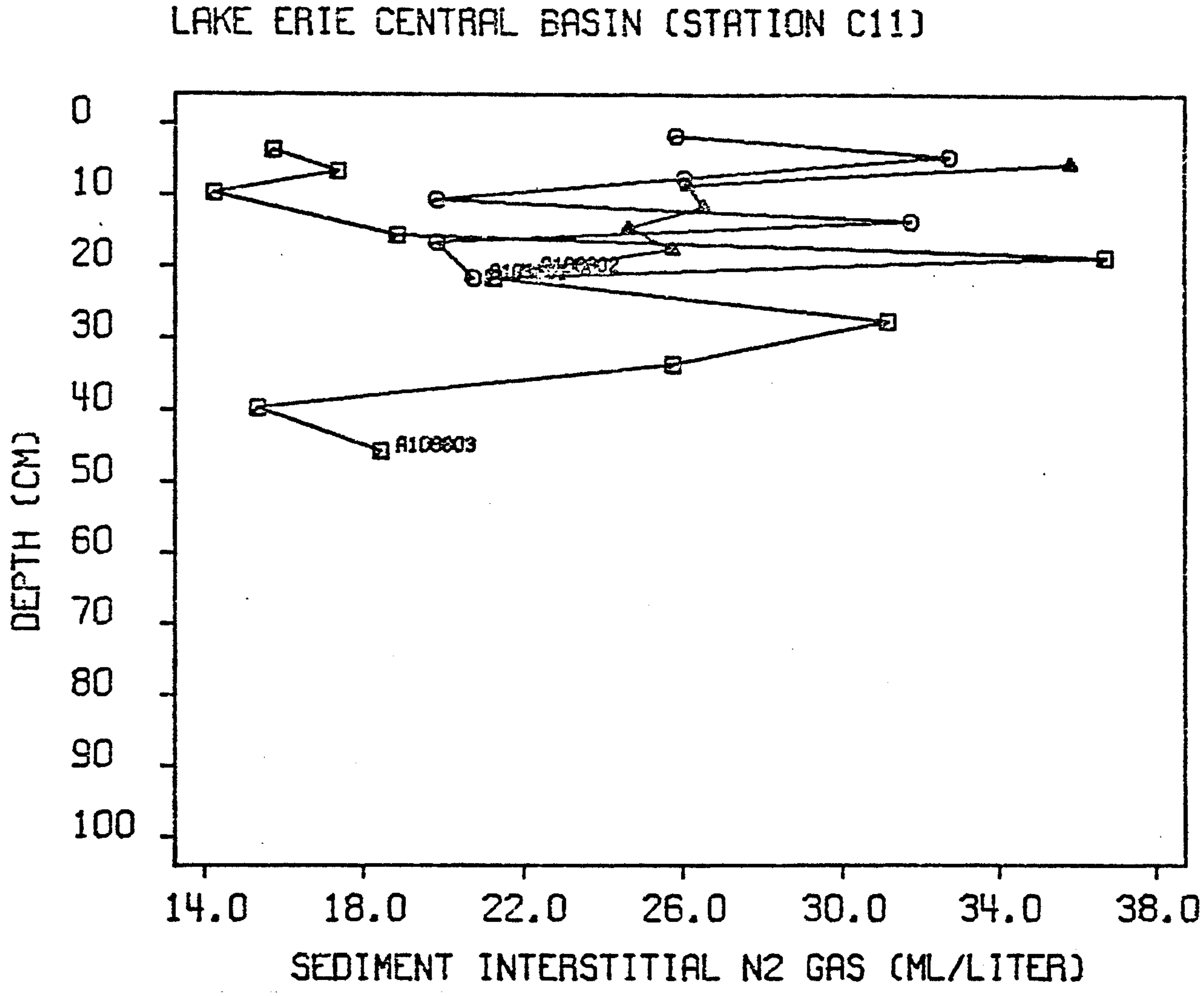


Figure 32b. Profiles for sediment interstitial water concentrations of dissolved nitrogen gas at station C-11 in the central basin of Lake Erie. The three cores were collected in August 1980 by means of SCUBA. Cores A108801 (o) and A108802 (Δ) were obtained side by side while A108803 (◻) was located about 0.5 km from the other two.

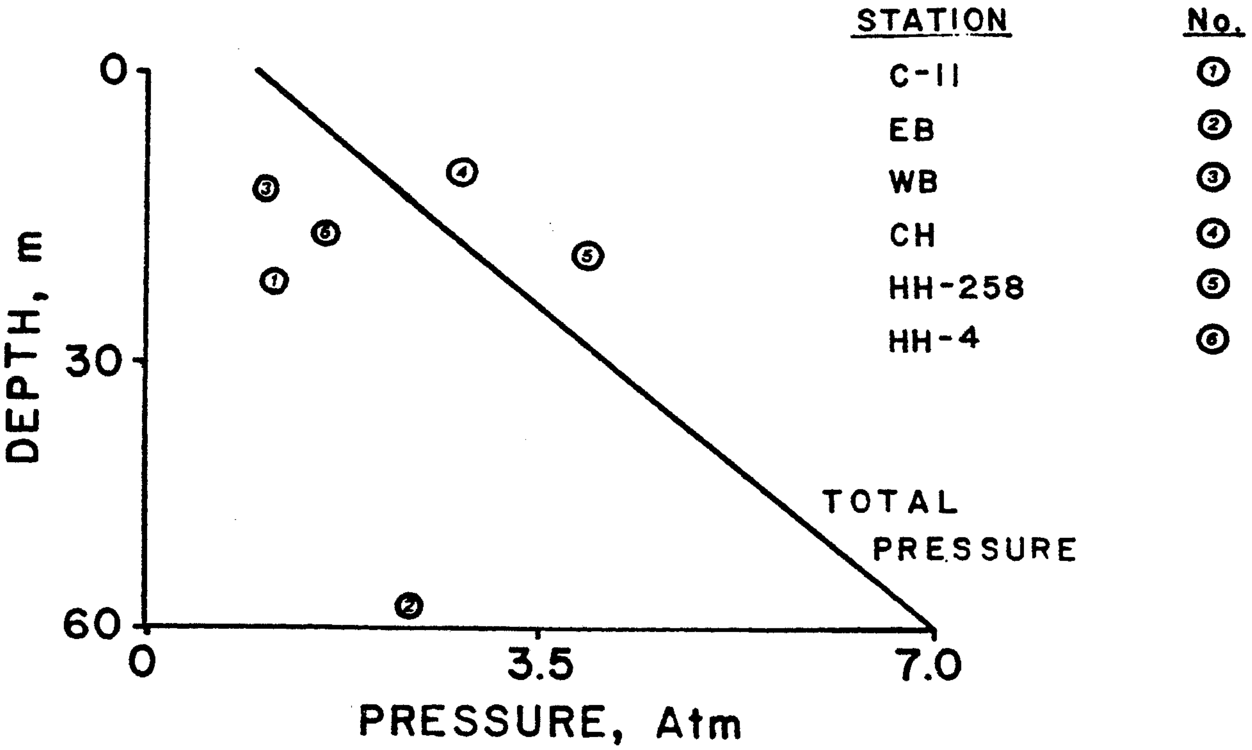


Figure 33. Depth (meters) versus the sum of partial pressures (atmospheres) of nitrogen and methane gases dissolved in the sediment interstitial water at the different stations in Lake Erie, Cleveland Harbor and Hamilton Harbour. The total pressure line includes the sum of both hydrostatic and atmospheric pressures.

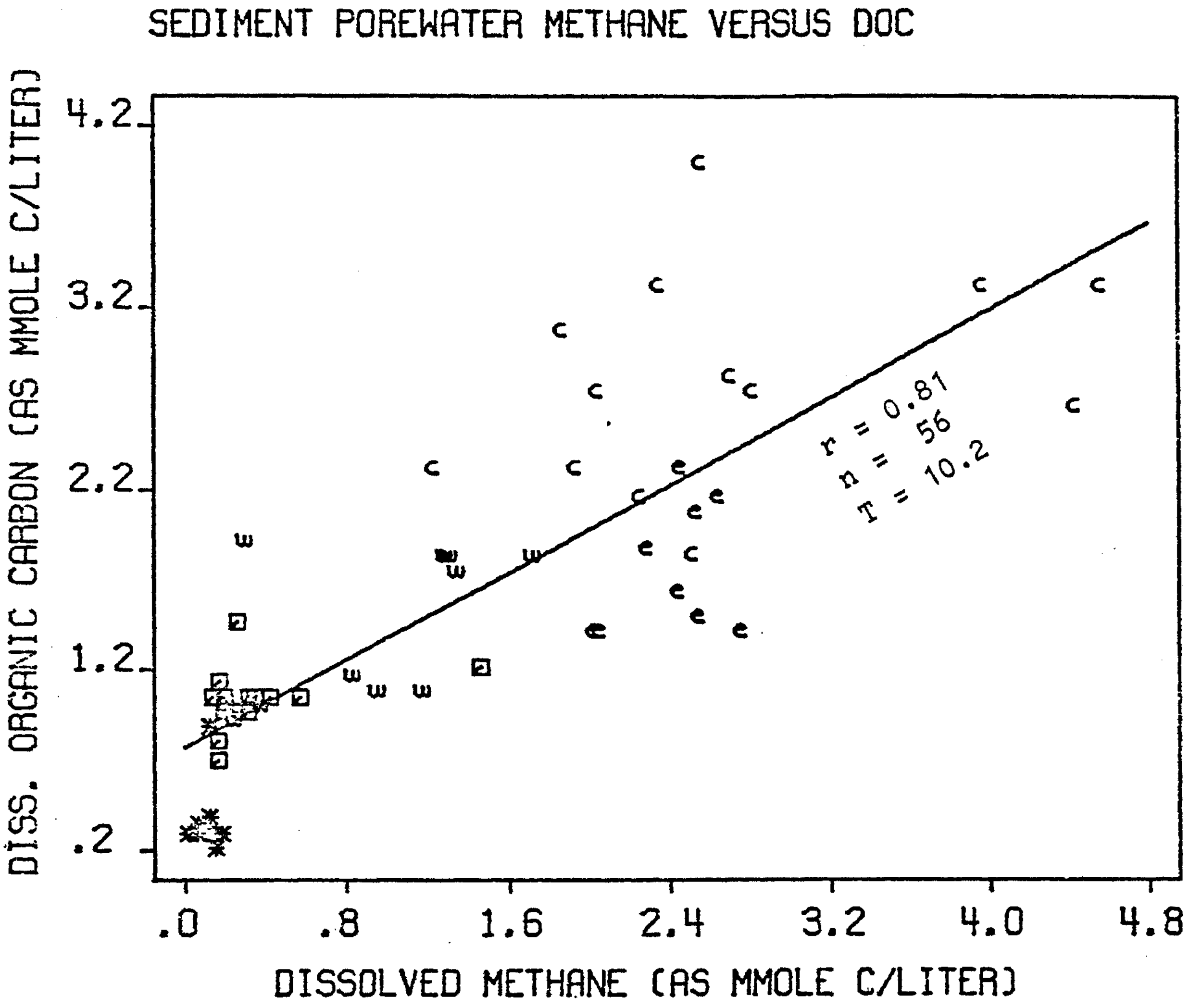


Figure 34a. Relationship between sediment interstitial water dissolved methane and dissolved organic carbon for the three basins of Lake Erie and Cleveland Harbor. Station symbols are western basin (w), central basin (* = station 83, ⊡ = stations A-1 & C-11), eastern basin (e) and Cleveland Harbor (c, 2 locations = CH0879 and CH0780). Without Cleveland Harbor samples: r = 0.75, n = 43, T value = 7.3 for the linear least squares fit.

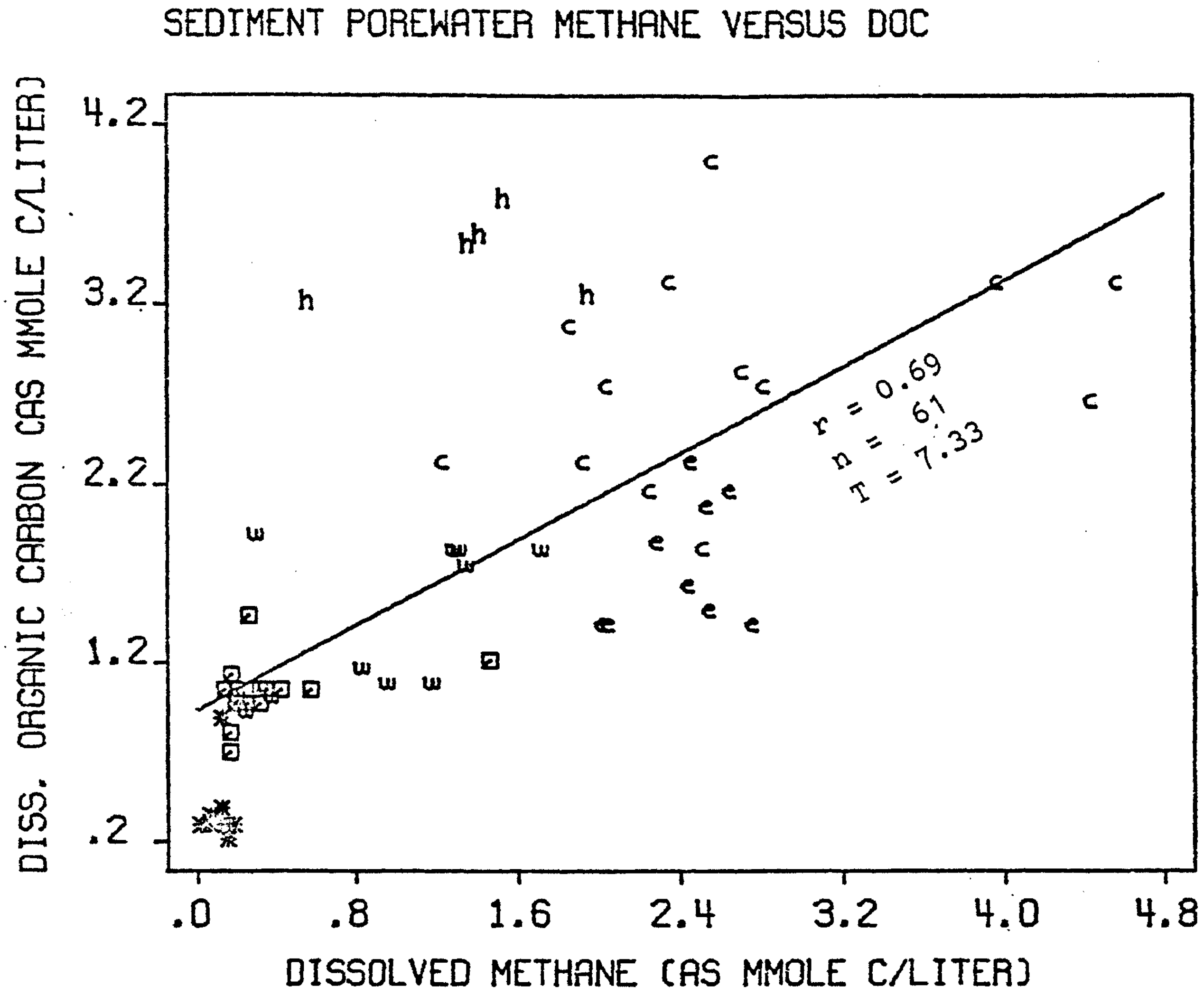


Figure 34b. Same as Figure 34a except with the inclusion of Hamilton Harbour sample data. Symbols are (h) for H20580 (station 258 in the middle of Hamilton Harbour.

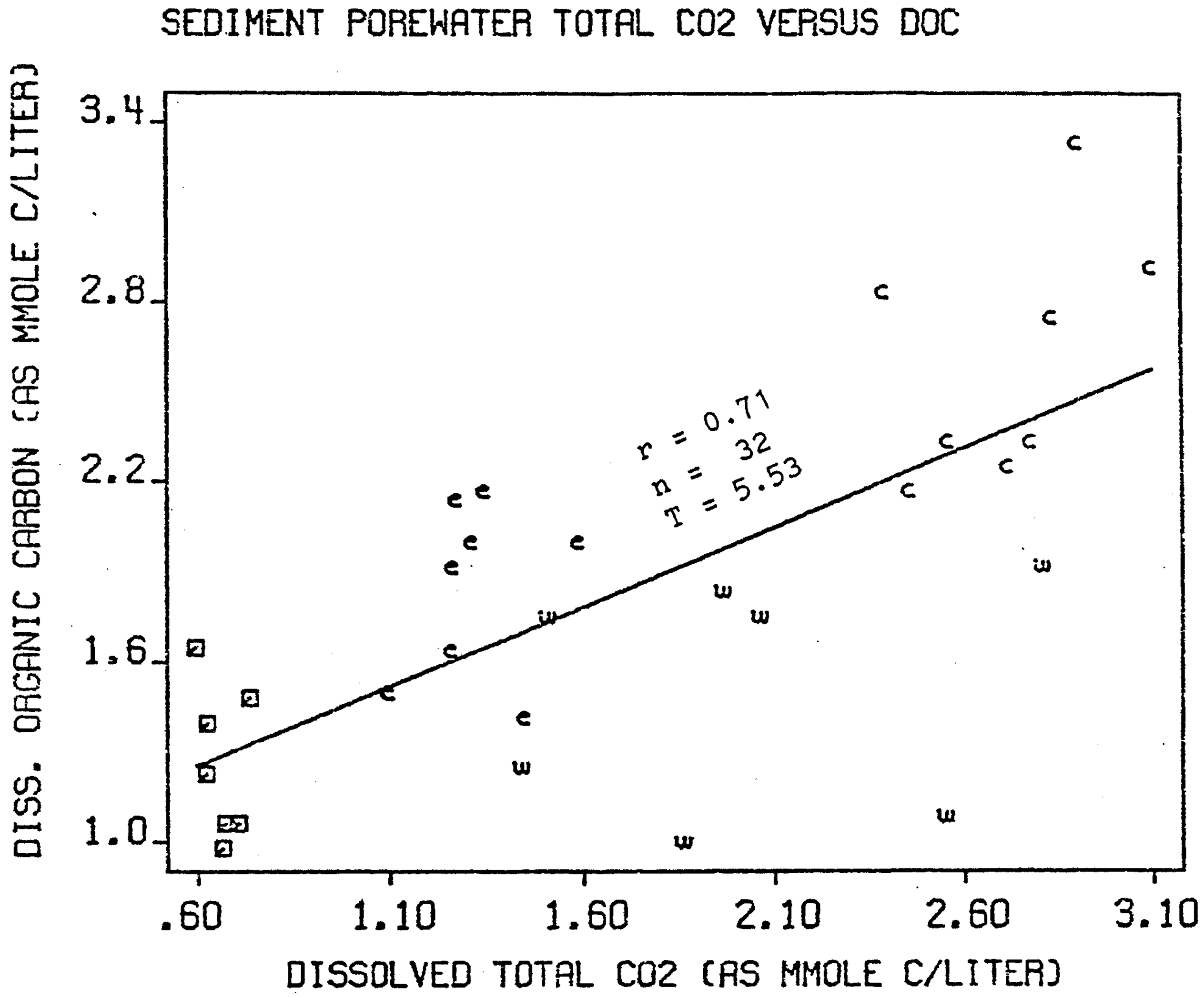


Figure 35a. Relationship between sediment interstitial water dissolved total carbon dioxide and dissolved organic carbon for the three basins of Lake Erie and Cleveland Harbor. Station symbols are western basin (w), central basin station C-11 (⊡), eastern basin (e) and Cleveland Harbor (c). The linear least squares correlation was not significant without Cleveland Harbor samples: r = 0.29, n = 24, and T value = 1.40.

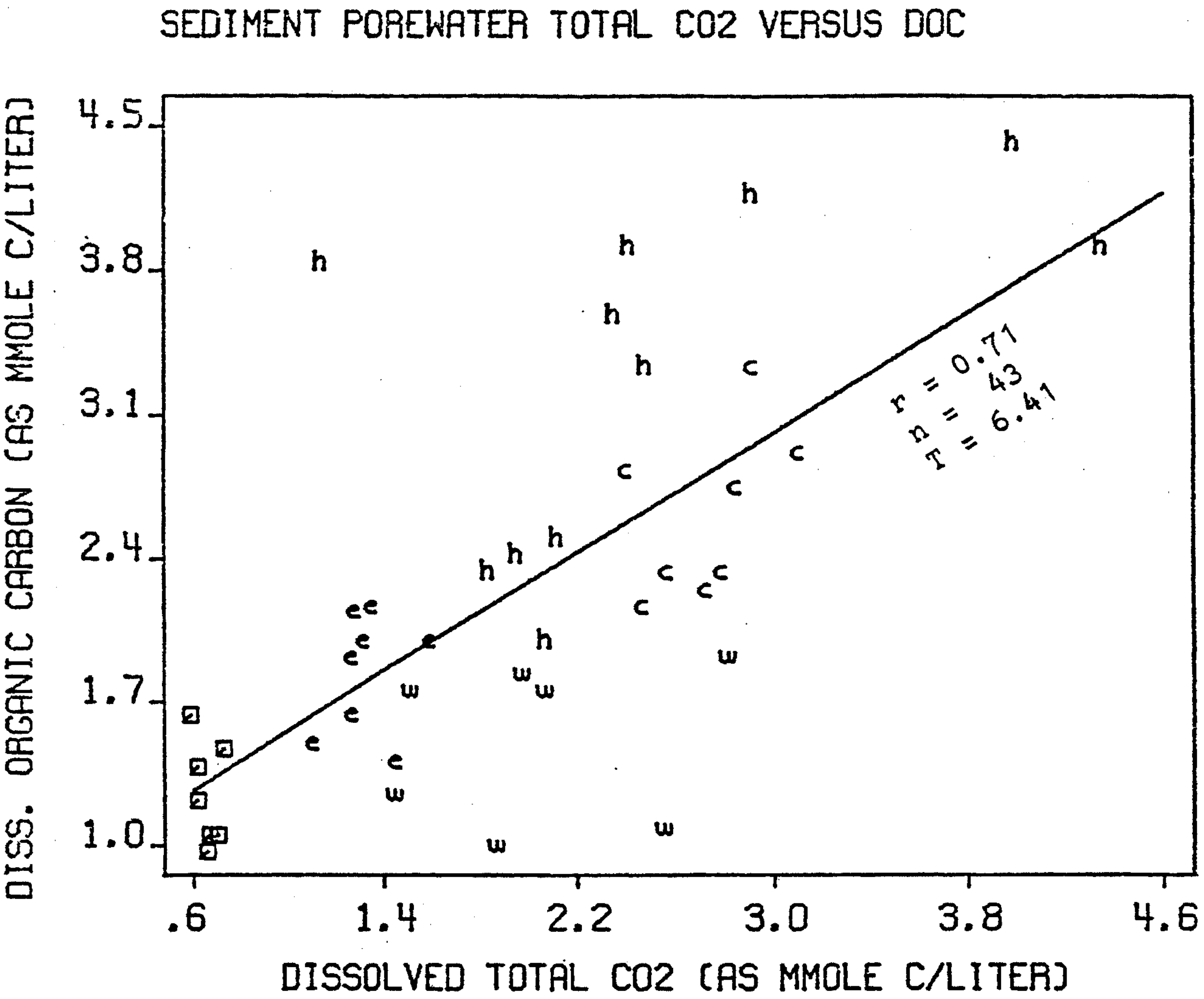


Figure 35b. Same as Figure 35a except with the inclusion of Hamilton Harbour sample data. Symbols are (h) for H20880 (station 258) in the middle of Hamilton Harbour.

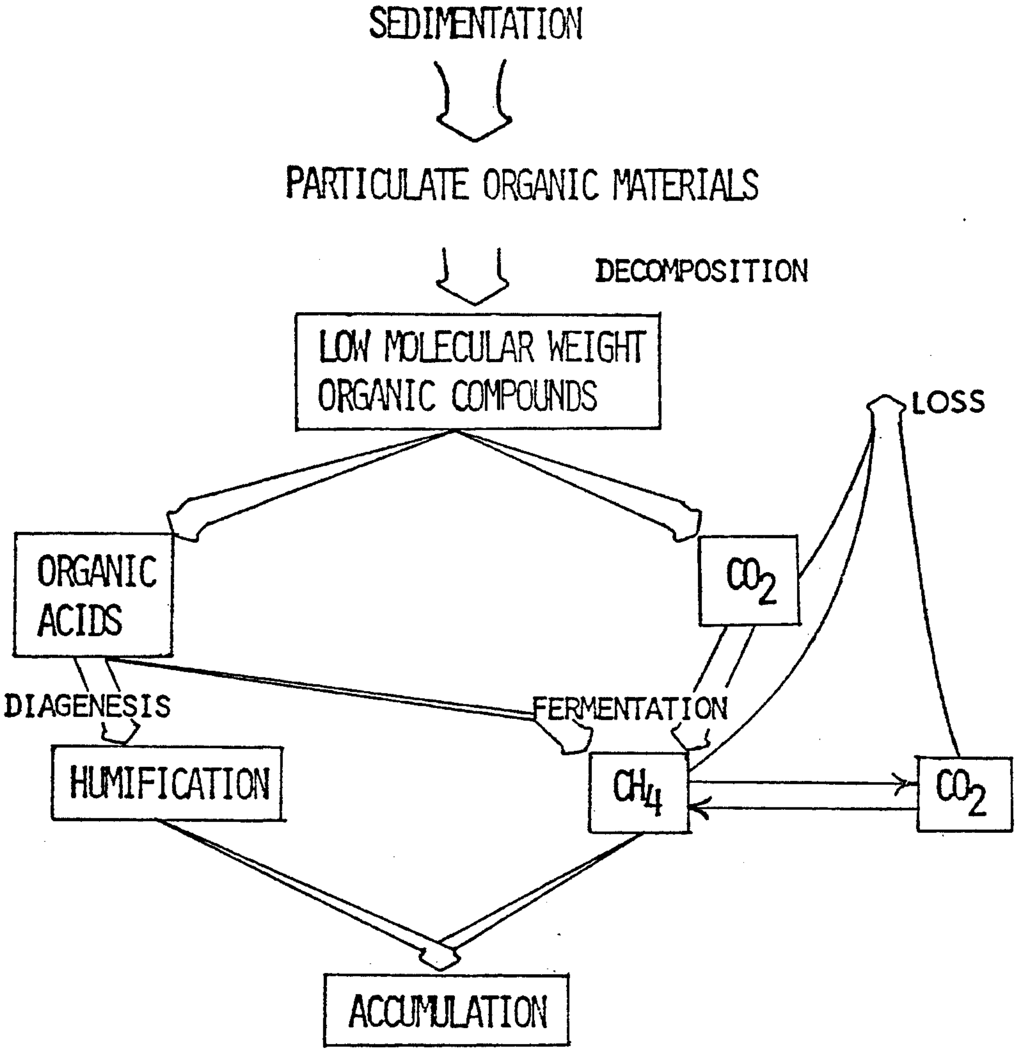


Figure 36. A schematic diagram for a proposed carbon cycle in the sediments of Lake Erie. The principle source of carbon is sedimentation of detrital and eroded materials from overlying waters. The major mechanisms for carbon loss are through diffusion and ebullition of methane and carbon dioxide gases.

APPENDIX A

DATA TABULATION

Station Coding System:

Digits	Information
1,2	station number
2,3	month
4,5	year
6	cruise core number

Note: Because of the short distance between stations A-1 and C-11, the station coded as A-1 in 1980 was in actuality station C-11. This was only for the 1980 (digits 4,5 for station code) cruise.

Concentration coding system:

mL of gas per L of sediment interstitial water

mg of carbon per L of sediment interstitial water

percent of volatile matter calculated for sediment dry weight

porosity is unitless (see equation 1 for calculations)

Depth coding system:

cm of depth in the sediment measured during core processing

corrections were not made for compaction

INTERSTITIAL DISSOLVED METHANE GAS

STATION CODE	CONC. (ML/LITER)	DEPTH (CM)
A108791	5.70	3.0
A108791	5.72	8.0
A108791	20.0	23.0
A108791	32.9	38.0
A108791	28.3	43.0
A108791	47.1	68.0
A108791	44.6	73.0
A109791	6.92	2.0
A109791	17.1	12.0
A109791	22.2	17.0
A109791	30.5	22.0
A109791	37.6	32.0
A109791	34.3	52.0
A109791	36.5	57.0
A109791	46.1	62.0
A109791	45.7	67.0
A109791	44.7	72.0
A109791	48.4	77.0
A109791	51.0	82.0
A109791	46.6	92.0
A109791	44.2	97 0
8310791	2.70	2.0
8310791	1.05	7.0
8310791	4.57	12.0
8310791	2.77	17.0
8310791	4.46	22.0
8310791	5.48	27.0
8310791	4.82	32.0
8310791	6.34	42.0
8310791	4.39	52.0
8310791	9.73	57.0
A108792	11.2	8.0
A108792	39.2	38.0
A108792	39.6	43.0
A108792	42.3	78.0
H208803	76.2	3.0
H208803	100.3	6.0
H208803	149.6	9.0
H208803	126.9	12.0
H208803	136.4	17.0
H208803	82.4	21.0
H208803	140.8	27.0
H208803	181.4	33.0
H208803	155.1	39.0
H208803	155.8	45.0
CH08791	74.5	15.0
CH08791	131.8	35.0
CH08791	83.4	45.0
CH08791	76.0	55.0
CH08791	135.7	60.0
A10979P	8.0	0.0
A10979P	12.2	1.0
A10979P	11.4	2.0
A10979P	2.9	3.0
A10979P	17.6	4.0
A10979P	23.6	5.0
A10979P	7.05	6.0
A10979P	1.8	7.0
A10979P	2.5	8.0
A10979P	8.5	9.0
A10979P	9.4	10.0
A10979P	2.2	12.0
A10979P	12.9	14.0
A10979P	8.5	16.0
A10979P	10.7	18.0
A10979P	22.4	20.0
A10979P	17.2	24.0
A10979P	22.2	40.0
A10979P	16.4	50.0
A10979P	51.9	60.0
A10979P	31.9	70.0
A10979P	16.9	80.0
A10979P	74.6	90.0
A108803	3.18	3.0
A108803	3.60	6.0
A108803	3.91	9.0
A108803	5.60	15.0
A108803	10.14	18.0
A108803	9.46	21.0
A108803	11.26	27.0
A108803	17.01	33.0
A108803	22.2	39.0
A108803	22.7	45.0
A108802	10.2	5.0
A108802	17.9	8.0
A108802	6.61	11.0
A108802	6.66	14.0
A108802	6.12	17.0
A108802	8.39	20.0
A108801	9.65	1.0
A108801	8.56	4.0
A108801	13.3	7.0
A108801	11.2	10.0
A108801	4.91	13.0
A108801	8.18	16.0
A108801	10.2	21.0
H405801	58.1	9.0
H405801	58.7	12.0
H405801	50.2	18.0
H405801	36.8	21.0
H405801	58.0	24.0
H405801	64.4	27.0
H405801	7.24	30.0

WB08801	5.72	2.5
WB08801	7.04	5.5
WB08801	10.88	8.5
WB08801	8.56	11.5
WB08801	28.29	14.5
WB08801	34.91	17.5
WB08801	24.66	20.5
WB08801	39.98	26.5
WB08801	51.12	32.5
WB08801	38.13	38.5
WB08801	39.0	44.5
H405802	68.7	5.0
H405802	58.0	8.0
H405802	48.4	17.0
H405802	40.95	20.0
H405802	39.1	26.0
H405802	36.0	32.0
EB06804	59.9	4.0
EB06804	81.6	7.0
EB06804	72.5	10.0
EB06804	75.3	13.0
EB06804	78.3	16.0
EB06804	67.4	19.0
EB06804	74.9	21.0
EB06804	72.3	33.0
EB06804	65.8	39.0
EB06804	60.7	51.0
H205805	16.2	8.0
H205805	40.0	11.0
H205805	41.8	14.0
H205805	45.3	20.0
H205805	57.8	23.0
H205805	19.2	51.0
H205805	40.8	57.0
H205805	40.6	64.0
CH07801	51.0	2.0
CH07801	60.4	5.0
CH07801	66.7	11.0
CH07801	69.6	14.0
CH07801	57.1	17.0
CH07801	54.9	20.0
CH07801	36.1	26.0
CH07801	80.1	32.0
CH07801	117.9	38.0
H208801	92.9	6.0
H208801	69.2	9.0
H208801	78.0	12.0
H208801	70.1	15.0
H208801	102.2	18.0
H208801	64.4	21.0
H208801	147.3	27.0
H208801	93.8	33.0
H208801	89.0	39.0
H208801	134.5	51.0
H208801	119.4	57.0
H208801	90.5	69.0

INTERSTITIAL DISSOLVED NITROGEN GAS

STATION CODE	CONC. (ML/LITER)	DEPTH (CM)
WB08801	18.14	2.5
WB08801	16.68	5.5
WB08801	17.15	8.5
WB08801	19.46	11.5
WB08801	19.54	14.5
WB08801	19.01	17.5
WB08801	25.64	20.5
WB08801	15.42	26.5
WB08801	18.35	32.5
WB08801	15.70	38.5
WB08801	11.86	44.5
CH07801	58.26	2.0
CH07801	38.44	5.0
CH07801	9.39	11.0
CH07801	19.87	14.0
CH07801	15.00	17.0
CH07801	13.51	20.0
CH07801	22.30	32.0
CH07801	8.89	38.0
H208801	20.86	6.0
H208801	17.43	9.0
H208801	15.19	12.0
H208801	21.22	15.0
H208801	15.64	18.0
H208801	16.13	21.0
H208801	22.79	27.0
H208801	32.30	33.0
H208801	20.24	39.0
H208801	21.83	51.0
H208801	18.12	57.0
H208801	17.89	69.0
A108801	26.09	1.0
A108801	32.93	4.0
A108801	26.26	7.0
A108801	20.00	10.0
A108801	31.90	13.0
A108801	20.04	16.0
A108801	20.94	21.0
A108802	36.06	5.0
A108802	26.30	8.0
A108802	26.71	11.0
A108802	24.81	14.0
A108802	25.97	17.0
A108802	22.28	20.0
H405801	39.93	9.0
H405801	32.53	12.0
H405801	14.46	18.0
H405801	19.12	21.0
H405801	29.27	24.0
H405801	20.73	27.0

H405802	19.86	5.0
H405802	38.04	8.0
H405802	31.70	17.0
H405802	74.90	20.0
H405802	27.27	26.0
H405802	43.40	32.0
EB06804	24.46	4.0
EB06804	25.16	7.0
EB06804	20.69	10.0
EB06804	20.84	13.0
EB06804	21.47	16.0
EB06804	20.07	19.0
EB06804	18.71	21.0
EB06804	18.68	39.0
EB06804	18.08	51.0
H205805	9.55	8.0
H205805	18.86	11.0
H205805	19.31	14.0
H205805	15.86	20.0
H205805	16.95	23.0
H205805	14.81	32.0
H205805	24.28	51.0
H205805	28.70	57.0
H205805	24.68	64.0
A108803	15.93	3.0
A108803	17.52	6.0
A108803	14.42	9.0
A108803	19.06	15.0
A108803	36.97	18.0
A108803	21.43	21.0
A108803	31.31	27.0
A108803	25.96	33.0
A108803	15.55	39.0
A108803	18.67	45.0

INTERSTITIAL DISSOLVED TOTAL CO2 GAS

STATION CODE	CONC. (ML/LITER)	DEPTH (CM)
EB06802	89.3	2.0
EB06802	103.7	5.0
EB06802	107.0	11.0
EB06802	89.1	14.0
EB06802	109.6	17.0
EB06802	129.6	26.0
EB06802	102.8	32.0
EB06802	102.9	38.0
EB06802	118.0	50.0
WB08802	152.7	3.5
WB08802	209.3	6.5
WB08802	123.7	9.5
WB08802	118.3	12.5
WB08802	169.3	27.5
WB08802	161.4	33.5
WB08802	230.6	39.5
WB08802	298.5	45.5
A108804	61.7	3.0
A108804	59.1	6.0
A108804	59.4	9.0
A108804	56.6	12.0
A108804	55.9	15.0
A108804	50.1	27.0
A108804	52.6	33.0
A108804	52.5	51.0
H208802	149.2	1.5
H208802	168.5	4.5
H208802	166.0	7.5
H208802	158.8	10.5
H208802	202.1	13.5
H208802	92.2	16.5
H208802	196.7	19.5
H208802	237.9	25.5
H208802	192.0	31.5
H208802	354.6	37.5
H208802	356.2	43.5
H208802	326.6	49.5
CH07802	232.2	6.0
CH07802	190.4	9.0
CH07802	200.8	12.0
CH07802	237.9	15.0
CH07802	227.3	18.0
CH07802	209.3	27.0
CH07802	195.4	32.0
CH07802	222.3	45.0
CH07802	253.7	51.0

INTERSTITIAL DISSOLVED ORGANIC CARBON

STATION CODE	CONC. (MG/LITER)	DEPTH (CM)
IA10792	4.0	0.5
IA10792	4.0	1.5
IA10792	4.2	2.5
IA10792	4.7	3.5
IA10792	2.3	4.5
IA10792	7.0	5.5
IA10792	5.8	6.5
IA10792	9.8	7.5
IA10792	7.1	8.5
IA10792	8.8	9.5
IA10792	3.0	11.0
IA10792	9.9	13.0
IA10792	7.7	15.3
IA10792	6.5	17.5
IA10792	6.4	21.5
IA10792	8.4	23.5
IA10792	10.7	28.0
IA10792	15.0	30.0
IA10792	12.9	32.0
IA10792	16.3	35.5
IA10792	15.1	40.5
IA10792	7.3	45.5
IA10792	9.6	50.5
IA10792	12.6	56.3
8310793	3.5	1.0
8310793	5.6	3.0
8310793	8.2	5.0
8310793	4.0	7.0
8310793	10.0	9.0
8310793	4.0	11.0
8310793	11.0	13.0
8310793	4.0	15.0
8310793	4.0	17.0
8310793	2.0	19.0
8310793	5.0	22.5
8310793	3.0	27.5
8310793	4.0	32.5
8310793	14.0	37.5
8310793	4.0	42.5
A108792	9.0	0.5
A108792	7.3	1.5
A108792	8.7	2.8
A108792	7.0	4.0
A108792	5.3	5.0
A108792	9.7	6.0
A108792	12.0	7.0
A108792	10.1	8.0
A108792	6.5	9.0
A108792	12.7	10.0
A108792	14.1	24.5
A108792	12.0	32.5
A108792	15.0	48.3
A108792	12.6	52.5
A108792	12.0	58.5
A108792	15.0	71.3
A108792	15.0	73.5
CH08792	11.0	0.5
CH08792	18.0	1.5
CH08792	19.0	2.5
CH08792	25.0	3.5
CH08792	31.0	4.5
CH08792	20.6	5.5
CH08792	42.0	6.5
CH08792	20.0	7.5
CH08792	21.0	8.5
CH08792	37.0	9.5
CH08792	29.0	13.0
CH08792	22.2	15.0
CH08792	28.0	17.0
CH08792	38.0	19.0
CH08792	24.0	21.0
CH08792	36.0	23.0
CH08792	35.0	25.0
CH08792	32.0	27.0
CH08792	22.7	29.3
CH08792	24.0	31.5
CH08792	26.0	33.5
CH08792	32.0	35.5
CH08792	33.0	37.5
CH08792	32.0	39.5
CH08792	26.0	41.5
CH08792	24.4	43.5
CH08792	33.0	45.5
CH08792	29.9	47.5
CH08792	25.9	49.5
CH08792	44.0	51.8
CH08792	48.0	54.3
CH08792	39.0	56.5
CH08792	39.0	58.5
CH08792	40.0	60.5
CH08792	27.0	62.5
CH08792	41.0	64.5
CH08792	42.0	66.5
CH08792	40.0	68.8
CH08793	16.0	0.5
CH08793	25.0	2.5
CH08793	20.0	3.5
CH08793	24.0	4.5
CH08793	16.0	5.5
CH08793	21.0	6.5
CH08793	16.0	7.5
CH08793	25.0	8.5
CH08793	21.0	9.5
CH08793	17.0	11.5
CH08793	20.0	14.5
CH08793	22.0	17.5
CH08793	30.0	20.5
CH08793	21.0	23.5
CH08793	33.0	26.5
CH08793	33.0	29.5
CH08793	39.0	32.5
CH08793	43.0	35.5
CH08793	28.0	38.5
CH08793	37.0	41.5

H407792	46.0	0.5
H407792	48.0	1.5
H407792	46.0	2.5
H407792	32.0	3.5
H407792	45.0	4.5
H407792	34.0	5.5
H407792	33.0	6.5
H407792	41.0	7.5
H407792	53.0	8.5
H407792	40.0	9.5
H407792	34.0	11.0
H407792	59.7	13.0
H407792	63.0	17.0
H407792	60.0	19.0
H407792	74.0	21.0
H407792	107.0	23.0
H407792	94.0	25.0
H407792	68.0	27.0
H407792	102.0	32.0
H407792	119.0	34.0
H407792	135.0	36.0
H407792	103.0	38.0
H407792	96.0	40.0
H407792	191.0	42.0
H407792	180.0	44.5
H407792	257.0	48.5
H407792	193.0	54.0
H407792	130.0	56.0
H407792	229.0	58.5
H407792	132.0	61.0
H407792	56.0	64.5
A108804	18.0	3.0
A108804	13.0	6.0
A108804	13.0	9.0
A108804	13.0	12.0
A108804	12.0	15.0
A108804	14.0	18.0
A108804	12.0	21.0
A108804	20.0	27.0
A108804	17.0	33.0
A108804	14.0	39.0
A108804	23.0	45.0
A108804	15.0	51.0
A108804	15.0	57.0
H208802	28.0	1.5
H208802	24.0	4.5
H208802	30.0	7.5
H208802	29.0	10.5
H208802	40.0	13.5
H208802	46.0	16.5
H208802	47.0	19.5
H208802	50.0	25.5
H208802	43.0	31.5
H208802	47.0	43.5
H208802	53.0	49.5
H207792	31.0	0.5
H207792	24.0	1.5
H207792	21.0	2.5
H207792	29.0	3.5
H207792	22.0	4.5
H207792	38.0	5.5
H207792	30.0	6.5
H207792	53.0	7.5
H207792	64.0	9.5
H207792	65.0	11.0
H207792	35.0	13.0
H207792	79.4	15.0
H207792	51.9	17.0
H207792	51.0	19.0
H207792	33.0	21.0
H207792	33.0	23.0
H207792	57.0	25.0
H207792	59.0	27.0
H207792	38.0	29.0
H207792	40.0	31.0
H207792	78.0	33.5
H207792	27.0	38.5
H207792	34.0	41.0
H207792	30.0	43.0
H207792	30.0	45.0
H207792	35.0	47.0
H207792	31.0	49.0
H207792	38.0	51.0
H207792	25.0	53.0
H207792	29.0	55.0
H207792	33.0	57.0
H207792	29.0	59.0
H207792	30.0	61.5
H207792	30.0	65.0
H207792	26.0	67.5
H207792	65.0	69.5
WB08803	12.0	0.5
WB08803	11.0	1.5
WB08803	12.0	2.5
WB08803	13.0	3.5
WB08803	11.0	4.5
WB08803	11.0	5.5
WB08803	10.0	7.0
WB08803	12.0	8.5
WB08803	17.0	9.5
WB08803	23.0	11.0
WB08803	14.0	13.0
WB08803	13.0	15.0
WB08803	13.0	17.0
WB08803	15.0	19.0
WB08803	14.0	21.0
WB08803	16.0	24.5
WB08803	22.0	29.5
WB08803	16.0	34.5
WB08803	22.0	39.5
WB08803	22.0	44.5
WB08803	19.0	49.5

A106791	48.1	0.5
A106791	45.0	1.5
A106791	45.9	3.5
A106791	37.4	4.5
A106791	28.9	5.5
A106791	36.1	6.5
A106791	33.0	7.5
A106791	38.7	8.5
A106791	39.8	9.5
A106791	45.9	11.0
A106791	34.8	13.0
A106791	38.1	17.0
A106791	38.7	19.0
A106791	42.6	21.0
A106791	44.9	23.0
A106791	42.3	25.0
A106791	46.5	27.0
A106791	45.0	29.0
A106791	47.0	31.0
A106791	50.3	33.0
A106791	47.7	35.0
A106791	37.1	37.0
A106791	45.3	39.0
A106791	40.9	41.0
A106791	50.0	45.0
A106791	49.8	47.0
A106791	55.4	49.0
A106791	46.1	51.0
A106791	49.2	53.0
A106791	51.5	55.0
A106791	45.1	57.0
A106791	51.4	59.5
WB08802	12.0	3.5
WB08802	13.0	6.5
WB08802	21.0	9.5
WB08802	15.0	12.5
WB08802	16.0	15.5
WB08802	16.0	18.5
WB08802	18.0	21.5
WB08802	21.0	27.5
WB08802	22.0	33.5
WB08802	23.0	39.5
WB08802	19.0	51.5
CH07802	33.0	6.0
CH07802	26.0	12.0
CH07802	40.0	15.0
CH07802	28.0	18.0
CH07802	37.0	21.0
CH07802	28.0	27.0
CH07802	34.0	32.0
CH07802	40.0	39.0
CH07802	27.0	45.0
CH07802	35.0	51.0

EB06801	16.2	1.0
EB06801	15.0	3.0
EB06801	32.0	5.0
EB06801	8.1	7.0
EB06801	12.4	9.0
EB06801	31.8	12.5
EB06801	16.5	17.5
EB06801	12.0	22.5
EB06801	18.5	27.5
EB06801	25.0	32.5
EB06801	23.3	37.5
H205801	21.3	0.5
H205801	31.2	1.5
H205801	30.0	2.5
H205801	30.7	3.5
H205801	29.7	4.5
H205801	34.2	5.5
H205801	35.0	6.5
H205801	37.3	7.5
H205801	38.5	8.5
H205801	40.3	9.5
H205801	42.3	11.0
H205801	37.3	13.0
H205801	43.0	15.0
H205801	40.0	17.0
H205801	45.3	19.0
H205801	39.0	22.5
H205801	48.0	27.5
H205801	38.5	32.5
H205801	41.0	37.5
H205801	48.0	42.5
H405801	27.0	0.5
H405801	28.0	1.5
H405801	34.6	2.5
H405801	30.3	3.5
H405801	29.6	4.5
H405801	30.0	5.5
H405801	38.8	6.5
H405801	49.0	7.5
H405801	43.3	8.5
H405801	58.5	9.5
H405801	37.0	10.5
H405801	26.0	12.0
A306791	32.8	3.5
A306791	36.4	4.5
A306791	39.5	6.5
A306791	33.4	11.0
A306791	42.1	21.0
A306791	42.4	23.0
A306791	38.5	27.0
A306791	47.8	36.0
A306791	46.9	38.0
A306791	43.9	40.0
A306791	41.8	44.0

EB06803	17.0	0.5
EB06803	18.0	1.5
EB06803	17.0	3.5
EB06803	30.3	4.5
EB06803	25.7	5.5
EB06803	20.5	6.5
EB06803	17.0	7.5
EB06803	31.7	8.5
EB06803	28.0	9.5
EB06803	24.0	11.0
EB06803	18.0	13.0
EB06803	26.0	17.0
EB06803	22.5	19.0
EB06803	25.0	22.5
EB06803	24.0	27.5
EB06803	19.7	32.5
EB06803	23.0	37.5
EB06803	15.3	42.5
EB06803	16.0	47.5
EB06803	17.0	52.5
EB06803	20.5	57.5

INTERSTITIAL DISSOLVED INORGANIC CARBON

STATION CODE	CONC. (MG/LITER)	DEPTH (CM)
EB06803	37.6	0.5
EB06803	34.5	1.5
EB06803	37.0	3.5
EB06803	22.2	4.5
EB06803	32.3	5.5
EB06803	36.0	6.5
EB06803	36.0	7.5
EB06803	27.8	8.5
EB06803	35.7	9.5
EB06803	49.5	11.0
EB06803	47.5	13.0
EB06803	32.5	17.0
EB06803	36.5	19.0
EB06803	33.5	22.5
EB06803	33.5	27.5
EB06803	37.3	32.5
EB06803	31.5	37.5
EB06803	49.0	42.5
EB06803	50.0	47.5
EB06803	45.0	52.5
EB06803	43.5	57.5
WB08802	18.0	3.5
WB08802	19.0	6.5
WB08802	13.0	9.5
WB08802	20.0	12.5
WB08802	30.0	15.5
WB08802	26.0	18.5
WB08802	34.0	21.5
WB08802	31.0	27.5
WB08802	26.0	33.5
WB08802	30.0	39.5
WB08802	29.0	51.5
CH07802	13.0	6.0
CH07802	41.0	12.0
CH07802	19.0	15.0
CH07802	32.0	18.0
CH07802	9.0	21.0
CH07802	35.0	27.0
CH07802	48.0	32.0
CH07802	12.0	39.0
CH07802	32.0	25.0
CH07802	18.0	51.0
A108804	4.0	3.0
A108804	2.0	6.0
A108804	7.0	9.0
A108804	2.0	12.0
A108804	1.0	15.0
A108804	4.0	18.0
A108804	5.0	21.0
A108804	5.0	27.0
A108804	6.0	33.0
A108804	16.0	39.0
A108804	18.0	51.0
A108804	12.0	57.0

H208802	39.0	1.5
H208802	30.0	4.5
H208802	44.0	7.5
H208802	32.0	10.5
H208802	31.0	13.5
H208802	39.0	16.5
H208802	46.0	19.5
H208802	43.0	25.5
H208802	53.0	31.5
H208802	40.0	43.5
H208802	46.0	49.5

INTERSTITIAL DISSOLVED TOTAL CARBON (INORGANIC AND ORGANIC CARBON)

STATION CODE	CONC. (MG/LITER)	DEPTH (CM)
EB06803	54.7	0.5
EB06803	52.5	1.5
EB06803	54.0	3.5
EB06803	52.5	4.5
EB06803	58.0	5.5
EB06803	56.5	6.5
EB06803	53.0	7.5
EB06803	59.5	8.5
EB06803	63.7	9.5
EB06803	73.5	11.0
EB06803	65.5	13.0
EB06803	58.5	17.0
EB06803	59.0	19.0
EB06803	58.5	22.5
EB06803	57.5	27.5
EB06803	57.0	32.5
EB06803	54.5	37.5
EB06803	64.0	42.5
EB06803	66.5	47.5
EB06803	62.0	52.5
EB06803	64.0	57.5
WB08802	30.0	3.5
WB08802	32.0	6.5
WB08802	34.0	9.5
WB08802	35.0	12.5
WB08802	46.0	15.5
WB08802	42.0	18.5
WB08802	52.0	21.5
WB08802	52.0	27.5
WB08802	48.0	33.5
WB08802	53.0	39.5
WB08802	48.0	51.5
CH07802	81.5	3.0
CH07802	46.0	6.0
CH07802	67.0	12.0
CH07802	59.0	15.0
CH07802	60.0	18.0
CH07802	46.0	21.0
CH07802	63.0	27.0
CH07802	82.0	32.0
CH07802	52.0	39.0
CH07802	59.0	45.0
CH07802	53.0	51.0

A108804	22.0	3.0
A108804	15.0	6.0
A108804	20.0	9.0
A108804	15.0	12.0
A108804	13.0	15.0
A108804	18.0	18.0
A108804	17.0	21.0
A108804	25.0	27.0
A108804	23.0	33.0
A108804	33.0	39.0
A108804	23.0	45.0
A108804	33.0	51.0
A108804	27.0	57.0
H208802	67.0	1.5
H208802	54.0	4.5
H208802	74.0	7.5
H208802	61.0	10.5
H208802	71.0	13.5
H208802	85.0	16.5
H208802	93.0	19.5
H208802	93.0	25.5
H208802	96.0	31.5
H208802	90.0	43.5
H208802	99.0	49.5

STATION CODE	SEDIMENT VOLATILE SOLIDS (PERCENT)	DEPTH (CM)
8311781	4.75	1.0
8311781	4.24	2.0
8311781	3.32	3.0
8311781	3.91	4.0
8311781	3.41	5.0
8311781	2.95	6.0
8311781	2.94	7.0
8311781	3.63	8.0
8311781	3.32	10.0
8311781	2.06	12.0
8311781	1.83	14.0
8311781	2.42	16.0
8311781	2.29	18.0
8311781	2.33	20.0
8311781	2.75	22.0
8311781	2.23	24.0
8311781	2.37	26.0
8311781	2.06	28.0
8311781	2.22	30.0
8311781	2.30	32.0
8311781	2.20	34.0
8311781	1.92	36.0
8311781	2.04	38.0
8311781	2.00	40.0
A108803	12.4	3.0
A108803	12.2	6.0
A108803	12.8	9.0
A108803	9.98	12.0
A108803	9.49	15.0
A108803	8.85	18.0
A108803	8.14	21.0
A108803	7.56	27.0
A108803	7.50	33.0
A108803	7.33	39.0
A108803	7.12	45.0
A108803	6.70	51.0
EB06802	8.30	2.0
EB06802	7.97	5.0
EB06802	6.11	8.0
EB06802	6.55	11.0
EB06802	7.10	14.0
EB06802	6.96	17.0
EB06802	7.07	20.0
EB06802	6.05	26.0
EB06802	5.59	32.0
EB06802	6.71	38.0
EB06802	6.23	50.0
EB06802	5.32	62.0

CH07801	7.82	2.0
CH07801	7.45	5.0
CH07801	7.24	8.0
CH07801	8.12	11.0
CH07801	8.03	14.0
CH07801	7.18	17.0
CH07801	7.10	20.0
CH07801	9.02	26.0
CH07801	7.43	32.0
CH07801	7.07	38.0
CH07801	6.73	48.0
H208802	16.5	1.5
H208802	15.4	4.5
H208802	16.0	7.5
H208802	16.0	10.5
H208802	17.6	13.5
H208802	19.8	16.5
H208802	16.8	19.5
H208802	7.90	25.5
H208802	13.2	31.5
H208802	9.40	37.5
H208802	3.77	43.5
H208802	10.4	49.5
WB08801	8.80	2.5
WB08801	8.88	5.5
WB08801	9.14	8.5
WB08801	8.49	14.5
WB08801	7.98	17.5
WB08801	8.50	20.5
WB08801	9.44	23.5
WB08801	7.06	26.5
WB08801	7.26	29.5
WB08801	7.99	32.5
WB08801	5.05	35.5
WB08801	4.91	38.5
H205805	11.91	2.0
H205805	17.00	5.0
H205805	17.47	8.0
H205805	16.25	11.0
H205805	16.87	14.0
H205805	17.22	17.0
H205805	19.03	20.0
H205805	20.65	23.0
H205805	9.29	32.0
H205805	8.84	38.0
H205805	10.64	44.0
H205805	10.64	51.0
H205805	10.29	57.0
H205805	9.65	64.0

EB06804	7.69	4.0
EB06804	7.48	7.0
EB06804	5.97	10.0
EB06804	5.37	13.0
EB06804	5.27	16.0
EB06804	4.90	19.0
EB06804	6.15	21.0
EB06804	5.73	27.0
EB06804	5.31	33.0
EB06804	3.66	39.0
EB06804	5.67	51.0
EB06804	5.95	63.0
H405802	14.51	2.0
H405802	13.56	5.0
H405802	14.42	8.0
H405802	14.90	11.0
H405802	15.44	14.0
H405802	16.64	17.0
H405802	4.48	20.0
H405802	4.57	26.0
H405802	2.10	32.0
H405802	0.87	38.0
H405802	1.28	44.0
H405802	3.00	56.0
IA10791	7.78	2.0
IA10791	5.07	7.0
IA10791	3.45	22.0
IA10791	4.27	27.0
IA10791	4.03	32.0
IA10791	5.68	37.0
IA10791	4.96	42.0
IA10791	5.03	47.0
IA10791	5.18	52.0

STATION CODE	SEDIMENT WATER CONTENT (PERCENT)	DEPTH (CM)
CH08792	70.03	1.0
CH08792	57.14	2.0
CH08792	65.18	4.0
CH08792	57.28	5.0
CH08792	46.52	6.0
CH08792	52.22	7.0
CH08792	53.33	8.0
CH08792	53.27	9.0
CH08792	54.49	10.0
CH08792	53.68	12.0
CH08792	50.01	14.0
CH08792	51.15	16.0
CH08792	50.86	18.0
CH08792	51.19	20.0
CH08792	47.25	22.0
CH08792	42.95	24.0
CH08792	48.57	26.0
CH08792	47.68	30.5
CH08792	39.35	32.5
CH08792	48.51	34.5
CH08792	52.16	36.5
CH08792	51.00	38.5
CH08792	50.01	40.5
CH08792	47.03	42.5
CH08792	47.89	44.5
CH08792	47.54	46.5
CH08792	39.97	50.5
CH08792	44.19	53.0
CH08792	47.98	55.5
CH08792	47.98	57.5
CH08792	48.32	59.5
CH08792	44.06	61.5
CH08792	50.08	65.5
CH08792	49.14	67.5
CH08792	47.93	70.0
A108793	85.40	1.0
A108793	84.48	2.0
A108793	84.98	3.5
A108793	84.81	4.5
A108793	82.20	5.5
A108793	82.31	6.5
A108793	85.14	7.5
A108793	84.24	8.5
A108793	83.77	9.5
A108793	82.85	10.5
A108793	82.84	12.5
A108793	81.03	14.5
A108793	77.94	17.0
A108793	76.35	19.0
A108793	75.51	21.0
A108793	76.02	23.0
A108793	76.21	25.5
A108793	74.73	27.5
A108793	69.00	29.5
A108793	67.47	31.5
A108793	66.89	33.5
A108793	67.64	35.5
A108793	67.13	37.5
A108793	68.04	39.5
A108793	68.93	41.5
A108793	67.78	43.5
A108793	67.18	45.5
A108793	65.92	47.5
A108793	64.98	49.5
A108793	65.56	51.5
A108793	66.20	53.5
A108793	64.39	57.5
A108793	65.68	59.5
A108793	65.36	63.5
A108793	66.18	66.0
A108793	65.16	68.0
A108793	64.89	70.5
A108793	63.96	74.5
A108793	63.01	76.5
A108793	63.95	78.5
A108793	64.12	80.5
A108793	64.14	82.5
A108793	63.52	84.5
A108793	62.29	89.5
A108793	62.93	90.5
IA10792	75.28	1.0
IA10792	73.49	2.0
IA10792	70.57	3.0
IA10792	68.76	4.0
IA10792	65.05	5.0
IA10792	60.42	6.0
IA10792	55.62	7.0
IA10792	50.38	8.0
IA10792	47.40	9.0
IA10792	45.01	10.0
IA10792	47.85	12.0
IA10792	45.50	14.0
IA10792	41.17	16.5
IA10792	43.37	18.5
IA10792	34.19	20.5
IA10792	36.48	22.5
IA10792	38.54	24.5
IA10792	42.46	29.0
IA10792	39.71	31.0
IA10792	42.82	33.0
IA10792	41.41	38.0
IA10792	41.91	43.0
IA10792	45.29	48.0
IA10792	45.47	53.0
IA10792	44.62	59.5
A107792	88.54	2.0
A107792	90.97	4.0
A107792	96.80	6.0
A107792	98.24	8.0
A107792	86.95	10.0

A107792	90.65	12.0
A107792	90.44	16.0
A107792	95.40	18.0
A107792	75.09	25.0
A107792	79.99	30.0
A107792	78.91	35.0
A107792	71.47	40.0
A107792	76.82	45.0
A107792	78.63	50.0
A107792	77.73	55.0
A107792	78.91	60.0
A107792	77.32	65.0
A107792	71.12	70.0
A107792	75.12	75.0
A107792	67.26	80.0
A107792	68.82	85.0
A107792	71.59	90.0
A107792	75.72	95.0
A107792	67.07	99.0
A109793	82.64	2.0
A109793	84.49	3.0
A109793	82.64	4.0
A109793	83.85	5.0
A109793	83.87	6.0
A109793	83.53	7.0
A109793	82.54	8.0
A109793	80.92	9.0
A109793	80.60	10.0
A109793	83.70	12.0
A109793	76.45	16.0
A109793	76.19	18.0
A109793	75.46	20.0
A109793	75.03	24.0
A109793	75.85	28.0
A109793	68.09	32.0
A109793	67.52	36.0
A109793	67.93	40.0
A109793	67.16	44.0
A109793	65.64	49.0
A109793	65.57	54.0
A109793	64.49	64.0
A109793	64.64	74.0
A109793	62.68	84.0
A106791	64.35	1.0
A106791	65.58	2.0
A106791	65.12	3.0
A106791	64.23	4.0
A106791	63.58	5.0
A106791	52.55	6.0
A106791	49.91	7.0
A106791	64.07	8.0
A106791	66.25	9.0
A106791	63.27	10.0
A106791	63.52	12.0
A106791	62.76	14.0
A106791	63.04	16.0
A106791	62.43	18.0
A106791	57.91	20.0
A106791	56.31	22.0
A106791	51.07	24.0
A106791	55.19	26.0
A106791	57.86	28.0
A106791	53.54	30.0
A106791	53.19	32.0
A106791	54.70	34.0
A106791	58.05	36.0
A106791	55.20	38.0
A106791	54.70	40.0
A106791	54.95	42.0
A106791	54.64	44.0
A106791	55.60	46.0
A106791	56.12	48.0
A106791	44.02	50.0
A106791	53.07	52.0
A106791	53.31	54.0
A106791	50.05	56.0
A106791	51.87	58.0
A106791	53.58	61.0
8310793	69.15	2.0
8310793	72.07	4.0
8310793	59.15	6.0
8310793	48.57	8.0
8310793	49.72	10.0
8310793	46.51	12.0
8310793	46.18	14.0
8310793	47.78	16.0
8310793	46.11	18.0
8310793	38.91	20.0
8310793	34.11	25.0
8310793	37.28	30.0
8310793	34.29	35.0
8310793	32.71	40.0
8310793	37.58	45.0
8307792	98.85	2.0
8307792	73.51	3.0
8307792	74.06	4.0
8307792	90.39	6.0
8307792	67.95	7.0
8307792	58.63	8.0
8307792	59.50	9.0
8307792	65.56	10.0
8307792	72.66	12.0
8307792	55.60	14.0
8307792	48.56	18.0
8307792	46.45	20.0
8307792	54.10	22.0
8307792	54.94	24.0
8307792	52.67	26.0
8307792	82.31	28.0
8307792	74.12	30.0
8307792	51.52	32.0
8307792	54.02	34.0
8307792	47.36	36.0
8307792	59.48	38.0

8307792	42.42	40.0
8307792	49.39	42.0
8307792	53.70	44.0
8307792	66.99	47.0
8307792	50.45	49.0
8307792	53.76	51.0
8307792	69.38	53.0
8307792	66.58	55.0
8307792	55.46	57.0
8307792	51.48	59.0
8307792	52.15	63.0
8307792	54.36	65.0
8307792	58.02	67.0
8307792	54.87	70.0
8307792	60.16	72.0
8307792	51.00	74.0
8307792	42.70	76.0
8307792	48.71	78.0
8307792	54.52	81.0
H208801	77.54	6.0
H208801	76.39	9.0
H208801	75.97	12.0
H208801	78.25	15.0
H208801	78.05	18.0
H208801	81.00	21.0
H208801	51.71	27.0
H208801	61.05	33.0
H208801	61.45	39.0
H208801	38.50	51.0
H208801	59.36	57.0
H208801	67.76	69.0
H208801	62.48	72.0
H208801	65.92	80.0
CH07801	55.56	2.0
CH07801	53.69	5.0
CH07801	50.15	8.0
CH07801	53.78	11.0
CH07801	54.29	14.0
CH07801	48.25	17.0
CH07801	47.63	20.0
CH07801	55.39	26.0
CH07801	51.68	32.0
CH07801	46.01	38.0
CH07801	52.75	42.0
CH07801	54.69	48.0
A108802	84.39	2.0
A108802	82.54	5.0
A108802	82.42	8.0
A108802	78.77	11.0
A108802	71.63	14.0
A108802	77.79	17.0
A108802	73.01	20.0
A108801	84.10	1.0
A108801	84.64	4.0
A108801	81.87	7.0
A108801	78.68	10.0
A108801	75.51	13.0
A108801	75.63	16.0
A108801	73.91	19.0
A108801	71.59	21.0
H208803	83.21	3.0
H208803	78.48	6.0
H208803	77.40	9.0
H208803	78.42	12.0
H208803	76.34	15.0
H208803	81.20	18.0
H208803	81.24	21.0
H208803	67.06	27.0
H208803	56.98	33.0
H208803	53.46	39.0
H208803	64.01	45.0
A108804	83.66	3.0
A108804	81.64	6.0
A108804	81.57	9.0
A108804	79.67	12.0
A108804	75.90	15.0
A108804	71.81	18.0
A108804	76.77	21.0
A108804	73.99	27.0
A108804	69.30	33.0
A108804	65.55	45.0
A108804	67.57	51.0
A108804	64.95	57.0
WB08802	74.77	3.5
WB08802	68.39	6.5
WB08802	65.27	9.5
WB08802	71.59	12.5
WB08802	65.93	15.5
WB08802	64.33	18.5
WB08802	68.30	21.5
WB08802	63.07	27.5
WB08802	63.34	33.5
WB08802	45.16	39.5
WB08802	44.11	45.5
WB08802	42.00	51.5
WB08801	74.81	2.5
WB08801	87.11	5.5
WB08801	68.75	8.5
WB08801	66.02	11.5
WB08801	65.04	14.5
WB08801	65.78	17.5
WB08801	65.61	20.5
WB08801	65.56	26.5
WB08801	59.21	32.5
WB08801	63.06	38.5
WB08801	64.69	44.5
WB08801	46.12	50.5
WB08801	45.71	56.5
CH07802	58.51	3.0
CH07802	53.04	6.0
CH07802	44.16	9.0
CH07802	54.44	12.0
CH07802	53.96	15.0
CH07802	48.18	18.0
CH07802	49.09	27.0
CH07802	51.81	33.0
CH07802	45.97	39.0
CH07802	50.58	45.0
CH07802	45.90	51.0

H208802	84.00	1.5
H208802	77.90	4.5
H208802	75.30	7.5
H208802	75.78	10.5
H208802	77.24	13.5
H208802	80.61	16.5
H208802	80.95	19.5
H208802	62.63	25.5
H208802	75.35	31.5
H208802	59.48	37.5
H208802	40.03	43.5
H208802	65.76	49.5
A108803	82.89	3.0
A108803	82.20	6.0
A108803	83.26	9.0
A108803	74.45	12.0
A108803	75.60	15.0
A108803	75.70	18.0
A108803	72.69	21.0
A108803	68.73	27.0
A108803	68.84	33.0
A108803	67.25	39.0
A108803	65.74	45.0
A108803	65.53	51.0
EB06801	73.75	1.0
EB06801	70.77	3.0
EB06801	69.21	5.0
EB06801	64.83	7.0
EB06801	63.85	9.0
EB06801	62.16	12.5
EB06801	60.98	17.5
EB06801	57.51	22.5
EB06801	45.65	27.5
EB06801	39.92	32.5
EB06801	50.19	37.5
EB06802	69.11	2.0
EB06802	69.40	5.0
EB06802	64.13	8.0
EB06802	61.50	11.0
EB06802	61.52	14.0
EB06802	62.65	17.0
EB06802	62.07	20.0
EB06802	57.66	26.0
EB06802	56.11	32.0
EB06802	57.31	38.0
EB06802	54.88	50.0
EB06802	54.27	62.0
EB06803	74.83	0.5
EB06803	72.80	1.5
EB06803	68.26	3.5
EB06803	72.39	4.5
EB06803	71.14	5.5
EB06803	68.96	6.5
EB06803	65.88	7.5
EB06803	64.59	8.5
EB06803	63.93	9.5
EB06803	63.22	11.0
EB06803	62.14	13.0
EB06803	62.99	15.0
EB06803	61.69	17.0
EB06803	62.15	19.0
EB06803	61.87	22.5
EB06803	58.02	27.5
EB06803	56.58	32.5
EB06803	56.41	37.5
EB06803	55.87	42.5
EB06803	56.12	47.5
EB06803	55.24	52.5
EB06803	56.31	57.5
EB06804	70.39	4.0
EB06804	69.56	7.0
EB06804	65.08	10.0
EB06804	62.36	13.0
EB06804	63.18	16.0
EB06804	61.02	19.0
EB06804	62.64	21.0
EB06804	59.24	27.0
EB06804	56.49	33.0
EB06804	58.00	39.0
EB06804	54.83	51.0
EB06804	54.08	63.0
H405801	79.71	3.0
H405801	77.76	6.0
H405801	72.59	9.0
H405801	73.87	12.0
H405801	74.17	15.0
H405801	75.08	18.0
H405801	76.41	21.0
H405801	75.57	24.0
H405801	55.26	27.0
H405801	28.83	30.0
H405801	34.31	33.0
H405801	25.67	36.0
H405801	26.51	45.0
H405802	77.57	2.0
H405802	73.89	5.0
H405802	73.86	8.0
H405802	73.70	11.0
H405802	74.91	14.0
H405802	79.43	17.0
H405802	48.68	20.0
H405802	45.65	26.0
H405802	26.92	32.0
H405802	23.65	38.0
H405802	22.76	44.0
H405802	35.90	56.0
H405804	79.12	0.5
H405804	77.03	1.5
H405804	77.04	2.5
H405804	74.07	3.5
H405804	74.64	4.5
H405804	75.08	5.5

H405804	76.56	6.5
H405804	75.17	7.5
H405804	59.59	8.5
H405804	57.15	9.5
H405804	22.23	10.5
H405804	26.28	12.0
H405804	24.23	13.0
H205805	82.71	5.0
H205805	77.27	8.0
H205805	75.39	11.0
H205805	76.94	14.0
H205805	77.25	17.0
H205805	79.75	20.0
H205805	81.96	23.0
H205805	59.74	32.0
H205805	63.29	38.0
H205805	64.08	44.0
H205805	63.41	51.0
H205805	66.13	57.0
H205805	64.57	64.0
H205806	85.16	0.5
H205806	84.60	1.5
H205806	83.49	2.5
H205806	77.62	3.5
H205806	77.23	4.5
H205806	76.77	5.5
H205806	76.02	6.5
H205806	75.90	7.5
H205806	76.70	8.5
H205806	77.38	9.5
H205806	78.61	11.0
H205806	76.47	13.0
H205806	81.33	15.0
H205806	82.26	17.0
H205806	80.80	19.0
H205806	77.05	22.5
H205806	62.56	27.5
H205806	54.97	32.5
H205806	55.70	37.5
H205806	45.03	42.5
H205806	60.85	47.5
H205806	63.67	52.5
H205806	63.41	57.5

STATION CODE	SEDIMENT POROSITY	DEPTH (CM)
CH08792	.854	1.0
CH08792	.769	2.0
CH08792	.824	4.0
CH08792	.770	5.0
CH08792	.685	6.0
CH08792	.732	7.0
CH08792	.741	8.0
CH08792	.740	9.0
CH08792	.750	10.0
CH08792	.743	12.0
CH08792	.714	14.0
CH08792	.724	16.0
CH08792	.721	18.0
CH08792	.724	20.0
CH08792	.691	22.0
CH08792	.653	24.0
CH08792	.702	26.0
CH08792	.695	30.5
CH08792	.619	32.5
CH08792	.702	34.5
CH08792	.732	36.5
CH08792	.722	38.5
CH08792	.714	40.5
CH08792	.689	42.5
CH08792	.697	44.5
CH08792	.694	46.5
CH08792	.625	50.5
CH08792	.664	53.0
CH08792	.698	55.5
CH08792	.697	57.5
CH08792	.700	59.5
CH08792	.663	61.5
CH08792	.715	65.5
CH08792	.707	67.5
CH08792	.697	70.0
A108793	.936	1.00
A108793	.932	2.0
A108793	.934	3.5
A108793	.933	4.5
A108793	.920	5.5
A108793	.921	6.5
A108793	.935	7.5
A108793	.930	8.5
A108793	.928	9.5
A108793	.923	10.5
A108793	.923	12.5
A108793	.914	14.5
A108793	.898	17.0
A108793	.890	19.0
A108793	.885	21.0
A108793	.888	23.0
A108793	.889	25.5
A108793	.881	27.5
A108793	.848	29.5

A108793	.838	31.5
A108793	.835	33.5
A108793	.839	35.5
A108793	.836	37.5
A108793	.842	39.5
A108793	.847	41.5
A108793	.840	43.5
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A108793	.829	47.5
A108793	.823	49.5
A108793	.826	51.5
A108793	.830	53.5
A108793	.819	57.5
A108793	.827	59.5
A108793	.825	63.5
A108793	.830	66.0
A108793	.824	68.0
A108793	.822	70.5
A108793	.816	74.5
A108793	.810	76.5
A108793	.816	78.5
A108793	.817	80.5
A108793	.817	82.5
A108793	.813	84.5
A108793	.805	89.5
A108793	.809	90.5
IA10792	.884	1.0
IA10792	.874	2.0
IA10792	.857	3.0
IA10792	.846	4.0
IA10792	.823	5.0
IA10792	.758	7.0
IA10792	.717	8.0
IA10792	.692	9.0
IA10792	.672	10.0
IA10792	.696	12.0
IA10792	.676	14.0
IA10792	.657	18.5
IA10792	.565	20.5
IA10792	.589	22.5
IA10792	.611	24.5
IA10792	.648	29.0
IA10792	.622	31.0
IA10792	.652	33.0
IA10792	.639	38.0
IA10792	.643	43.0
IA10792	.674	48.0
IA10792	.676	53.0
IA10792	.668	59.5
A107792	.951	2.0
A107792	.962	4.0
A107792	.987	6.0
A107792	.993	8.0
A107792	.943	10.0
A107792	.960	12.0
A107792	.959	16.0
A107792	.981	18.0
A107792	.909	30.0
A107792	.903	35.0
A107792	.862	40.0
A107792	.892	45.0
A107792	.902	50.0
A107792	.897	55.0
A107792	.903	60.0
A107792	.895	65.0
A107792	.860	70.0
A107792	.883	75.0
A107792	.837	80.0
A107792	.847	85.0
A107792	.863	90.0
A107792	.886	95.0
A107792	.836	99.0
A109793	.922	2.0
A109793	.932	3.0
A109793	.922	4.0
A109793	.928	5.0
A109793	.928	6.0
A109793	.927	7.0
A109793	.922	8.0
A109793	.914	9.0
A109793	.912	10.0
A109793	.928	12.0
A109793	.890	16.0
A109793	.889	18.0
A109793	.885	20.0
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A109793	.887	28.0
A109793	.842	32.0
A109793	.839	36.0
A109793	.841	40.0
A109793	.836	44.0
A109793	.827	49.0
A109793	.826	54.0
A109793	.819	64.0
A109793	.820	74.0
A109793	.808	84.0
8310792	.849	2.0
8310792	.866	4.0
8310792	.783	6.0
8310792	.702	8.0
8310792	.712	10.0
8310792	.685	12.0
8310792	.682	14.0
8310792	.696	16.0
8310792	.681	18.0
8310792	.614	20.0
8310792	.564	25.0
8310792	.598	30.0
8310792	.566	35.0
8310792	.549	40.0
8310792	.601	45.0

8307792	.995	2.0
8307792	.874	3.0
8307792	.877	4.0
8307792	.959	6.0
8307792	.841	7.0
8307792	.800	8.0
8307792	.786	9.0
8307792	.826	10.0
8307792	.869	12.0
8307792	.758	14.0
8307792	.684	20.0
8307792	.747	22.0
8307792	.753	24.0
8307792	.736	26.0
8307792	.921	28.0
8307792	.877	30.0
8307792	.727	32.0
8307792	.746	34.0
8307792	.692	36.0
8307792	.786	38.0
8307792	.648	40.0
8307792	.709	42.0
8307792	.744	44.0
8307792	.835	47.0
8307792	.718	49.0
8307792	.744	51.0
8307792	.850	53.0
8307792	.833	55.0
8307792	.757	57.0
8307792	.726	59.0
8307792	.731	63.0
8307792	.749	65.0
8307792	.775	67.0
8307792	.752	70.0
8307792	.791	72.0
8307792	.722	74.0
8307792	.651	76.0
8307792	.704	78.0
8307792	.750	81.0
H208801	.896	6.0
H208801	.890	9.0
H208801	.888	12.0
H208801	.900	15.0
H208801	.899	18.0
H208801	.914	21.0
H208801	.728	27.0
H208801	.797	33.0
H208801	.799	39.0
H208801	.610	51.0
H208801	.785	57.0
H208801	.840	69.0
H208801	.806	72.0
H208801	.829	80.0
H208802	.929	1.5
H208802	.898	4.5
H208802	.884	7.5
H208802	.887	10.5
H208802	.895	13.5
H208802	.912	16.5
H208802	.914	19.5
H208802	.807	25.5
H208802	.884	31.5
H208802	.786	37.5
H208802	.625	43.5
H208802	.828	49.5
H208803	.925	3.0
H208803	.901	6.0
H208803	.895	9.0
H208803	.901	12.0
H208803	.890	15.0
H208803	.915	18.0
H208803	.915	21.0
H208803	.836	27.0
H208803	.768	33.0
H208803	.742	39.0
H208803	.816	45.0
A108801	.930	1.0
A108801	.932	4.0
A108801	.919	7.0
A108801	.902	10.0
A108801	.885	13.0
A108801	.886	16.0
A108801	.876	19.0
A108801	.863	21.0
A108802	.931	2.0
A108802	.922	5.0
A108802	.921	8.0
A108802	.903	11.0
A108802	.863	14.0
A108802	.897	17.0
A108802	.871	20.0
A108803	.924	3.0
A108803	.920	6.0
A108803	.925	9.0
A108803	.879	12.0
A108803	.886	15.0
A108803	.886	18.0
A108803	.869	21.0
A108803	.846	27.0
A108803	.847	33.0
A108803	.827	39.0
A108803	.826	45.0
A108804	.927	3.0
A108804	.917	6.0
A108804	.917	9.0
A108804	.907	12.0
A108804	.887	15.0
A108804	.864	18.0
A108804	.892	21.0
A108804	.877	27.0
A108804	.849	33.0
A108804	.826	45.0
A108804	.837	51.0
A108804	.822	57.0

CH07801	.758	2.0
CH07801	.743	5.0
CH07801	.715	8.0
CH07801	.744	11.0
CH07801	.748	14.0
CH07801	.700	17.0
CH07801	.694	20.0
CH07801	.756	26.0
CH07801	.728	32.0
CH07801	.681	38.0
CH07801	.736	42.0
CH07801	.751	48.0
CH07802	.779	3.0
CH07802	.738	6.0
CH07802	.664	9.0
CH07802	.749	12.0
CH07802	.745	15.0
CH07802	.699	18.0
CH07802	.707	27.0
CH07802	.729	33.0
CH07802	.680	39.0
CH07802	.719	45.0
CH07802	.680	51.0
WB08801	.881	2.5
WB08801	.944	5.5
WB08801	.846	8.5
WB08801	.829	11.5
WB08801	.823	14.5
WB08801	.828	17.5
WB08801	.827	20.5
WB08801	.826	26.5
WB08801	.784	32.5
WB08801	.810	38.5
WB08801	.821	44.5
WB08801	.681	50.5
WB08801	.678	56.5
WB08802	.881	3.5
WB08802	.844	6.5
WB08802	.824	9.5
WB08802	.863	12.5
WB08802	.829	15.5
WB08802	.818	18.5
WB08802	.843	21.5
WB08802	.810	27.5
WB08802	.812	33.5
WB08802	.673	39.5
WB08802	.664	45.5
WB08802	.644	51.5
EB06801	.875	1.0
EB06801	.858	3.0
EB06801	.849	5.0
EB06801	.822	7.0
EB06801	.815	9.0
EB06801	.804	12.5
EB06801	.796	17.5
EB06801	.772	22.5
EB06801	.677	27.5
EB06801	.624	32.5
EB06801	.716	37.5
EB06802	.848	2.0
EB06802	.850	5.0
EB06802	.817	8.0
EB06802	.800	11.0
EB06802	.800	14.0
EB06802	.807	17.0
EB06802	.804	20.0
EB06802	.773	26.0
EB06802	.762	32.0
EB06802	.770	38.0
EB06802	.752	50.0
EB06802	.748	50.0
EB06803	.881	0.5
EB06803	.870	1.5
EB06803	.843	3.5
EB06803	.868	4.5
EB06803	.860	5.5
EB06803	.847	6.5
EB06803	.828	7.5
EB06803	.820	8.5
EB06803	.816	9.5
EB06803	.811	11.0
EB06803	.804	13.0
EB06803	.810	15.0
EB06803	.801	17.0
EB06803	.804	19.0
EB06803	.802	22.5
EB06803	.775	27.5
EB06803	.765	32.5
EB06803	.764	37.5
EB06803	.760	42.5
EB06803	.762	47.5
EB06803	.755	52.5
EB06803	.763	57.5
EB06804	.856	4.0
EB06804	.851	7.0
EB06804	.823	10.0
EB06804	.805	13.0
EB06804	.812	16.0
EB06804	.796	19.0
EB06804	.807	21.0
EB06804	.784	27.0
EB06804	.764	33.0
EB06804	.775	39.0
EB06804	.752	51.0
EB06804	.746	63.0
H405801	.908	3.0
H405801	.897	6.0
H405801	.869	9.0
H405801	.876	12.0
H405801	.878	15.0
H405801	.883	18.0
H405801	.890	21.0
H405801	.885	24.0
H405801	.755	27.0
H405801	.503	30.0
H405801	.566	33.0
H405801	.463	36.0
H405801	.474	45.0

H405802	.896	2.0
H405802	.876	5.0
H405802	.876	8.0
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H405802	.479	32.0
H405802	.436	38.0
H405802	.424	44.0
H405802	.583	56.0
H405804	.904	0.5
H405804	.893	1.5
H405804	.893	2.5
H405804	.877	3.5
H405804	.880	4.5
H405804	.883	5.5
H405804	.891	6.5
H405804	.883	7.5
H405804	.787	8.5
H405804	.769	9.5
H405804	.417	10.5
H405804	.471	12.0
H405804	.444	13.0
H205805	.923	5.0
H205805	.895	8.0
H205805	.884	11.0
H205805	.893	14.0
H205805	.895	17.0
H205805	.908	20.0
H205805	.919	23.0
H205805	.788	32.0
H205805	.812	38.0
H205805	.817	44.0
H205805	.812	51.0
H205805	.830	57.0
H205805	.820	64.0
H205806	.935	0.5
H205806	.932	1.5
H205806	.927	2.5
H205806	.897	3.5
H205806	.895	4.5
H205806	.892	5.5
H205806	.888	6.5
H205806	.887	7.5
H205806	.892	8.5
H205806	.895	9.5
H205806	.902	11.0
H205806	.890	13.0
H205806	.916	15.0
H205806	.921	17.0
H205806	.913	19.0
H205806	.894	22.5
H205806	.807	27.5
H205806	.753	32.5
H205806	.759	37.5
H205806	.672	42.5
H205806	.795	47.5
H205806	.814	52.5
H205806	.812	57.5