AN ABSTRACT OF THE THESIS OF

Harry R. Beller for the degree of Master of Science

in Oceanography presented on June 7, 1985

Title: Distributions of Polychlorinated Biphenyls (PCB's), Hydrocarbons and Fatty Acids Among Sedimentary Organic Matter Fractions

Abstract approved: Redacted for privacy

Bernd R.T. Simoneit

Previous field and laboratory studies have established that sedimentary organic matter plays an important role in the association of hydrophobic pollutants with aquatic sediments, yet very little attention has been paid to the importance of individual organic matter fractions in this process. In this study, selective extraction was used to examine the quantitative and qualitative distributions of PCB's and saturated hydrocarbons among free lipid (FL), humic acid (HA), and humin (HU) fractions of five estuarine sediments. The distributions of fatty acids among FL, HA, and HU were also examined to yield additional information on the biogenic sources of lipid material in these fractions.

In all samples, over 90% of the total sedimentary PCB's and hydrocarbons were easily extracted with FL (unbound) fractions. Fatty acids and two polar, chlorinated pollutants also detected in this study, hexachlorophene (HCP) and pentachlorophenol (PCP), were proportionately more concentrated in bound (HA and HU) fractions than the non-polar compounds. Such distributions are suggestive of chemical binding to refractory organic matter, particularly for HCP, which

was recovered only with HA fractions. Qualitative distributions of PCB's, hydrocarbons, and fatty acids indicated that unbound and bound assemblages may derive from different sources.

Selective extraction is a promising technique for investigating strongly bound polar pollutants, such as HCP, which apparently are not recovered by conventional solvent extraction.

DISTRIBUTIONS OF POLYCHLORINATED BIPHENYLS (PCB'S), HYDROCARBONS AND FATTY ACIDS AMONG SEDIMENTARY ORGANIC MATTER FRACTIONS

by

Harry R. Beller

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed June 7, 1985
Commencement June 1986

APPROVED:

Redacted for privacy

Professor of Oceanography in charge of major

Redacted for privacy

Dean of College of Oceanography

Redacted for privacy

Dean of Graduate School

Date of thesis presentation June 7, 1985

Typed by Harry R. Beller

To my parents, Joan and Bob

ACKNOWLEDGEMENTS

I am very grateful to my major advisor, Bernie Simoneit, for his support and guidance throughout my career at OSU.

I thank Orest Kawka, Jim Butler, Fred Prahl, Laurel Standley, and Monica Mazurek for their friendship, encouragement, and invaluable technical assistance, especially in times of dire crisis (weekdays from 9 - 5). Orest and Jim spent a great deal of time assisting me in a quixotic struggle against my two mechanical nemeses (a Finnigan mass spectrometer and an Osborne impersonal computer). I also thank Jeff Paduan and Roger Samelson for accompanying me in a musical exploration of white jazz.

I gratefully acknowledge those who provided samples, standards, and technical advice essential to this study. Samples were generously provided by Bruce Brownawell and John Farrington (WHOI), Richard Bopp (Lamont-Doherty Geological Observatory), and Tony Phillips (Hyperion, City of Los Angeles). Francis I. Onuska (National Water Research Institute, Ontario, Canada) provided a PCB standard and David Schmedding and Donald Griffin (both of Agricultural Chemistry, OSU) provided technical advice and some laboratory equipment. Dreas Nielsen (Oceanography, OSU) devised software to construct the histograms for figures in this thesis.

I also thank Louis Gordon for providing office space throughout my stay at OSU.

Nature is, above all, profligate. Don't believe them when they tell you how economical and thrifty nature is, whose leaves return to the soil. Wouldn't it be cheaper to leave them on the tree in the first place? This deciduous business alone is a radical scheme, the brainchild of a deranged manic-depressive with limitless capital. Extravagance! Nature will try anything once. This is what the sign of the insects says. No form is too gruesome, no behavior too grotesque. If you're dealing with organic compounds, then let them combine.... This is a spendthrift economy; though nothing is lost, all is spent.

-Annie Dillard, Pilgrim at Tinker Creek

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

DISTRIBUTIONS OF POLYCHLORINATED BIPHENYLS (PCB's), HYDROCARBONS AND FATTY ACIDS AMONG SEDIMENTARY ORGANIC MATTER FRACTIONS

INTRODUCTION

General

Environmental organic geochemistry properly includes the study of both biogenic ("natural") and anthropogenic compounds since these compounds often interact and are subject to the same natural processes. Relationships and interactions between natural and anthropogenic compounds are often neglected because they complicate our understanding of processes that are not well understood even under simple laboratory conditions.

This study focuses on the distributions of several classes of compounds among sedimentary organic matter fractions. The compound classes studied were polychlorinated biphenyls (PCB's), a class of synthetic anthropogenic compounds, saturated hydrocarbons, a class of compounds which comprises anthropogenic and biogenic constituents, and fatty acids, which are of biogenic origin.

PCB's, a ubiquitous and persistent class of pollutants, have been the object of considerable study since their identification in environmental samples by Soren Jensen (1966). The class of PCB's comprises 209 isomers, which are distinguished by the number and ring position of chlorine substituents on the biphenyl carbon skeleton (Figure 1).

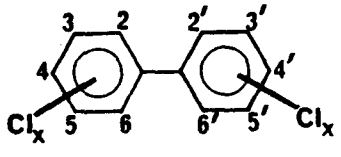

Figure 1. Generalized PCB molecule

PCB's were first synthesized in 1881 but were not commercially introduced until the 1930's. Appproximately 1.4 billion pounds of PCB's were produced in the US between 1929 and 1977, with a peak in production in 1970. Several properties of PCB's make them excellent for industrial use: they are non-flammable, thermally and chemically inert, and electrically and thermally insulating. For most major industrial uses, PCB's were added to oils and were used in electrical transformers and capacitors and in heat transfer systems. More detailed information on the production and use of PCB's is available (Miller, 1982; National Academy of Sciences, 1979; Nisbet and Sarofim, 1972).

Monsanto, the sole manufacturer of PCB's in the US, marketed mixtures of PCB isomers under the trade name Aroclor. Aroclor mixtures were of approximately known bulk chlorine content and were designated by four digit numbers (e.g., Aroclor 1242 or Aroclor 1254). The first two digits, 12, designated the general class of biphenyls (12 carbon atoms) and the last two digits denoted the approximate chlorine content of the mixture (as weight percent). The exception to this numbering system was Aroclor 1016, a mixture similar to Aroclor 1242 but lacking isomers containing more than five chlorines.

Under public pressure, Monsanto voluntarily limited sales of PCB's to closed electrical equipment applications in 1971. A partial ban was imposed on PCB use and manufacture in 1976 (Section 6(e) of the Toxic Substances Control Act) and was revised and finalized on May 31, 1979. The final ban prohibited the manufacturing, processing, distribution in commerce, and use of PCB's except in totally

enclosed systems (with certain exemptions) after July 2, 1979. An estimated 750 million pounds of PCB's were still in use in closed electrical systems in 1983. Roughly 70 million pounds of PCB's had accumulated in marine, estuarine, and freshwater sediments in and adjacent to North America by 1970 (Nisbet and Sarofim, 1972).

For the purposes of this study, sedimentary organic matter was separated into three fractions, free lipids (FL), humic acid (HA) and humin (HU). This established classification system is based on operational definitions. Free lipids are, by definition, compounds that are easily extractable with organic solvents (e.g., hydrocarbons and fatty acids). Although lipids are usually thought of as being biogenic (e.g., oils or waxes of organisms), many synthetic organic compounds are easily extractable and are included in free lipid extracts.

Humic acids are complex biogeopolymers soluble in alkali but not in acid whose genesis and structure are subjects of considerable debate and uncertainty. Humic acids are thought to be formed from biological detritus by some combination of several processes: chemical condensation reactions (e.g., Abelson and Hare, 1971; Hedges, 1978; Hoering, 1973), microbial activity (e.g., Flaig, 1964; Kawamura and Ishiwatari, 1984; Martin and Haider, 1971), oxidative free radical reactions (Harvey et al., 1983), and/or aggregation related to complexation (Tipping and Ohnstad, 1984; Wershaw et al., 1977). Certain constituents of organic detritus are thought to be important precursors of humic acids: amino acids and carbohydrates (e.g., Hedges, 1978; Hoering, 1973), lipids (Harvey et al., 1983; Hatcher, VanderHart et al., 1980; Stuermer and Harvey, 1978), and lignin

(e.g., Ertel and Hedges, 1984; Flaig, 1964). Unlike lipids, humic acids cannot be characterized in terms of specific molecular structures; they can only be characterized by bulk chemical properties (e.g., elemental composition, percent aliphatic carbon, total carboxyl or phenoxyl content). Humic acid structure and formation processes are probably dependant on the environment in which the polymers are formed (Degens and Mopper, 1975; Nissenbaum and Kaplan, 1972). For example, the availability of certain kinds of organic detritus (e.g., terrestrially-derived lignin vs. marine planktonic detritus) may influence the character of humic acids.

Humin (or protokerogen) is generally regarded as a diagenetically altered form of humic acid which is similar in overall structure but is more closely associated with sedimentary mineral matter (Hatcher, VanderHart et al., 1980; Nissenbaum and Kaplan, 1972; Wershaw et al., 1977). Humin is operationally distinguished from humic acid in that it is insoluble in both acid and base. Humic acid and humin constitute most of the organic matter in Recent sediments and soils (Bordovskiy, 1965).

Humic acid and humin have their own lipid assemblages, often referred to as "bound" lipids, which are operationally distinguished from free lipids in that they are not easily extractable with organic solvents. Functionalized, polar lipids may be chemically bound to humic substances whereas hydrophobic, non-polar lipids are thought to be sorbed to humic substances or entrapped within void spaces known to be prevalent in humic polymers (Khan and Schnitzer, 1972; 1978).

The objective of this study was to determine, by selective extraction, whether or not non-polar, non-ionic pollutants (namely,

PCB's and petroleum hydrocarbons) can become "bound" in estuarine sediments, and if so, whether their qualitative distributions reflect the nature of the incorporation process. Quantitative and qualitative fatty acid distributions among FL, HA, and HU were also analyzed to discern the natural lipid sources to each of these fractions. Similar studies have been carried out for some polar, biogenic lipids (e.g., fatty acids and sterols) in aquatic sediments and to a lesser extent, for hydrocarbons, but no such studies have been performed for PCB's or other non-polar, synthetic pollutants.

The incorporation of non-polar compounds into sedimentary organic matter is of interest in a pure geochemical sense, but also has practical environmental implications. "Bound" pollutants would be undetected in many environmental studies because such studies typically employ simple solvent extraction; the quantitative significance of bound pollutants must be ascertained to produce an accurate assessment of contamination. Also, biological availability of sedimentary pollutants could depend on the nature of their association with organic matter. For example, "bound" PCB's entrapped in humic matrices might be less accessible to benthic fauna than "free" PCB's.

The absence of detailed field studies of PCB-sedimentary organic matter interactions is unusual because existing research indicates that organic matter, and in particular, humic substances, play a critical role in PCB sediment geochemistry. The following literature review provides an overview of field and laboratory studies that address PCB-sediment associations in the greatest detail.

PCB-Sediment Associations - Literature Review

Introduction

Suspended and bottom sediments are widely regarded as a sink for hydrophobic pollutants released into aquatic systems. The mechanism offered to explain the "preference" of PCB's for sediments rather than water is equilibrium sorption or partitioning, a function of the aqueous solubility of PCB isomers and the attractiveness of the sedimentary matrix to PCB's (Bopp et al., 1981; Chiou et al., 1979; Dexter and Pavlou, 1978a; Pavlou and Dexter, 1979). The results of research in PCB geochemistry indicate the importance of equilibrium sorption for controlling PCB behavior in aquatic systems: there is strong agreement between field and laboratory observations of the quantitative distributions of PCB's between water and sediments (Bopp et al., 1981; Dexter and Pavlou, 1978a; Pavlou and Dexter, 1979; West and Hatcher, 1980).

Field Studies

The Roles of Organic Matter and Particle Size- Field studies of aquatic sediments indicate that PCB concentrations correlate directly with sedimentary organic carbon content and inversely with particle size in lacustrine (Simmons et al., 1980), fluvial (Sawhney et al., 1981), estuarine (Abdullah et al., 1982; Choi and Chen, 1976), and marine (Halcrow et al., 1974) sediments. In fact, considerable evidence suggests that the entire class of non-polar, chlorinated organic compounds, to which PCB's belong, associates preferentially with organic-rich, silt- or clay-size sediments. Our understanding

of the relative importance of particle size and organic carbon content for PCB associations is impaired because these properties tend to co-vary in sediments (Choi and Chen, 1976; Sawhney et al., 1981; Simmons and Kotz, 1982). However, there is disagreement among researchers regarding this issue. For example, Goerlitz and Law (1974) found that PCB distributions in stream sediments did not correlate as well with particle size as they did with organic carbon content, whereas Glooschenko et al. (1976) found no correlation among PCB concentration, particle size and organic carbon content in lacustrine samples.

Choi and Chen (1976) found that sedimentary PCB and DDT concentrations were linearly related to the humic acid content of estuarine sediments from Los Angeles Harbor. To the best of this author's knowledge, this is the only field study of PCB-sediment associations that addresses a fraction of organic matter other than free lipids. There are no published field studies of the distribution of PCB's among the established sedimentary organic matter fractions, namely, the free lipid (solvent extractable) , humic acid (base soluble, acid insoluble) and humin (solvent, acid and base insoluble) fractions.

Lab Studies

Methods- Most lab studies involve batch sorption experiments in which the distribution of PCB between a substrate (usually sediment) and water is examined (e.g., Griffin and Chou, 1981; Haque and Schmedding, 1976; Hiraizumi et al., 1979; Steen et al., 1978; Wildish et al., 1980). In general, PCB's (Aroclor mixtures or pure isomers) and sediment of known organic carbon content and particle size distribution are equilibrated with water in a centrifuge tube. Small

amounts of moderately polar solvents (such as acetone) are sometimes used to facilitate PCB dissolution into water. The PCB concentrations are kept well below their maximum water solubilities (ppb range) to eliminate the possibility of forming a crystalline phase. Once equilibrated, the mixture is centrifuged and the water and sediment phases are solvent extracted and analyzed. Sorption isotherms are generated by running successive samples while systematically varying either the sediment or initial PCB concentrations. Desorption isotherms are generated by decanting the supernatant from the sorption experiment and adding an equal volume of uncontaminated water.

The data for these experiments are described by an empirical relation, the Freundlich isotherm:

$$x/m = k_d C_{eq},$$

where x/m is the amount of PCB sorbed per unit mass of sediment, C_{eq} is the equilibrium concentration of PCB in water and k_d is a distribution coefficient. Another distribution coefficient, k_{oc}, is used to describe the distribution of PCB between water and sedimentary organic carbon (representative of organic matter). In the relation

$$x/m = k_{oc} C_{eq},$$

x/m represents the amount of PCB sorbed per unit mass of sedimentary organic carbon. This relation can also be expressed as $k_{oc} = k_d/(\text{fraction of organic carbon})$. The description of data in terms of k_{oc} standardizes sediments in terms of organic carbon content and is thus an indication of the importance of sedimentary organic matter in sorption. The use of k_{oc} is premised on the implicit assumption that PCB's associate preferentially with the organic matter of sediments;

the validity of this assumption is tested by the extent to which a single k_{oc} value can apply to sediments of various organic carbon contents.

The Roles of Organic Matter and Particle Size- The correlation of sedimentary organic carbon content to sedimentary PCB concentrations observed in field studies is strongly supported by sorption studies (e.g., Griffin and Chou, 1981; Hiraizumi et al., 1979; Karickhoff et al., 1979; Schwarzenbach and Westall, 1981; Steen et al., 1978; Wildish et al., 1980). Plots of k_d vs. fraction of organic carbon (slope = k_{oc}) for various sediments are presented in all but one of these studies (Hiraizumi et al., 1979) and are linear with very little data scatter on log-log plots. Other non-polar organic compounds tested in two of these studies behaved similarly (Karickhoff et al., 1979; Schwarzenbach and Westall, 1981).

The results of sorption studies also support the inverse correlation of particle size to PCB concentration found in field studies (Hiraizumi et al., 1979; Karickhoff et al., 1979; Steen et al., 1978; Wildish et al., 1980). Hiraizumi et al. (1979), like most other authors, explain this relationship in terms of specific surface area, in that fine particles generally have greater specific surface area and thus, higher sorptive capacity, than larger particles.

Laboratory sorption studies yield interesting information about the relative importance of particle size and organic carbon content for sorption of non-polar, non-ionic compounds. Strek and Weber (1982) compared the sorption capacity of an untreated terrestrial soil to that of the same soil treated with H_2O_2 and found that the former soil, higher in organic carbon but lower in specific surface

area, demonstrated greater sorption of PCB's. These authors commented that the type of surface (i.e., organic vs. inorganic) is as important as the amount of surface area for PCB sorption. Indeed, the findings of this and other sorption studies indicate that the type of surface (expressed as sedimentary organic carbon content) is more important than specific surface area (expressed as particle size) for PCB sorption. For example, Karickhoff et al. (1979) reported that for a given particle size isolate, differences in sorption were largely related to organic carbon content; the data of Steen et al. (1978) reveal a similar pattern. Wildish et al. (1980) found that estuarine sediments of identical organic carbon content but different particle size had identical k_d values.

In light of the observed correlations of sediment texture and composition to PCB sorption, it is not surprising that the sorption capacities of natural sorbents follow the order: humic acid > bulk natural sediments > sediments with organic carbon removed > clay minerals > sand (Haque and Schmedding, 1976; Sawhney et al., 1981). This ranking of sorbents relates decreasing sorption capacity with decreasing organic carbon content and, roughly, with decreasing specific surface area.

The Roles of Various Types of Organic Matter- Pierce et al. (1974) examined in detail the roles of specific sedimentary organic matter fractions in the sorption of a hydrophobic pollutant (p,p'-DDT). The study consisted of a series of sorption experiments using separate aliquots of a homogenized sediment from which various organic matter fractions had been removed. Thus, the sorbents used in the experiment were the original sediment, the sediment with free lipids re-

moved by Soxhlet extraction with benzene:methanol, the sediment with humic acid removed by 0.5 N NaOH extraction, and the sediment with oxidizable carbon removed by treatment with H_2O_2. Removal of these organic matter fractions had the following effects in reducing the sorption capacity of the original sediments: removal of free lipids - 6% reduction in k_d value relative to the original sediment, removal of humic acid - 63% reduction in k_d, and removal of all oxidizable organic matter - 75% reduction in k_d. Similar results were obtained in a comparable study of hexachlorobutadiene (HCBD) sorption, where free lipids, humic acid and oxidizable organic matter accounted for 26, 56 and 90% of the total sedimentary sorption capacity (Diachenko, 1981). These results indicate the overall importance of humic substances for the sorption of hydrophobic compounds.

Pierce et al. (1974) also examined the importance of lipoidal material associated with humic acid for sorption by Soxhlet extracting some isolated humic acid to remove the "free lipids" and then removing the more tightly held (humic acid-bound) lipids by acid hydrolysis followed by Soxhlet extraction. Soxhlet extraction of the humic acid reduced its original k_d by 63% and subsequent hydrolysis and extraction reduced the k_d by 67% relative to the original humic acid. Because DDT is structurally very similar to PCB's and behaves similarly in the environment, these results should be applicable to PCB's at least in a qualitative sense. The data indicate that lipids, both free and humic acid-associated, play an important role in the sorption of non-polar, non-ionic compounds. To wit, it could be estimated from the Pierce et al. study that the humic acid-associated lipids, which constitute far less than 1% of the total sediment

weight, are responsible for approximately 42% of the total sedimentary sorption capacity.

In addition to providing information about the differential sorption capacities of various sedimentary organic matter fractions, sorption experiments have also demonstrated how bulk chemical properties of organic matter, such as paraffinicity, can influence the sorption capacity of organic matter for hydrophobic compounds. Diachenko (1981) compared the sorption capacities of several humic acids from different locations and found that paraffinicity (as determined by ^{13}C NMR) was positively correlated with sorption capacity for hexachlorobutadiene. Hance (1969) observed that the sorption capacities of synthetic adsorbents increased logarithmically with increasing alkyl chain lengths. This relationship was derived from experiments with three non-ionic, nitrogen-containing herbicides (atrazine, EPTC and linuron) and may have implications for PCB-sediment associations in natural systems. The aliphatic character of sedimentary humic acid, which is related to the source of this material (marine vs. terrestrial; Hatcher et al., 1981; Hatcher, Rowan, et al., 1980), may influence the nature and extent of PCB associations with sedimentary organic matter.

Proposed Association Mechanisms- While they are largely descriptive, laboratory sorption experiments may provide some information about the mechanism of PCB-sediment associations. Lambert (1967; 1968) suggested that the sorption of a non-polar organic compound is analogous to the partitioning of the compound between water and an immiscible organic solvent, with sedimentary organic matter acting as a solvent in natural systems. This idea has been advocated by Briggs

(1973) and Chiou et al. (1979; 1983).

The observation that liquid-liquid partition coefficients (such as k_{ow}, the octanol-water partition coefficient) of non-polar compounds agree well with the k_{oc} values for these compounds is used to implicate a partitioning mechanism for PCB-sediment associations. Several studies have reported highly significant linear correlations between log k_{oc} and log k_{ow} for PCB and other non-polar compounds of the form

$$\log k_{oc} = a \log k_{ow} + b$$

(Briggs, 1973; Chiou et al., 1983; Karickhoff et al.; 1979, Schwarzenbach and Westall, 1981). This equation, derived theoretically by Lambert (1967; 1968), relates the partition coefficients of a given compound for two different immiscible water/organic solvent systems. The fact that the k_{oc} and k_{ow} values of PCB isomers obey this relation indicates that sedimentary organic matter may indeed act as a solvent for these compounds in the environment.

Chiou et al. (1979) cite the commonly reported observation that sorption isotherms of PCB's and other non-polar, non-ionic compounds show no indication of curvature (i.e., of site saturation) even at relatively high concentrations as evidence which is consistent with a partitioning model and which invalidates a surface adsorption model. Linear isotherms over broad concentration ranges have been found for PCB's (Chiou et al., 1983; Haque and Schmedding, 1976; Steen et al., 1978; Wildish et al., 1980; Voice et al., 1983), DDT (Pierce et al., 1974), and a variety of non-polar compounds (Schwarzenbach and Westall, 1981). An exception to this trend is the sorption to coarse sand, which is very low in organic carbon and appears to become

saturated at low solute concentrations (Karickhoff et al., 1979; Wildish et al., 1980).

Associations With Dissolved Organic Matter (DOM)

Whereas sedimentary organic matter associations tend to remove PCB's from the water column, DOM associations may have an inverse effect. Ballard (1971) and Wershaw et al. (1969) were among the first to suggest that dissolved humic substances could act as surfactants for hydrophobic compounds like DDT and dramatically enhance their aqueous solubilities in natural systems. A more recent study by Hayase and Tsubota (1983) supports the contention that dissolved humic substances are surface active. Hassett and Anderson (1979) used gel permeation chromatography to demonstrate that a tetrachlorobiphenyl isomer could associate with natural dissolved organic matter. This conclusion was based on the fact that the PCB isomer eluted at a volume corresponding to a molecular weight much greater than that of the free compound with a fraction that showed very high UV absorbance.

The liquid-liquid partitioning mechanism suggested for sedimentary organic matter associations is also implicated for DOM associations. Carter and Suffet (1982), using a dialysis technique, generated linear isotherms of free DDT vs. organic matter-associated DDT. Landrum et al. (1984), using reverse-phase column chromatography, found that the observed distributions of p,p'-DDT and 2,5,2',5'-PCB between DOM and water approximated their k_{ow} values. The procedure used for this study was to allow the pollutant to equilibrate with an aqueous DOM solution and to elute this solution through a column; free hydrophobic solutes adsorbed while humic-

associated solutes passed through the column.

MATERIALS AND METHODS

Introduction

The experimental objective of this study was to chemically isolate compound classes of interest (polychlorinated biphenyls, saturated hydrocarbons, and fatty acids) from a sediment matrix by isolating the organic matter fractions with which they were associated. This approach, more commonly used in studies of metals, is referred to as selective extraction and relies heavily on the operational definitions of sedimentary fractions. The extraction scheme used in this experiment roughly follows that of Van Vleet and Quinn (1978; 1979) in their studies of the distributions of hydrocarbons and fatty acids among free lipid, humic acid and humin fractions of sediments. Figure 2 provides a streamlined schematic diagram of the experimental procedure used of this study. As in the Van Vleet and Quinn studies, sediments were successively extracted with organic solvents and dilute base and then saponified, although in the present study, the extractions were designed to be more exhaustive and a more "pure" humic acid fraction (free of fine mineral matter and fulvic acid) was obtained.

The emphasis on operational definitions in this experiment involves some implicit ambiguities. For example, free lipids are broadly defined as organic solvent-soluble compounds while humic acid is defined as a base-soluble, acid-insoluble substance. It is possible that a portion of lipid material could be extracted with free lipids during solvent extraction and, if sediments are not pre-extracted, also with humic acid during base extraction. The problematic question thus arises: should these be classified as free or

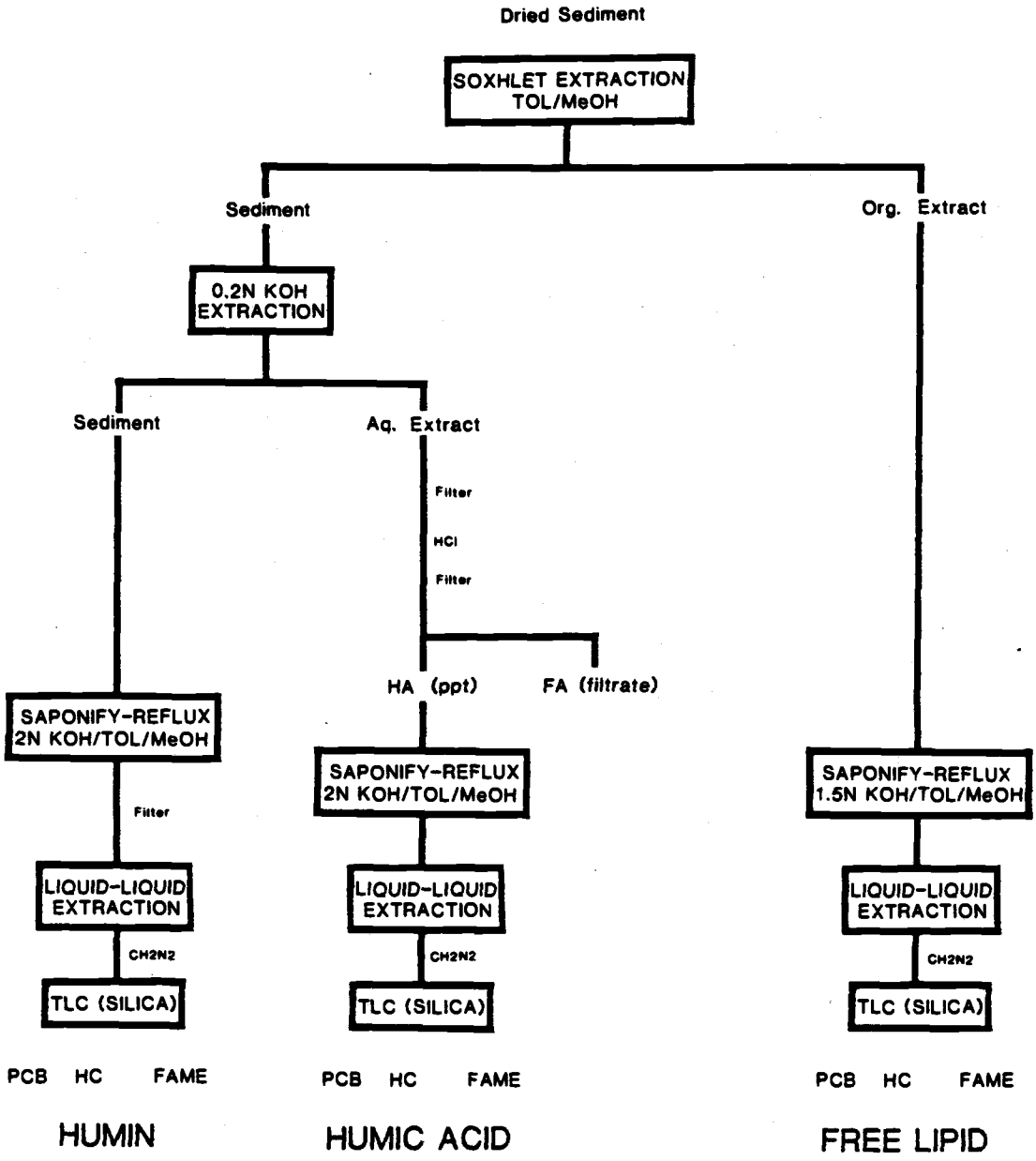

Figure 2. Schematic diagram of selective extraction procedure

humic acid-associated lipids? This experiment was designed with the consideration that bound lipid concentrations would be low relative to free lipid concentrations and thus, an attempt was made to efficiently remove any material that could be considered a free lipid from the sediment prior to humic acid extraction. In this way, the qualitative composition of the least accessible, most entrapped lipid material would be minimally obscured.

Free Lipid Fraction

Soxhlet Extraction

All samples were placed in large, pre-extracted cellulose thimbles (Whatman 62x180 mm, single thickness; cleaned for 30 hr with toluene/methanol, 1:3, v/v) in a large Soxhlet apparatus (500 ml capacity to the top of the siphon). The solvent mixture used was azeotropic toluene/methanol (1:3, v/v; bp=63.5^{o} C), which has been shown to be extremely efficient at extracting hydrocarbons from freeze-dried sediments (Rohrback and Reed, 1975). All solvents were distilled-in-glass, pesticide grade (Burdick and Jackson) and were used as received. For all but the Yaquina Bay sample, 700 ml of the azeotrope was cycled through the sediment for 30 to 40 hr, at which time the extract was stored and 700 ml of fresh azeotrope was added for further extraction. The solvent was not changed for the Yaquina Bay sample, which yielded a clear extract after only 8 hr of running time. Total running time for the Yaquina Bay sample was 53 hr, while the other samples, much richer in organic matter, were each extracted for 95 to 107 hr (depending on when the extract coming off the sediment appeared clear). The final volume of extract was measured

when the extraction was completed.

Saponification of Extract

The free lipid extract was saponified to make it comparable with the humic acid and humin lipid fractions, both of which underwent saponification. A 200 to 300 ml aliquot of the total free lipid extract was put in a 1 l round bottom flask along with 40 ml of 1.5 N KOH. The round bottom flask was attached to a Soxhlet condenser via a glass adapter and the mixture was saponified under reflux for 30 minutes.

When the saponified extract had cooled, it was poured into a 1 l separatory funnel along with 200 ml of lipid-free reagent water. The toluene layer was released, the remaining extract was acidified to pH 2 with solvent-cleaned, concentrated HCl and repeatedly extracted with toluene and hexane. More specifically, 50 ml of toluene, 50 ml of hexane and then 35 ml portions of toluene and hexane were used until the organic layers were colorless (from 3 to 8 solvent additions for a total solvent volume of 205 to 315 ml).

The combined organic extract (a mixture of toluene and hexane) was rotoevaporated to near dryness and transferred to a solvent-cleaned, pre-weighed vial with a Teflon cap liner. The extract was then methylated with an excess of diazomethane in 3 ml of diethyl ether and was blown down under N_2 to a volume of about 3 ml (Fales et al., 1973). The purpose of methylation was to derivatize fatty acids as methyl esters, thus facilitating chromatographic separations and analyses.

It should be noted that while strong base can alter some chlorinated hydrocarbons by dehydrohalogenation, it does not affect the

chemically inert class of PCB's (Hutzinger et al., 1974; Young and Burke, 1972). DDT (dichlorodiphenyltrichloroethane), however, is susceptible to dehydrohalogenation in the presence of base (Choi and Chen, 1976) due to the acidic tertiary hydrogen on its trichloroethane group. Thus, DDT in samples of this study is reported as DDE (dichlorodiphenyldichloroethylene).

Preparatory TLC

A portion of the derivatized extract was subjected to thin layer chromatography (TLC) to separate compound classes for subsequent gas chromatographic analyses. The TLC plates were coated with silica gel (Analtech, GHL) of 250 um thickness and were cleaned by successive elution with methanol (twice), diethyl ether (once) and hexane (twice). The silica was activated at 130^{o}C for 30 minutes. The elution solvent mixture was hexane:diethyl ether (185:13), which was found to adequately separate the hydrocarbon and methyl ester bands. Combined sample and vial weights were taken on a Mettler BH26 immediately before and after TLC application to determine the percent of extract applied to the plate.

Bands were visualized by exposing the plates to iodine vapor for several minutes. Saturated hydrocarbon and fatty acid methyl ester (FAME) fractions were identified by comparing the R_f values of sample bands to those of a standard eluted alongside the sample. Preliminary TLC tests indicated that PCB's in Aroclors 1242 and 1254 eluted in a broad band beneath the solvent front. Saturated hydrocarbons and PCB's were thus collected together in a broad band.

Hydrocarbon (both saturated and chlorinated together) and FAME fractions were scraped off the TLC plate and rinsed through a Buchner funnel with hexane (for the hydrocarbon band) or hexane and methanol

(for the FAME band). Hexane was used for the hydrocarbon/PCB fraction because it has been shown to efficiently separate PCB's and DDE from interfering chlorinated compounds on activated silica (Snyder and Reinert, 1971). The extracts were collected in 50 ml pear flasks and rotoevaporated to near dryness. The concentrated extracts were then transferred to solvent-cleaned vials with Teflon cap liners and were blown down under N_2 and stored until gas chromatographic analysis. The sample fractions that eluted below the ketone fraction of the TLC standard were stored in glass vials in silica-sorbed form.

Examination of TLC fractions beneath hydrocarbon/PCB bands in several samples indicated that preliminary TLC tests were not sufficiently detailed and that certain isomers eluted beneath collected bands and were excluded from all PCB analyses. Thus, PCB concentrations and chromatograms presented in this study are not entirely representative of actual assemblages. However, collection techniques were consistent and qualitative and quantitative intrasample comparisons are based on the same pool of isomers.

Because hydrocarbons were collected in a broad band to include chlorinated aromatics, some non-chlorinated aromatics were included in this fraction; this will be discussed further in the RESULTS AND DISCUSSION section. For the sake of brevity, hydrocarbons will be referred to as saturated despite the occurrence of some aromatics in some of these fractions. This is reasonable since these fractions consisted mostly of saturated hydrocarbons. Most polycyclic aromatic hydrocarbons eluted near the FAME band.

Sulfur Removal

One additional step was required before gas chromatographic analyses for samples containing sulfur (NB(0-3), NB(29-31) and LA). Hydrocarbon extracts from these samples were treated with several small drops of metallic mercury to precipitate the sulfur as HgS (Choi and Chen, 1976; Goerlitz and Law, 1971). Samples requiring treatment were easily identified during the TLC procedure by yellow bands which eluted in the hydrocarbon/FAME region of the plates. Mercury treatment effectively eliminated sulfur interferences from electron capture traces of all samples except LA (HU fraction), which retained large amounts of sulfur despite extensive mercury treatment. The mercury was cleaned with hexane before use and presented no contamination problems.

Procedural Blank

A procedural blank was performed by carrying solvents through the entire free lipid laboratory procedure (from Soxhlet extraction through gas chromatography) in the absence of sediments.

Humic Acid Fraction

Humic Acid Extraction

After Soxhlet extraction, the sediments (still in cellulose thimbles) were dried under vacuum for at least 30 hr to remove toluene and methanol. The sediments were then poured into a 1 gallon, solvent-cleaned glass jar with 1 l of 0.2N KOH. The jar was then sealed with a Teflon gasket, shaken vigorously for several hours and left to settle overnight. The supernatant KOH (humic and fulvic acid) solution was siphoned off the next day with a glass suction assembly connected to a vacuum line and was stored in a 4 l

glass beaker. The process of addition of 1 l of 0.2N KOH, vigorous shaking, gravitational settling overnight, and removal and storage of supernatant was repeated four times. A total of five extractions was deemed sufficient since the final extracts were much lighter in color than the initial extracts. Such exhaustive humic acid extraction was considered necessary in this study to make an accurate assessment of the proportion of total sedimentary PCB's, hydrocarbons, and fatty acids associated with humic acid. Van Vleet and Quinn (1978; 1979), who carried out a 2 hr. humic acid extraction with only 200 ml of alkali, may have underestimated the amount of total hydrocarbons and fatty acids in their humic acid fraction by insufficiently extracting humic acid. KOH was chosen as the extraction solvent because a similar base, NaOH, was shown to be efficient at isolating humic substances of widely ranging molecular weights (Hayes et al., 1975). NaOH could not be used in this study because it presented excessive contamination problems.

Filtration of Humic Extracts

The combined humic extract was then filtered through a large Buchner funnel assembly fitted with a GF/A glass fiber filter (Whatman, effective retention of 1.6um) and attached to a vacuum line. The extract was filtered to prevent the inclusion of fine particulate matter in humic solution. It should be noted that the true effective retention size of the glass fiber filter was clearly less than 1.6um soon after filtration started since fine particulate matter quickly coated the filter and significantly reduced the rate of filtration.

The filtered extract was then acidified with solvent-cleaned, concentrated HCl and the humic acid precipitate was allowed to settle for at least 24 hr. The acidified solution was passed through the

large Buchner funnel to separate humic acid (the precipitate) from fulvic acid (the acidic solution). The humic acid precipitate trapped on the glass fiber was rinsed into a 500 ml round bottom flask with 150 ml of 0.2N KOH. This step was intended to trap any residual mineral matter on the filter, removing it from the humic acid fraction. The material left on the filters after rinsing was light gray for all samples, visually confirming that the brown humic matter had been effectively re-dissolved. The glass fiber filters and the material they trapped were added to the residual sediment, which was saponified to yield the humin fraction. In this way, PCB's, hydrocarbons, and fatty acids associated with the fine particulate matter were carried through the procedure.

A 10% (vol.) aliquot of the liquid humic extract was saved while the remaining 90% of the extract was acidified and left to precipitate in a glass jar overnight. The supernatant was siphoned off the next day and the humic acid precipitate in the glass jar was frozen and then freeze-dried.

Saponification of Humic Acid

The purpose of saponifying the humic acid was to disperse it as much as possible in the presence of organic solvents and thus to release entrapped and sorbed lipids (i.e., PCB's, hydrocarbons, and fatty acids). It was assumed that the base would deprotonate the humic acid, increasing its ionic character and reducing possible H-bonding within the humic matrix. The freeze-dried humic acid was weighed and an aliquot (0.9 to 1.0g) was rinsed into a 1 l round bottom flask and dissolved in 150 ml of 2N KOH. 150 ml of methanol and 75 ml of toluene were added to the flask and the mixture was

refluxed for 1 hr, allowed to cool, and poured into a 1 l separatory funnel along with 100 ml of lipid-free reagent water. Liquid-liquid extraction and TLC separations of humic acid hydrolysates were carried out as for the free lipid extracts.

The choice of 2N KOH saponification was based on favorable results of studies by Neyroud and Schnitzer (1975), where high yields of fatty acids were produced by repeated saponification of a humic acid with 2N NaOH at 170^{o}C. Surprisingly, Schnitzer and Neyroud (1975) also showed that hydrolysis of a humic acid with 2N NaOH was less effective at releasing alkanes than neutral hydrolysis (in pH 7 water). Nonetheless, as Van Vleet and Quinn (1977) noted, saponification of humic acid in the presence of toluene, methanol, and water must be at least as efficient for hydrocarbon extraction as hydrolysis in water alone. It is likely that the inclusion of toluene in the saponification mixture enhances the solubility of non-polar, non-ionic compounds released from the humic acid and thus retards their re-association with colloidal matter during refluxing (Farrington and Quinn, 1971; Van Vleet and Quinn, 1977). To wit, Van Vleet and Quinn (1977) found that re-saponification of humic acid or sediments in a KOH/toluene/methanol mixture yielded less than 1% of the hydrocarbons generated from the first saponification. Similarly, Farrington et al. (1971; 1977) showed that re-saponification of sediments yielded less than 5% of the fatty acids generated from the first saponification.

A procedural blank for the humic acid procedure revealed that freeze-drying had resulted in significant contamination of the hydrocarbon fraction, obscuring the low levels of hydrocarbons contained

in these fractions. Thus, the 10% (vol.) liquid aliquots of humic acid that had not been freeze-dried were saponified in 75 ml of a 2:2:1 (2N KOH:MeOH:toluene ; v/v/v) mixture. Liquid-liquid extraction and TLC were carried out as for the extracts from the freeze-dried humic acid. The 10% (vol.) extracts were analyzed only for hydrocarbons, as freeze drying did not introduce fatty acid or chlorinated hydrocarbon contamination.

Procedural Blank

A procedural blank was performed for the entire humic acid procedure from KOH extraction through gas chromatographic analysis. Cleaned sand (annealed at 550° C for 4 hr and solvent rinsed) was carried through the blank procedure to account for the possibility that sediments and humic acid may have acted as sorbents for contaminants during the extensive handling steps.

Humic Acid Extraction of Untreated Sediments: A Procedural Test

An unextracted portion of sediments from Yaquina Bay, Oregon (hereafter referred to as YB-Q) was carried through the humic acid extraction procedure to assess the qualitative and quantitative significance of "carryover" of easily extractable lipids into the humic acid fraction. The humic acid procedure was identical to that used for other samples. Another portion of the Yaquina Bay sediment (sample YB) was carried through the entire experimental procedure and provided a basis for comparison of lipids in YB-Q humic acid to those in YB humic acid.

Ash Content Determination

The ash contents of freeze-dried humic acids were determined by measuring the weight loss of 20 to 80 mg humic acid aliquots after

combustion in a muffle furnace at 700-750° C for 3 hr (Povoledo and Pitze, 1979).

The ash contents were high, from 47 to 71%, due to a white precipitate that was present in all samples after freeze-drying. This material is presumed to be KCl, which could have been formed from the KOH and HCl used during the extraction and isolation procedure. The fact that this material was found to be almost completely soluble in water suggests that it could indeed have been a salt. Some of the ash may also have been due to silica leached from the soft glass containers during base extraction, which would have precipitated upon acidification.

Humin Fraction

Saponification of Sediments

The final treatment for the sediments was saponification with a strong base (2N KOH), a procedure intended to disperse humic acid-like polymers that were not affected by treatment with a more dilute base (0.2N KOH). Sediments that had undergone both free lipid and humic acid extraction were split into fractions of 45 to 70g and were saponified under reflux for 1 hr in 500 ml of a 2:2:1 (v/v/v) mixture of 2N KOH:MeOH:toluene. (Recall that the humic acid saponification was carried out in an identical mixture.)

The saponified slurries were allowed to cool and were then passed through a filter assembly like that used in the humic acid procedure. The filtered extracts were then poured into 1 l glass separatory funnels and liquid-liquid extracted as in the free lipid and humic acid procedures. The filtered, saponified extracts were extracted with toluene and hexane aliquots from 3 to 8 times using

150 to 425 ml of total solvent, depending on when the organic layers became clear. The organic extracts from all aliquots of a given sediment were combined, rotoevaporated, methylated, and applied to TLC plates as were the organic extracts from the free lipid and humic acid procedures.

Procedural Blank

A procedural blank was performed by carrying solvents through the entire process of saponification, filtration, preparative TLC, and GC in the absence of sediments.

Ancillary Procedures

Organic Carbon Analyses

Total carbon analyses were carried out for all five sediment samples and their humic acids by dry oxidation at >1200°C in a LECO induction furnace carbon analyzer (Weliky et al., 1983). The sediment samples were also analyzed for carbonate carbon by a wet oxidation (phosphoric acid) technique (Weliky et al., 1983). Sedimentary organic carbon values were determined by subtracting carbonate carbon measurements from total sedimentary carbon. The total carbon measurements for humic acids were assumed to be equivalent to organic carbon contents.

Cleaning of Glassware

Standard laboratory glassware (e.g., Soxhlet extractors, separatory funnels, flasks, transfer syringes) was cleaned by soap water rinsing followed by soaking for at least 12 hr in a solution of concentrated H_2SO_4 and NOCHROMIX (a strong oxidizing agent distri-

buted by Godax Laboratories, Inc.). After soaking in acid, the glassware was rinsed with tap water and deionized water and was left to dry. Before use, glassware was rinsed thoroughly with methanol, methylene chloride, and then hexane.

The large Buchner funnel assembly used to filter humic acid extracts and sediment slurries required an additional cleaning procedure. The glass fiber filter was placed in the assembly and the entire apparatus was rinsed with a series of solutions: KOH (0.2N for humic substances and 1.0 N for saponified sediments), followed by distilled water (to a neutral pH), methanol, and methylene chloride. After the methylene chloride had dried, the rinsing procedure was repeated and a final hexane rinse was made. Liquid cleaning of the filter was preferred to annealing because the latter may not be effective for refractory, chlorinated compounds like PCB's (Bevenue et al., 1971).

Cleaning of Acids and Bases

Preparation of sufficiently clean base was a significant problem in this study as fatty acids are major contaminants in commercial KOH and NaOH pellets. The following procedure was found to be sufficient, although a blank for each batch of KOH had to be performed to verify cleanliness: KOH pellets sufficient to make about 800 ml of 4N KOH were sonicated for several minutes in methylene chloride (twice) and hexane (once). The pellets were then slowly dissolved in lipid-free water and the solution was poured into a separatory funnel. The solution was extracted with 3 x 50 ml of methylene chloride and 2 x 50 ml of hexane. Care was taken to remove solvent from the solution after the last extraction.

Concentrated HCl was more effectively cleaned than KOH because acids existed in protonated form, not as K^+ salts, and partitioned into solvents more efficiently. 8 x 40 ml of methylene chloride was sufficient to clean 500 ml of HCl by liquid-liquid extraction.

Quantitation - Analyses by GC and GC-MS

Instrument Conditions

All gas chromatographic analyses were performed on high resolution, bonded, fused silica capillary columns.

Chlorinated hydrocarbons were analyzed by gas chromatography-electron capture detection (GC-ECD) on a Vista 44 GC system composed of a Varian Model 4600 GC and a Vista 401 Chromatography Data System Terminal. The DB-1701 capillary column (30 m, 0.25 mm i.d.; J & W Scientific) was temperature programmed from 65°C (held 1 min) to 230°C at 25°C/min, held at 230°C for 7.4 min, and then heated to 245°C at 10°C/min. The injector and detector temperatures were 260°C and 285°C. The ECD was a constant current, pulsed mode model. Helium was used as the carrier and nitrogen as the make-up gas; the linear velocity at 230°C was 50 cm/sec. All GC injections in this study were splitless with the split turned on 1 minute after injection. The retention time of decachlorobiphenyl under these conditions was approximately 26 minutes.

Non-chlorinated hydrocarbons and fatty acids (derivatized as methyl esters) were analyzed by gas chromatography-flame ionization detection (GC-FID) with a Hewlett-Packard Model 5890 GC interfaced with a Hewlett-Packard 3392 integrator. The DB-5 column (30 m, 0.25 mm i.d.; J & W Scientific) was programmed from 65°C (held 5 min) to 130°C at 10°C/min and then heated to 275°C at 5°C/min. Injector and detector temperatures were 290°C and 325°C, respectively. As for the ECD analyses, helium and nitrogen were the carrier and make-up gases; the linear velocity at 275°C was approximately 20 cm/sec.

Gas chromatography-mass spectrometry (GC-MS) was carried out on

selected samples either to confirm compounds identified by retention times on GC-FID or GC-ECD or to investigate the identities of unknown peaks of interest. Samples were run on a Finnigan 4000 GC-MS system composed of a Finnigan Model 9610 GC interfaced with a Finnigan Model 4021 quadrupole mass spectrometer. Mass spectrometric data were acquired and processed with a Finnigan-INCOS 2300 data system. The column and chromatographic conditions were comparable to those used for GC-FID. The mass spectrometer was run in electron impact mode with 70 eV electron energy. The ionizer temperature was 270°C, the transfer line (separator oven) was at 350°C and the manifold temperature was 135°C.

Quantitation Techniques

The quantitation of PCB's presents formidable difficulties to the analytical chemist and required special attention in this study. A reliable and feasible technique for accurate quantitiation of PCB's has not yet been developed. Early PCB research relied on packed column GC-ECD, which afforded poor separation of individual PCB isomers and thus provided an incomplete assessment of PCB behavior and distribution in the environment. Quantitation in such studies was performed by comparing selected peaks in samples to corresponding peaks in commercial Aroclor formulations that most closely resembled the sample. PCB concentrations were reported in terms of Aroclors (e.g., "ppm as Aroclor 1254"). This technique was predicated on the assumption that the relative isomeric compositions of environmental PCB assemblages did not differ from those of commercial mixtures or that ECD response to all PCB isomers was equal. Both of these assumptions are untenable: environmental PCB assemblages can differ considerably from commercial Aroclor mixtures due to the variable

physicochemical properties of isomers (e.g., aqueous solubility, volatility and susceptibility to biodegradation) (Duinker et al., 1980; Safe et al., 1983) and the ECD is known to have markedly variable response to PCB isomers depending on their degree of chlorination and secondarily, on their chlorine substitution patterns (Ballschmiter and Zell, 1980; Duinker and Hillebrand, 1983; Kerkhoff et al., 1982; Mullin and Filkins, 1981; Mullin et al., 1984; Mullin et al., 1983; Onuska and Comba, 1980; Onuska et al., 1983; Safe et al., 1983). Furthermore, commercial Aroclor mixtures are poor analytical standards because the PCB manufacturing process is not highly specific; molar percentages of isomers may differ from batch to batch even though mixtures may be qualitatively similar and of consistent bulk chlorine content (Albro et al., 1981; Duinker et al., 1980).

The recent development of capillary (high resolution) GC-ECD has improved our understanding of the behavior of individual PCB isomers by greatly enhancing chromatographic separation of complex PCB mixtures (Ballschmiter and Zell, 1980; Kerkhoff et al., 1982; Mullin and Filkins, 1981; Mullin et al., 1983; Onuska and Comba, 1980; Onuska et al., 1983; Safe et al., 1983). However, while capillary columns have mitigated the poor resolution problems of packed columns, the variable response of the ECD to PCB isomers still presents a major obstacle to accurate quantitation. One solution, proposed by Armour (1973), is to quantitatively perchlorinate all biphenyls in samples to decachlorobiphenyl so that total PCB's could be quantitated as one compound and variable ECD response would become irrelevant. The shortcoming of this technique is that the valuable qualitative information of isomeric distributions would be completely lost.

The most reliable way to quantitate PCB's by ECD is to use high resolution GC and sum all individual peaks corrected with their individual response factors. This approach, suggested by several authors (Ballschmiter and Zell, 1980; Mullin et al, 1983; Safe et al., 1983), requires complete separation of all PCB isomers, absolute identification of each peak, and knowledge of response factors for all possible PCB isomers (of which there are 209). These requirements are clearly impractical as no column phase has been found to completely resolve all isomers and many of the 209 isomers are virtually inaccessible and are quite expensive. Even though relative response factors have recently been determined for all 209 isomers (Mullin et al., 1984), the necessity to resolve and identify all PCB peaks still presents a problem. Thus, several researchers have developed techniques to establish relative response factors for resolved peaks (even if these peaks represent more than one isomer) (Albro et al., 1981; Webb and McCall, 1973; Zitko et al., 1971) or for homologous classes of PCB's (ie., di-, tri- tetrachlorobiphenyls, etc.) (Onuska et al., 1983; Rote and Murphy, 1971) and have quantitated on the basis of these response factors.

The PCB quantitation technique used in this study consisted of grouping sample peaks according to their retention times (strongly related to number of chlorine substituents) and correcting the summed area of each group with its appropriate response factor. This grouping technique was used because the inaccessibility and cost of authentic standards and the co-elution of isomers made identification of individual isomers impossible. Retention time boundaries for each homolog class of PCB's were constructed from the retention times of peaks of known chlorine content in a 1:1:1 (wt/wt/wt) standard

mixture of Aroclor 1242:1254:1260 (see Onuska et al., 1983 and Figure 3 for chromatograms of this standard). This technique was possible because retention times were very reproducible in this study and virtually all sample peaks had retention times corresponding to peaks in the 1:1:1 standard. Sample peaks were grouped within these retention time boundaries and summed to yield a total area for each homolog class. This grouping was subject to error because some isomers of different chlorine content co-eluted and because chlorine substitution patterns cause some variability in elution order trends normally controlled by chlorine content (e.g., a pentachloro isomer may elute after a hexachloro isomer even though most pentachloro isomers elute before most hexachloro isomers; see Mullin et al., 1984; Sissons and Welti, 1971; and Zitko et al., 1971 for details). This source of error was considered insignificant because all sample fractions were treated consistently and this experiment focuses on comparisons between sedimentary fractions, not on absolute isomer identification and quantification.

Accurate relative response factors for each homolog class of PCB's were needed to "level off" the differential response of the ECD across the range of homolog PCB classes. If no correction were made, then comparisons of PCB concentrations between sediment fractions with markedly different isomer distributions would be inaccurate. Relative response factors were estimated by using two types of data from recent PCB literature: (1) the quantitative isomer-specific compositions of commercial PCB mixtures (Aroclor 1242, 1254 and 1260) as reported by Albro et al. (1979; 1981) and (2) the response factors of each of these individual isomers, as reported by Mullin et al.

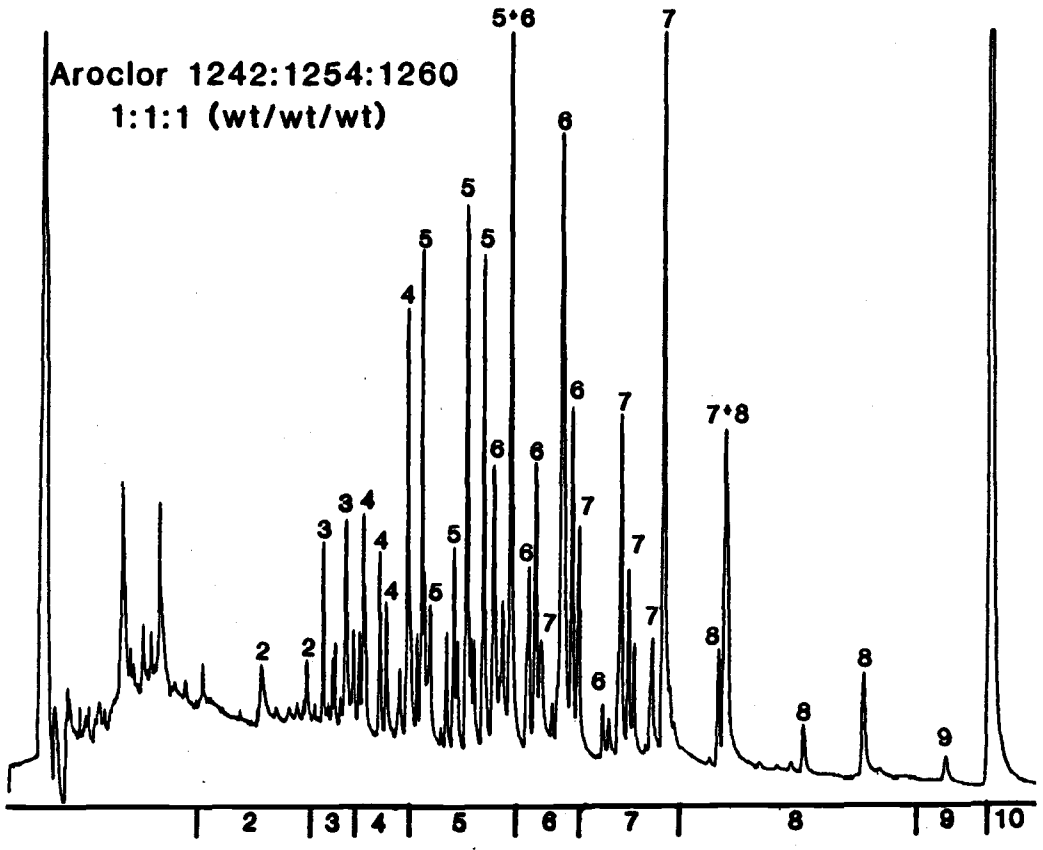

Figure 3. Capillary GC-ECD chromatogram of Aroclor 1242:1254:1260 standard. Approximate elution ranges of PCB homologs are delineated; numbering represents number of chlorine substituents.

(1984). The 45 isomers chosen from Albro et al., listed in Table 1, account for over 70 mole percent of the chlorobiphenyls in each of the common Aroclor mixtures and are assumed to represent most isomers found in environmental samples. Average response factors (relative to decachlorobiphenyl) for each homolog group were calculated from the 45 isomers, as shown in Table 1.

Table 1. Estimation of homolog RRF values based on selected isomers

Homolog Group	Isomer[a]	RRF[b] (avg.,std. dev.)
dichloro	4,8	0.107, 0.105
trichloro	16,17,18,20,22,28,31,32,33	0.18, 0.09[c]
tetrachloro	42,49,52,66,70,74,75	0.562, 0.097
pentachloro	85,86,91,97,99,101,110,118 120,121	0.618, 0.081
hexachloro	132,138,149,153,168	0.642, 0.096
heptachloro	171,180,181,183,185,193	1.156, 0.194
octachloro	194,196,201	1.14, 0.47
nonachloro	206,207,208	1.222, 0.224
decachloro	209	1.00 (by definition)

[a] isomer numbers according to Ballschmiter and Zell (1980)

[b] average relative response factor of homolog group to decachlorobiphenyl; response factors for isomers obtained from Mullin et al. (1984)

[c] corrected value, see text

Relative response factors were actually determined for several PCB isomers (numbers 8, 18, 28, 31, 116, 180, 194 according to the numbering system of Ballschmiter and Zell, 1980) and were used to

test the applicability of literature values to the ECD equipment used in this study. Agreement of experimentally determined values with literature values was good except for the trichloro isomers, so the average trichloro response factor was adjusted proportionately. The relative response factors used in this study, plotted in Fig 4, are illustrative of the linear trend of ECD resonse to chlorine content and the superimposed variability induced by different chlorine substitution patterns within a given homolog group. It is interesting that decachlorobiphenyl, which would be expected to have the highest response of all PCB isomers, has a lower response than the average hepta-, octa- and nonachloro isomers included in this study. Similar findings were published in another study of response factors (Onuska et al., 1983).

The quantitation technique was tested on a commercial mixture of known composition, Aroclor 1242. The weight percentages of each homolog class in the Aroclor were determined and compared to approximate values provided by the manufacturer (see Onuska et al., 1983). Table 2 displays the results and shows close agreement.

Table 2. Homolog Composition of Aroclor 1242 (wt. %)

	1Cl	2Cl	3Cl	4Cl	5Cl	6Cl	7Cl	8Cl	9Cl
Manufacturer	1.0	16.0	43.0	27.0	9.0	4.0	-	-	-
Determined	-	14.0	45.7	24.5	9.5	2.9	2.1	1.3	0.1

In summary, PCB's were quantified in this study by co-injecting decachlorobiphenyl (67.5 pg/ul) with each sample, summing areas within each retention time boundary and correcting these areas with their average group response factor. Concentrations of PCB's in each

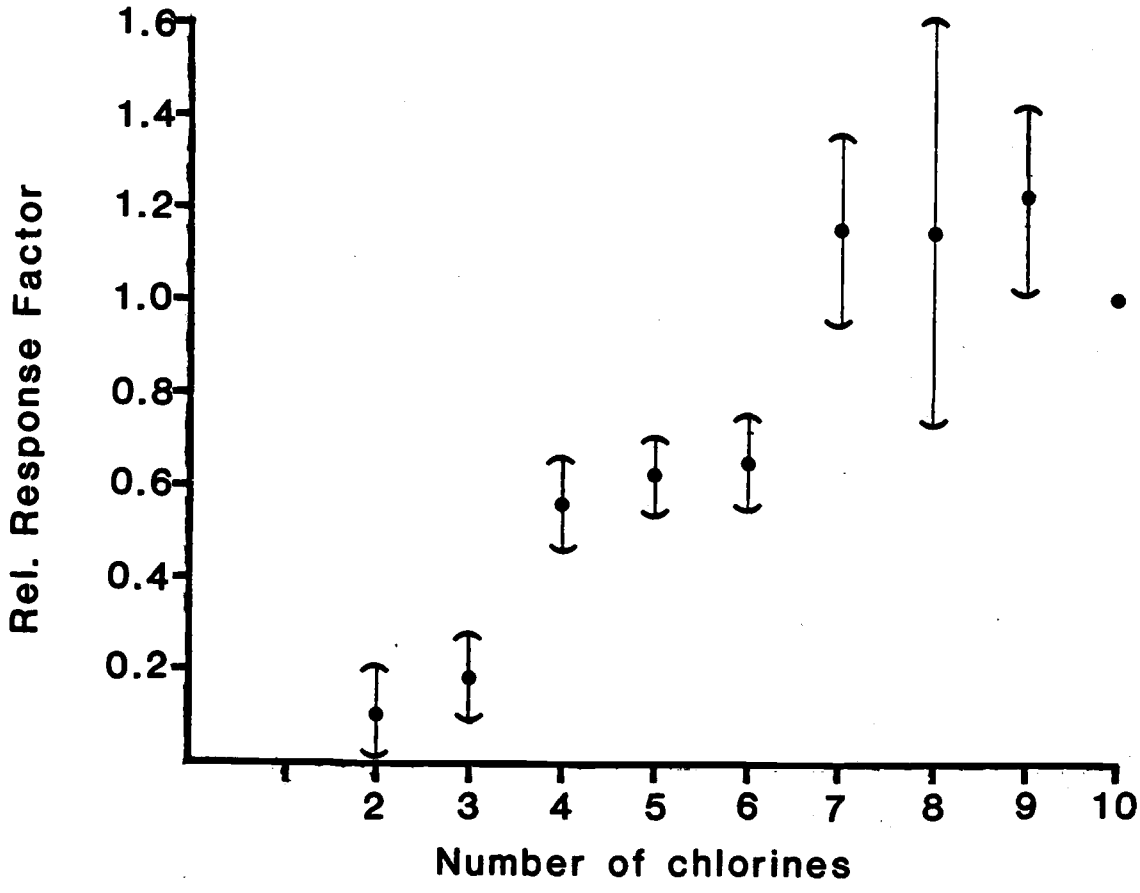

Figure 4. Response factors of PCB homologs (relative to decachlorobiphenyl) vs. chlorine content

sedimentary fraction were calculated according to the equations listed below:

Equation 1 - for a free lipid fraction

$$[Area_{homolog} \times RF_{std} \times RRF^{-1}] / [\text{total sed. wt. (dry)} \times \frac{\text{vol. extract aliquot}}{\text{vol. of total extract}} \times \frac{\text{wt. conc. extract applied to TLC}}{\text{wt. of total concentrated extract}} \times \frac{\text{vol. injected on GC}}{\text{total dilution volume for GC}}]$$

where: $Area_{homolog}$ = summed area of homolog group

RF_{std} = response factor of co-injection std., $wt._{std}/area_{std}$

RRF = relative response factor, $RF_{homolog}/RF_{std}$

Equation 2 - for a humic acid fraction

$$[Area_{homolog} \times RF_{std} \times RRF^{-1}] / [\text{total sed. wt. (dry)} \times \frac{\text{wt. dry HA saponified}}{\text{total dry wt. HA in sed.}} \times \frac{\text{wt. conc. extract applied to TLC}}{\text{wt. of total concentrated extract}} \times \frac{\text{vol. injected on GC}}{\text{total dilution volume for GC}}]$$

Equation 3 - for a humin fraction

$$[Area_{homolog} \times RF_{std} \times RRF^{-1}] / [\text{Total sed. wt. (dry)} \times \frac{\text{wt. conc. extract applied to TLC}}{\text{wt. of total concentrated extract}} \times \frac{\text{vol. injected on GC}}{\text{total dilution volume for GC}}]$$

For a number of samples, GC-MS was used in addition to retention time matching to confirm the presence of PCB's. PCB's are detectable by GC-MS even at very low concentrations in complex mixtures because of three distinctive features of chlorobiphenyl spectra: (1) intense M+ ions that make up a large percentage of the ion current, (2) clusters of ions separated by 2 mass units around chlorinated fragment ions that are due to the natural abundances of ^{35}Cl (75.8%) and ^{37}Cl (24.2%), and (3) successive expulsion of Cl atoms with odd electron ions (e.g., M+, M-Cl_2+, M-Cl_4+) being far more intense than even electron ions (e.g., M-Cl+, M-Cl_3+) (Hutzinger et al., 1974; Rote and Morris, 1973). Figure 5, a spectrum of a tetrachlorobiphenyl, is illustrative of the above characteristics. Thus, PCB's could be identified by mapping m/z values corresponding to the M+ ion for each homolog group of PCB's. As shown in Figure 6, PCB's could be identified by plotting m/z 222 (2 Cl), 256 (3 Cl), 292 (4 Cl), 326 (5 Cl), 360 (6 Cl), 394 (7 Cl), 430 (8 Cl), 464 (9Cl) and 498 (10 Cl). The map is slightly complicated by the fact that m/z values for M+ ions (e.g., m/z 290 for 4 Cl isomers) can also be M-Cl_2 + ions for higher isomers (e.g., m/z 290 for 6 Cl, M-Cl_2 ion). Some authors have suggested using selective ion monitoring for the above m/z values to increase the specificity and sensitivity of GC-MS analysis (Eichelberger et al., 1974; Liu et al., 1984). However, this technique would preclude data collection of non-PCB compounds (e.g., hydrocarbons, which were major components of extracts in this study) and would therefore be unsuitable for the present study.

Total hydrocarbon concentrations in each fraction were determined by electronically integrating the total area above the zero or

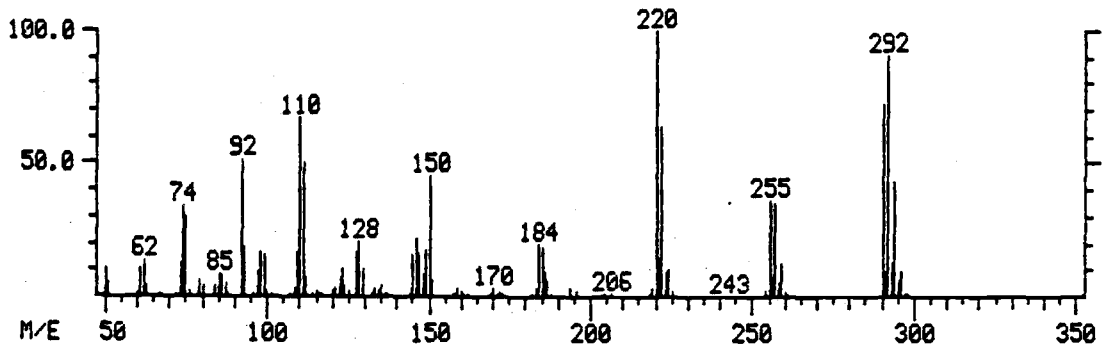

Figure 5. 70 eV mass spectrum of a tetrachlorobiphenyl

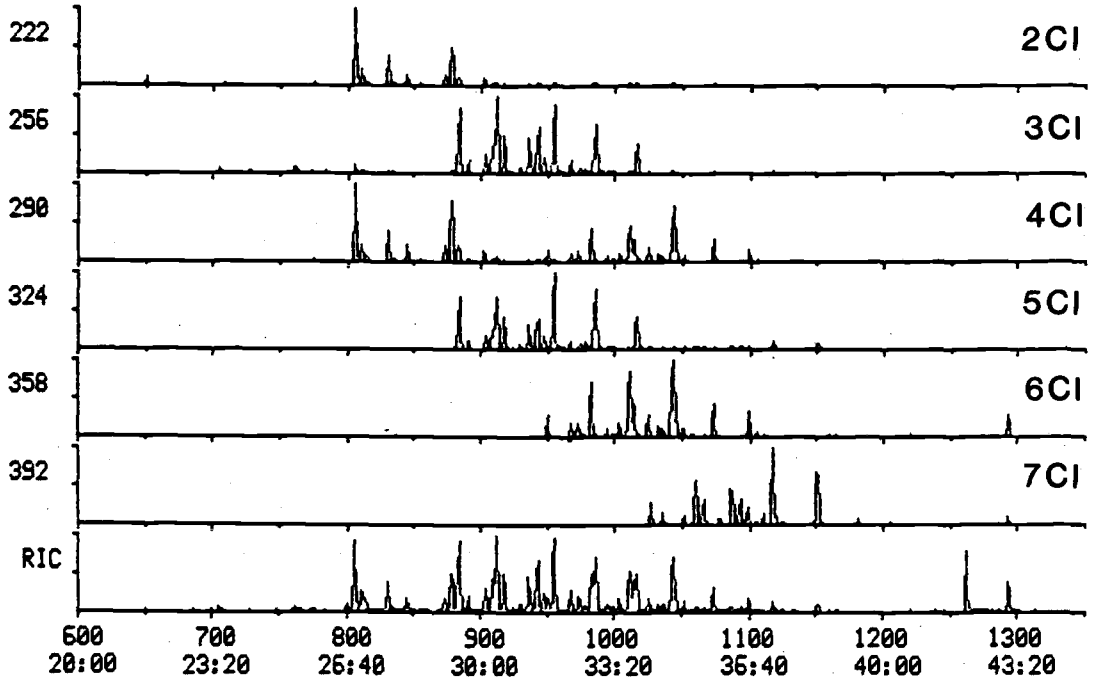

Figure 6. PCB "map" of an Aroclor 1254 standard

blank baseline; resolved hydrocarbon concentrations were determined by integrating peak areas above an unresolved envelope. Individual n-alkanes were identified by comparison of sample peak retention times to those of an external standard consisting of a homologous series of n-alkanes. Perdeuterated tetracosane (17.98 ng/ul) was co-injected with all sample fractions to establish an RF-std; equations analagous to Eq 1 - 3 were used to calculate hydrocarbon concentrations except that no relative response factors were used.

Fatty acid methyl ester (FAME) concentrations were quantified by comparing integrated peak areas of individual FAME components to the quantitative co-injection standard (perdeuterated tetracosane, as for the hydrocarbon fraction). Calculations analagous to Eq 1-3 were used and relative response factors were applied to FAME's of carbon chain length C_{24} and above. A quantitative standard consisting of a homologous series of n-fatty acid methyl esters provided retention times and response factors (relative to $C_{24}D_{50}$). GC-MS and ancillary standards (e.g., iso- and anteiso-15:0, n-16:1 and 18:1 methyl esters) were required for positive identification of peaks in some sample fractions. GC-MS analysis was necessary for FL fractions of NB(0-3), NB(29-31), and HR since polycyclic aromatic hydrocarbons (PAH's) co-eluted with the FAME band during TLC and individual PAH components co-eluted with FAME components during GC-FID analysis, particularly in the area of the branched C_{15} acids. These methyl ester components were determined by plotting a mass fragmentogram of m/z 74; iso- and anteiso- components could be distinguished by a comparison of (M-29)/(M-31) ratios (i.e., m/z 227/225) as described by Matsuda and Koyama (1977). Total FAME concentrations for each

fraction were calculated as the sum of all resolved, identified FAME's from C_{14} to C_{30} including quantitatively significant branched and unsaturated components (e.g., iso- and anteiso- 15:0, n-16:1 and n-18:1).

Sample Descriptions

Samples NB(0-3) and NB(29-31)

These samples were derived from the 0-3cm and 29-31cm horizons of a 0.25 m^2 large volume box core taken at Station 67 of Summerhayes et al. (1977) in Buzzards Bay, MA ($41^{o}36'30"N$, $70^{o}53'30"W$). The sedimentation rate at this site, which borders a dredged navigation channel, is unknown. Both samples consisted of fine-grained (silt/clay size), organic matter-rich sediments from a sulfate reducing environment. The samples were frozen after collection (September 1983) and were freeze-dried at OSU.

The Acushnet River and adjacent areas of Buzzards Bay are severely contaminated with PCB's, due predominantly to chronic releases from two electronic capacitor manufacturers, Aerovox, Inc. and Cornell-Dubilier Electronics Corp. Both companies used PCB's as impregnation fluids in capacitors from the 1940's (1941 for Cornell-Dubilier and 1947 for Aerovox) until 1978. The amount of PCB's used by just these two plants is staggering. To illustrate, Aerovox used approximately 500,000 kg/yr during its peak production year while Cornell-Dubilier used an estimated 1.4 million kg of Aroclor 1016 and 10,000 kg of Aroclor 1254 from 1971 to 1975 (Weaver, 1984). PCB's were released into the environment through various routes, but predominantly by direct discharge into the Acushnet River estuary and by indirect discharge through the New Bedford municipal wastewater treatment plant, whose effluent was released less than 1.5 miles from Station 67. The sludge from the municipal waste treatment plant was incinerated on site, resulting in significant atmospheric loadings of PCB's in this area (Weaver, 1984). Surface runoff of PCB-contaminated waste oils, used by the New Bedford public works department for

dust control on local roads (Weaver, 1982; 1984), may have been a significant source of PCB's to nearshore sediments. These and other releases of PCB's in New Bedford are well documented in published literature (Weaver, 1982; 1984; Metcalf and Eddy, Inc., 1983).

The New Bedford samples were donated by Bruce Brownawell and Dr. John Farrington of Woods Hole Oceanographic Institution.

Sample HR

Sample HR was collected with a Shipek grab sampler from a marginal cove approximately 59.8 river miles upstream from the southern tip of Manhattan, NY (May 1980). After collection, the sample was air-dried at room temperature, ground with a mortar and pestle, and then stored in an air-tight, teflon-lined aluminum can until extraction. The HR sediment was fine-grained and rich in organic matter. Judging from the apparent lack of sulfides in this sample, the sample site was not strongly reducing. The sample consisted of the top 10 cm of sediment, which, according to a ^{137}Cs profile of this core, encompassed 25 years of sedimentation (Richard Bopp, pers. comm.). The sediment was more fluvial than estuarine, as the salinity in the overlying water column ranged from 0 to 3% .

Point sources of PCB's in the Hudson River are well known. Two General Electric capacitor manufacturing plants (at Fort Edward and Hudson Falls, NY) released PCB's into the upper Hudson River from ca. 1950 to 1976. It has been estimated that these facilities used approximately 78 million pounds of PCB from 1966 to 1974, constituting roughly 15% of the U.S. domestic sales during that period (Hetling et al., 1978). The GE plants are situated far upriver from the HR site (nearly 140 miles), yet, removal of the Fort Edward Dam

in 1973 released and resuspended large amounts of heavily contaminated sediments and transported them far downstream. Documentation of PCB sources and distributions throughout the Hudson River is substantial (Bopp et al., 1981; 1982; Carcich et al., 1982; Hetling et al., 1978; Horn et al., 1979; Sloan et al., 1983)

Sample HR was provided by Dr. Richard Bopp (Lamont-Doherty Geological Observatory).

Sample LA

Sample LA was collected on December 14, 1983 from an area less than 0.75 miles from the Terminal Island sewage outfall in Los Angeles-Long Beach Harbor ($33^{o}43'51"$ N, $118^{o}14'27"$ W). This sample, a composite of several 0-2 cm sections of sediment cores, was frozen soon after collection and was freeze-dried at OSU. The sediment was fine-grained and rich in organic matter with significant amounts of sulfides indicative of reducing conditions.

Contamination by petroleum and chlorinated hydrocarbons (mostly DDT and derivatives) has been documented in the LA area (Venkatesan et al., 1980; Choi and Chen, 1976; Young et al., unpublished data); this is not surprising considering the intense industrial and shipping activity in and around the harbor. Dumping of dredge spoils has occurred around the LA site, so it is possible that this sample is not representative of pollutants introduced by the sewage effluent. Unpublished data of Young, Heesen, and McDermott provides evidence that, in the early 1970's, the major source of PCB's and DDT to LA-Long Beach Harbor was surface runoff (transported by the Los Angeles River) with less significant contributions from direct industrial discharges and aerial fallout.

Sample LA was collected and donated by Tony Phillips (Hyperion, City of Los Angeles).

Sample YB

Sample YB was collected with a stainless steel scoop from a tidal flat in the main drainage channel of King Slough, which feeds into Yaquina Bay near Newport, Oregon (approximately 44°36'14" N, 129°1'54" W). The sample consisted of surface sediments (approximately 0-2cm) that were covered by shallow water even during the low low tide that existed at the time of collection. YB was frozen soon after collection (July 1983) and later freeze-dried at OSU.

Sample YB is considered a pristine sample and was the first sample completed; it was used to test the feasibility of the experimental procedure.

All dried samples were passed through a 0.59 mm sieve to remove shell fragments and coarse debris. Small aliquots were saved for organic carbon analyses. The dry weights of the sample aliquots used for extraction were NB(0-3) - 91.2 g, NB(29-31) - 101 g, HR - 142 g, LA - 125 g, and YB - 200 g, although YB consisted of 873 g in total.

RESULTS AND DISCUSSION

Bulk Carbon-Related Sediment Properties

Bulk properties relating to organic carbon composition are presented in Table 3. All samples had relatively high sedimentary organic carbon contents, yet the humic acid yields were somewhat low relative to applicable literature values. A study of Terminal Island (Los Angeles-Long Beach Harbor) sediments reported C_{HA}/C_{org} values in the range of 2.4 to 53.8% with a median of 11.8% (Choi and Chen, 1976); another study reported a value of 2.7% for a sediment from Tanner Basin, on the southern California coast (Stuermer et al., 1978).

Table 3. Bulk Carbon-Related Properties of Samples

Sample	C_{org} (%)	C_{CaCO3} (%)	mg HA/g sed	C_{HA}/C_{org}[a] (%)	%C (HA)
NB(0-3)	5.76	0.15	8.6	5.2	35
NB(29-31)	4.79	0.12	9.3	2.9	15
HR	3.70	0.11	4.3	3.7	32
LA	3.71	0.44	6.2	1.2	7.0
YB	1.96	0.03	3.6	7.3	40

[a] humic acid carbon as percent of total carbon

All humic acid values are on an ash-free basis.

Literature values of the organic carbon contents of humic acids from a variety of environments (including coastal and littoral sediments) range from approximately 37 to 60% (Stuermer et al., 1978; Nissenbaum and Kaplan, 1972), whereas the values for humic acids in the present study range from 7 to 40%. One possible explanation for the low carbon contents of the humic acids in this study is that autoxidation occurred during the 5 day, 0.2 N KOH extraction pro-

cedure. A study of the autoxidation of humic acid dissolved in 1 N NaOH and exposed to oxygen for 30 days revealed that about 61% of the humic acid (as total weight) and 61% of the humic acid organic carbon was oxidized either to fulvic acid (with a relatively larger percentage of oxygenated functional groups) or to CO_2 (Swift and Posner, 1972).

Polychlorinated Biphenyls

Quantitative Results

Table 4 displays the distributions of PCB's and DDE among FL, HA and HU fractions (as percent of total sedimentary concentrations) and the total sedimentary concentrations on a dry weight basis. As discussed in the Experimental section, these values are not absolute and are intended only to denote relative trends in PCB distributions. Sample YB is not included because it contained only trace amounts of chlorinated compounds which could not be confirmed as PCB's. Significant peaks that were identified as being non-PCB's (such as methylated pentachlorophenol and hexachlorophene, to be discussed later) were not included in this quantitation.

Table 4. Relative PCB and DDE Distributions[a]

Sample	FL	HA	HU	Total
NB(0-3)	91%	0.96%	8.1%	1.3 ppm PCB
NB(29-31)	99%	0.12%	1.2%	6.5 ppm PCB
HR	98%	0.87%	1.4%	1.4 ppm PCB & DDE
LA	99.9%	-	0.10%	100 ppb DDE
	ca. 100%			91 ppb PCB

[a] as percent of total sedimentary concentrations

At least 90% of the total PCB's and DDE in these sediments was associated with free lipid fractions. This finding is not in accord with sorption experiments (e.g., Pierce et al., 1974), which indicate that at least half of the PCB's or DDT should be associated with humic fractions of the sediment. Thus, sorption may not be a controlling factor in the distribution of PCB's among sedimentary organic matter fractions.

The concentration data of the New Bedford samples also casts doubt upon the role of sorption as a prevailing process; it suggests

instead that free and bound fractions derived from different sources. The PCB concentrations of NB(0-3) and NB(29-31) humin fractions are similar, 102 and 77 ppb, whereas the free lipid PCB concentrations differ by over a factor of five, 1.1 and 6.4 ppm. If the sources for the free and bound fractions were the same and a concentration dependent process like sorption were operating, one would expect the PCB concentration ratios NB(0-3)FL/NB(29-31)FL and NB(0-3)HU/NB(29-31)HU to be similar. This argument requires that the concentrations of organic matter fractions be similar in both samples. While absolute concentrations of FL and HU were not determined, the HA concentrations of NB(0-3) and NB(29-31) were similar, 8.6 and 9.3 mg ash-free humic acid/g dry sediment (Table 3).

The absolute PCB concentrations for the Hudson River and New Bedford samples in Table 4 do not agree well with measurements made in other laboratories. R. Bopp, using packed column GC-ECD, reported a 10 ppm Aroclor 1254 concentration in the HR sample and B. Brownawell reported Aroclor 1254 concentrations of 10.1 and 22.8 ppm and Aroclor 1242 concentrations of 6.45 and 2.40 ppm for NB(0-3) and NB(29-31), respectively (pers. comm.). It is not unusual to find widely varying PCB analyses because of different quantitation techniques employed, yet the results for this study seem consistently low. Systematic losses of PCB's during the TLC procedure, discussed earlier, could not account for order of magnitude differences in quantitation. The concentrations of DDT compounds (analyzed as DDE in this study) and PCB's in the LA sample correspond well to values obtained in another study of Terminal Island sediments (Choi and Chen, 1976).

Reports of spatial distributions of PCB's are available for the Acushnet River (New Bedford)/Buzzards Bay area (Malcolm Pirnie, Inc., 1982; Metcalf and Eddy, Inc., 1983; New England Aquarium, 1973), the upper and lower Hudson River (Bopp et al., 1981; 1982; Carcich and Tofflemire, 1982; Hetling et al., 1978; Horn et al., 1979), Terminal Island (Los Angeles Harbor) (Choi and Chen, 1976), and Yaquina Bay (Fuhrer and Rinella, 1983).

Blanks - Procedural blanks revealed negligible chlorinated hydrocarbon contamination for the FL and HU fractions but a significant contamination problem for HA fractions. The apparent contamination values of HA fractions (as (PR BL/sample)x100) are 30% for NB(0-3), 33% for NB(29-31), 32% for HR, and 28% for LA. Appendix Figure 1A displays a chromatogram of the HA procedural blank.

Precision - The precision of gas chromatographic (ECD) analyses expressed as the coefficent of variation ((standard deviation/mean)x100) was found to be 6.2% (n=15). This value was determined by averaging the response factors for the quantitative decachlorobiphenyl standard that was co-injected with each sample fraction.

Qualititative Results

Relative isomeric distributions of PCB's in significantly contaminated samples , NB(0-3), NB(29-31), and HR, will be discussed in this section. The isomeric distributions of common commercial mixtures of PCB's, Aroclors 1242, 1254 and 1260, are presented for comparative purposes (Figure 7).

Figures 8 - 10 present the free lipid, humic acid and humin ECD

chromatograms from samples NB(0-3), NB(29-31), and HR. The abcissa is divided into the approximate homolog elution ranges discussed in the MATERIALS AND METHODS section. The histograms in these figures present the data in a more refined form, with PCB peaks summed within homolog groups and corrected with response factors.

The PCB distributions of the FL fractions of the New Bedford samples (Figures 8 and 9) don't closely resemble the commercial Aroclor mixtures that were used in this area (Aroclor 1242 and lesser amounts of Aroclor 1254 before 1972 and Aroclor 1016 from 1972 to 1978; Weaver, 1982; 1984). Sample NB(29-31) is more similar to Aroclor 1254 and may reflect the inputs of this commercial mixture that occurred before 1972. The most outstanding differences between these samples and commercial mixtures are the enrichment of pentachloro isomers and the relatively low levels of di- and trichloro isomers in the samples. These features have been noted in other studies (Abdullah et al., 1982; Bopp et al., 1981; Ballschmiter and Zell, 1980) and were attributed to water washing and/or preferential biodegradation of lower isomers (less than four chlorines); both water solubility and biodegradability tend to increase with decreasing chlorine content (Dexter and Pavlou, 1978b; Miller et al., 1984; Clark et al., 1979; Furukawa and Matsumura, 1976; Furukawa et al., 1978). Similarly, the FL fraction of sample HR, while sharing some of the characteristic early eluting components of commercial mixtures used in this area (Aroclor 1242 from 1966 to 1970 and Aroclor 1016 thereafter; Bopp et al., 1981), contains a more significant component of highly chlorinated isomers up to and including decachlorobiphenyl (Figure 10).

Qualitative PCB distributions of the New Bedford samples, like

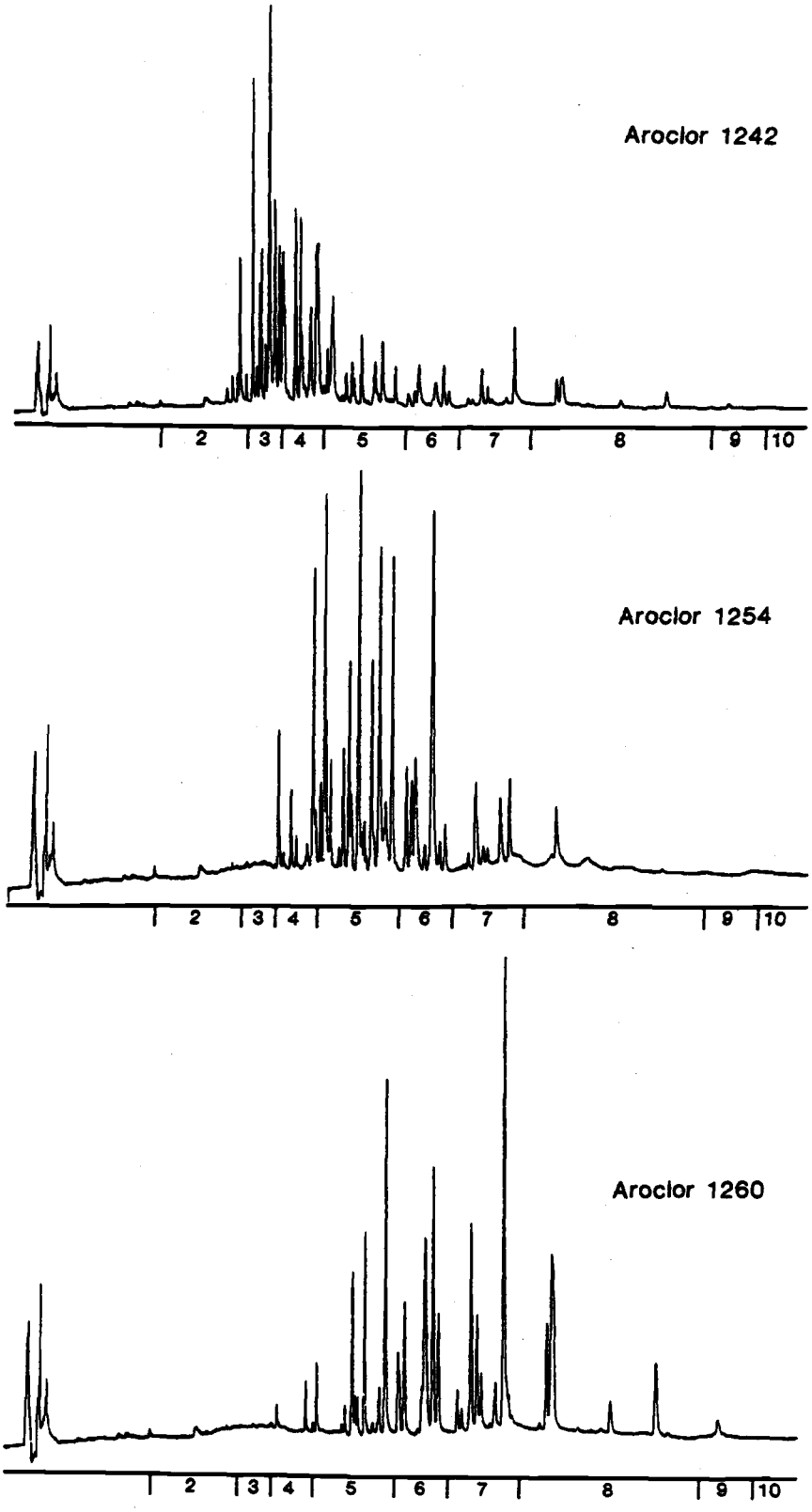

Figure 7. Capillary GC-ECD chromatograms of Aroclors 1242, 1254, and 1260

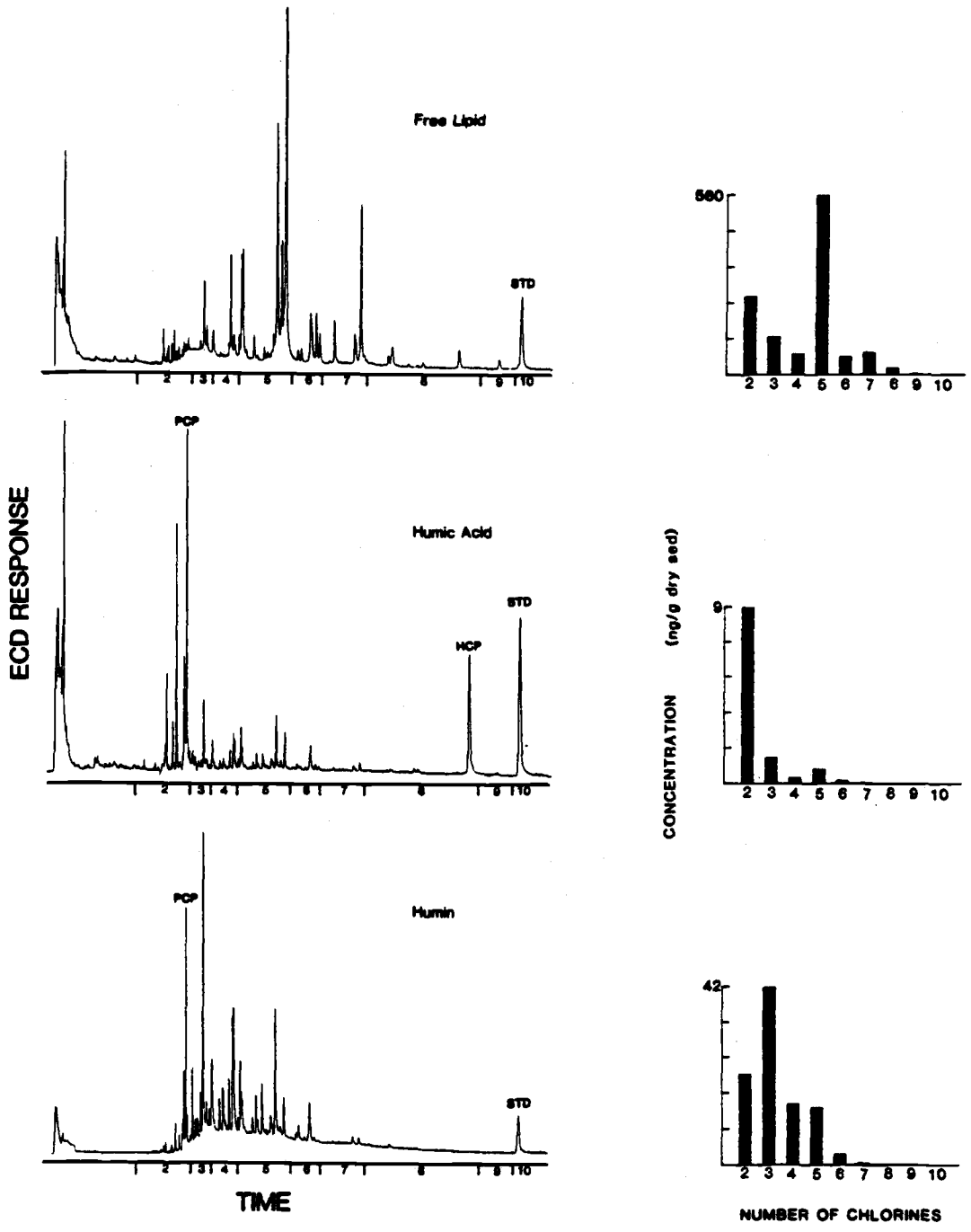

Figure 8. Capillary GC-ECD chromatograms of FL, HA, and HU fractions of sample NB(0-3). STD - co-injection standard, decachlorobiphenyl; PCP - pentachlorophenol (as methyl ether derivative); HCP - hexachlorophene (as dimethyl ether derivative). Homolog group concentrations, corrected with response factors, are presented in histograms.

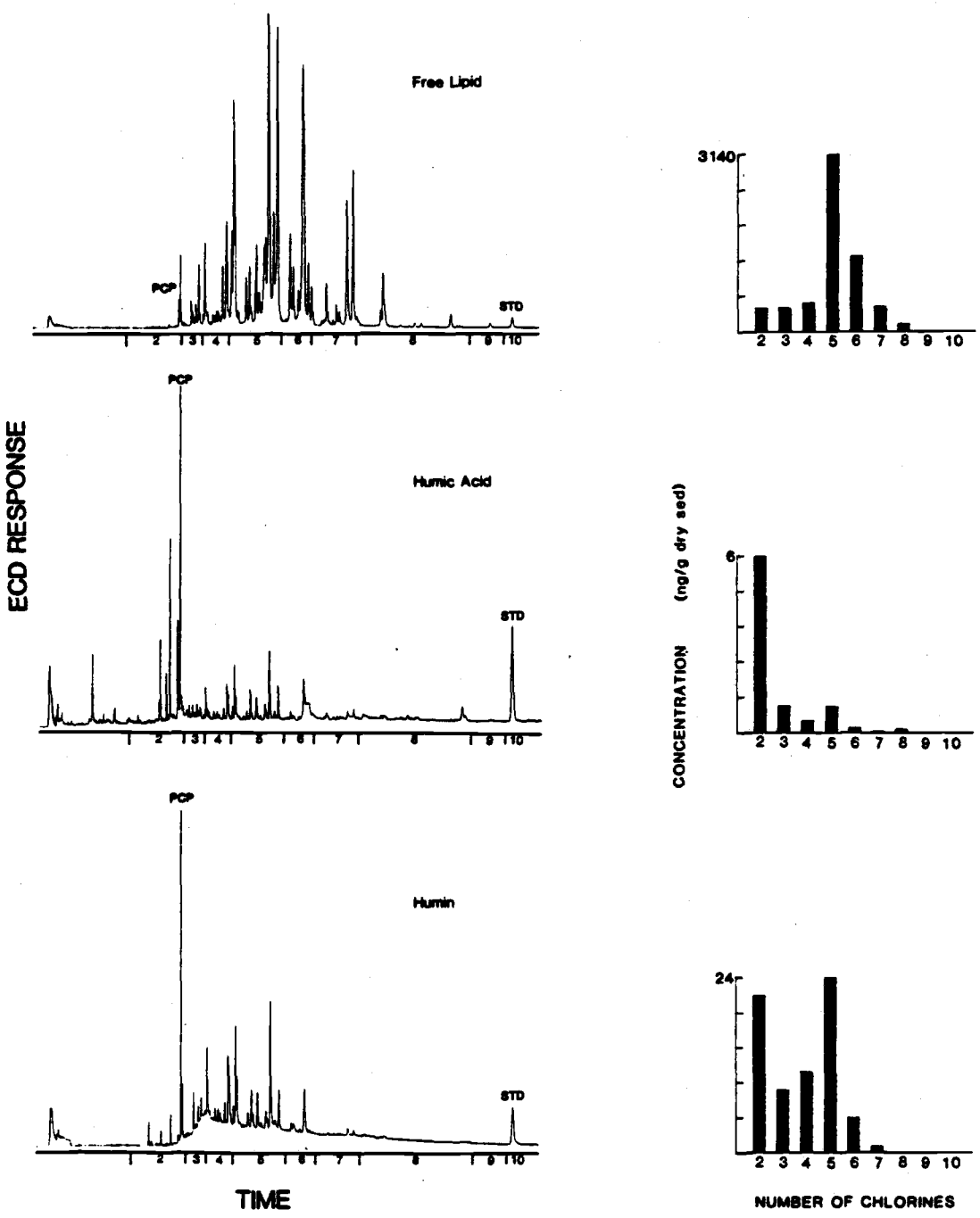

Figure 9. Capillary GC-ECD chromatograms of FL, HA, and HU fractions of sample NB(29-31). See legend of Figure 8.

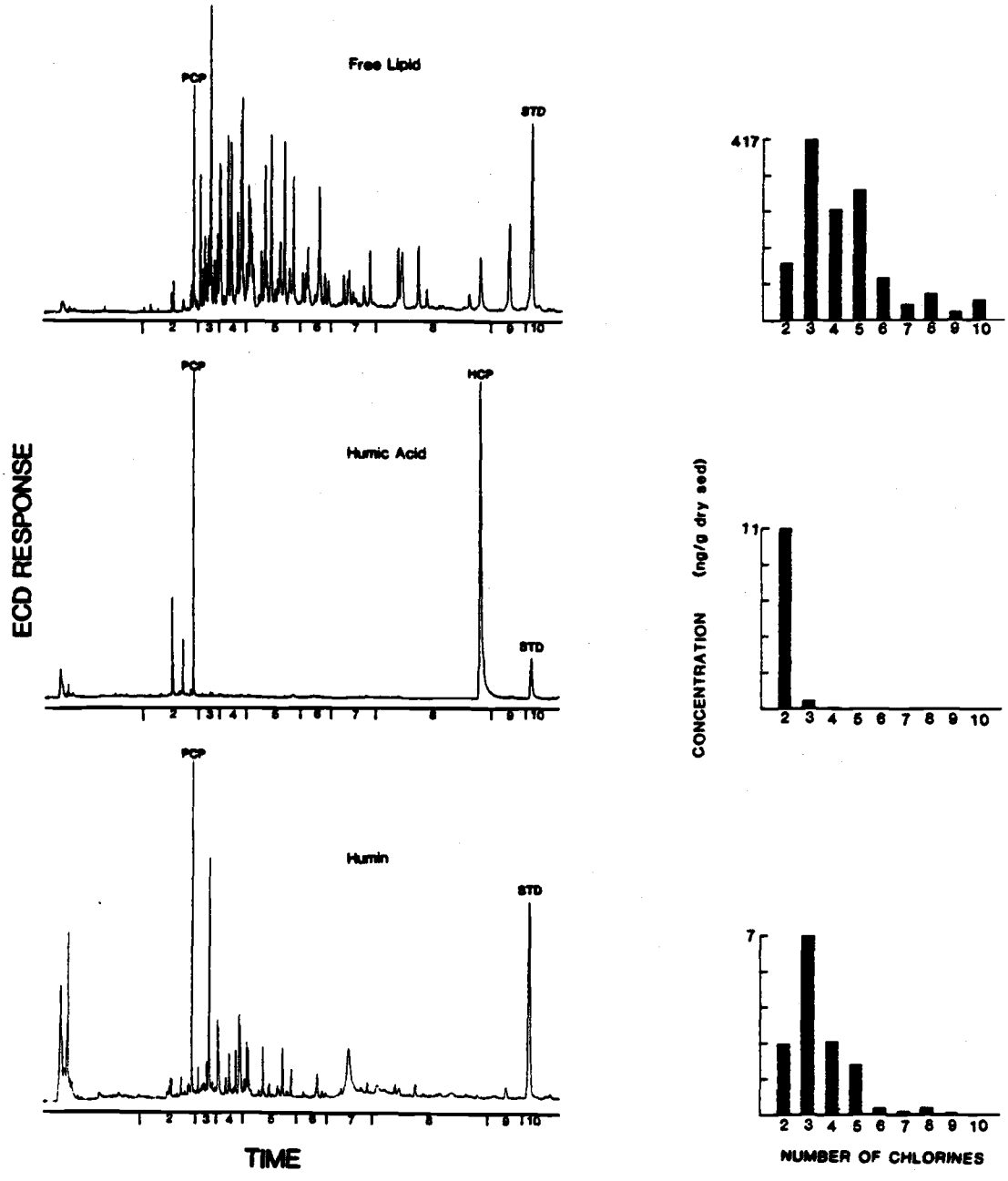

Figure 10. Capillary GC-ECD chromatograms of FL, HA, and HU fractions of sample HR. See legend of Figure 8.

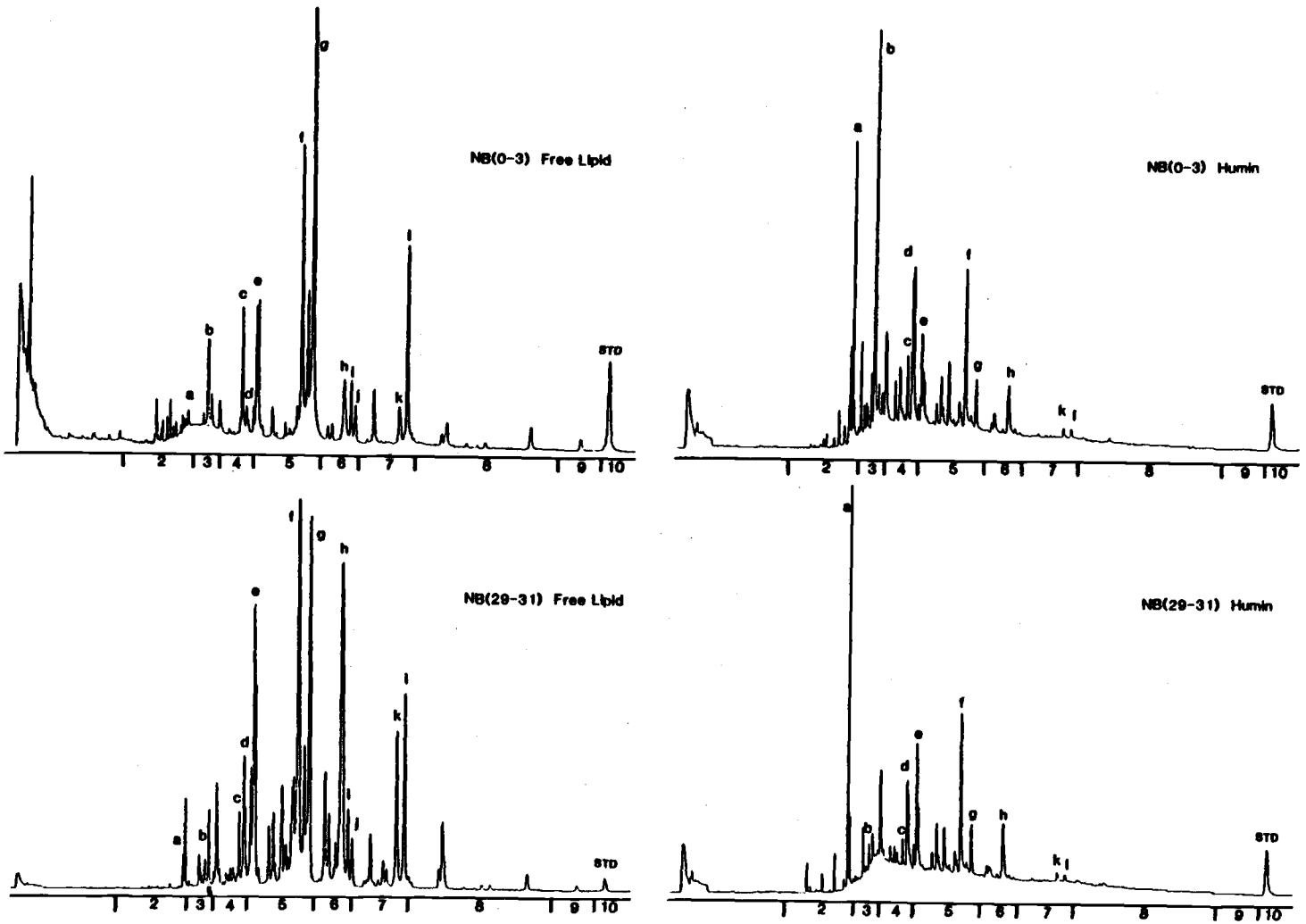

Figure 11. Capillary GC-ECD chromatograms of FL and HU fractions of samples NB(0-3) and NB(29-31). Peak a - pentachlorophenol (methyl ether); other labelled peaks are PCB's. STD - co-injection standard, decachlorobiphenyl.

the quantitative distributions, indicate that provenance rather than sorption controlled PCB distributions within sedimentary organic matter. Figure 11 presents capillary ECD chromatograms of the FL and HU fractions of samples NB(0-3) and NB(29-31). PCB's with five or more chlorine substituents, which are highly resistant to microbial degradation (Furukawa et al., 1978), provide a good basis for qualitative comparison of sample fractions. The assemblages of higher chlorinated isomers of the NB(0-3) and NB(29-31) humin fractions are very similar and may derive from the same source (see peaks f through l). The relative intensities of peaks f through l in the two free lipid fractions are markedly different than in the corresponding HU fractions (Figure 11). Furthermore, the relative intensities of several peaks differ considerably between the two FL fractions (e.g., peak clusters g,h and k,l), yet these differences are not apparent in the two HU fractions. If the PCB sources for the FL and HU fractions of each sample were the same, and if sorption were controlling the distributions of PCB's among the organic matter fractions, then a strong qualitative similarity between FL and HU fractions of a given sample would be expected. Even if sorption favored the incorporation of certain isomers over others, this could not explain the similarity of the HU fractions because the FL fractions reflect different ambient PCB assemblages.

Despite the similarity of the HU fractions of the New Bedford samples, there are some significant differences in relative compositions of less chlorinated isomers. The most striking difference between these humin fractions is the relative intensity of peak b (Figure 11). Based on its retention time, this peak is strongly suspected of being a combination of two co-eluting isomers, 2,4,4' and

2,4',5. Both isomers are major components of Aroclor 1242 and have been shown to be highly degradable in laboratory studies of microbial degradation (Furukawa and Matsumura, 1976; Furukawa et al., 1978). Thus, the relative intensity of this peak may be indicative of biodegradation downcore. Such a trend has been observed in FL fractions of samples taken from this box core (B. Brownawell, pers. comm.).

In all samples with significant PCB contamination, the bound fractions displayed narrower ranges of homolog groups and greater relative concentrations of less chlorinated isomers than did FL fractions (see histograms in Figures 8 - 10). Such comparisons are best made between FL and HU fractions, as laboratory contamination of HA fractions was predominantly in the dichloro range. The weight percent homolog compositions of FL and HU fractions of the New Bedford and Hudson River samples are presented in Table 5. The greater abundances of less chlorinated isomers in the bound fractions may be indicative of their origin. For example, it may indicate an atmospheric source, perhaps PCB's associated with carbonaceous, airborne particles. Laboratory studies of PCB's demonstrate that there is a trend toward higher vapor pressure with decreasing chlorine content (Bopp, 1983) and that photodecomposition selectively destroys highly chlorinated isomers (Hutzinger et al., 1974). These factors would tend to generate atmospheric PCB assemblages enriched in less chlorinated isomers. A possible source of atmospheric PCB's exists in the New Bedford area, as significant atmospheric loadings from incineration of PCB-contaminated sewage sludge have been reported near the sample site (Weaver, 1982; 1984).

Table 5. PCB Homolog Compositions of FL and HU Fractions (as wt. %)

Sample	Fraction	2Cl	3Cl	4Cl	5Cl	6Cl	7Cl	8Cl	9Cl	10Cl
NB(0-3)	FL	22	10	5.7	49	5.0	6.2	2.0	0.28	-
	HU	23	45	15	14	2.8	0.39	0.08	-	-
NB(29-31)	FL	6.7	6.7	8.0	49	21	6.9	2.2	0.09	-
	HU	30	12	15	34	6.8	1.3	0.29	-	-
HR	FL	9.4	31	19	22	7.1	2.7	4.4	1.4	3.4
	HU	18	46	19	13	1.8	0.75	2.0	0.61	-

An atmospheric source is not the only possible explanation for the HU PCB distributions, particularly for sample HR, which had free and bound assemblages that were more similar than those of the New Bedford samples. Another possibility is that lower chlorinated assemblages were entrapped in plant detritus and deposited in sediments in this form; Mrozek and Leidy (1981) demonstrated that estuarine vegetation (saltmarsh cordgrass) selectively incorporated early eluting components of an Aroclor 1254 mixture. The authors attributed this finding to the greater water solubility of lower chlorinated isomers.

The greater relative concentrations of lower chlorinated isomers in bound fractions suggest that bound PCB's are probably not diagenetic derivatives of free PCB's: aerobic microbial degradation would selectively reduce, not enhance, the relative concentations of less chlorinated isomers (Clark et al., 1979; Tucker et al., 1975; Furukawa and Matsumura, 1976; Furukawa et al., 1978). While reductive microbial dehalogenation would tend to preferentially diminish the amount of highly chlorinated isomers (Brown et al., 1984), it could not account for PCB distributions in sample HR, which was apparently not from a reducing environment; anaerobic bacteria capable of dechlorination require strictly anaerobic conditions (Brown et al., 1984). Furthermore, reductive dehalogenation is not evident in FL

fractions of New Bedford samples; indeed, these fractions are enriched in higher chlorinated isomers relative to PCB mixtures that were used in this area. It seems unlikely that anaerobic bacteria would affect bound fractions but not free fractions of the same sediment.

Sample LA was not included in the preceding discussion for several reasons: (1) the free lipid fraction was dominated by DDE and the PCB component was relatively minor, (2) the large, early eluting peaks in the bound fractions could not be definitvely identified as PCB's (Figure 12) and (3) the HU fraction was dominated by a sulfur peak that may obscure some PCB isomers eluting in this retention time area, although the FL fraction did not have any large peaks in this area (Figure 12).

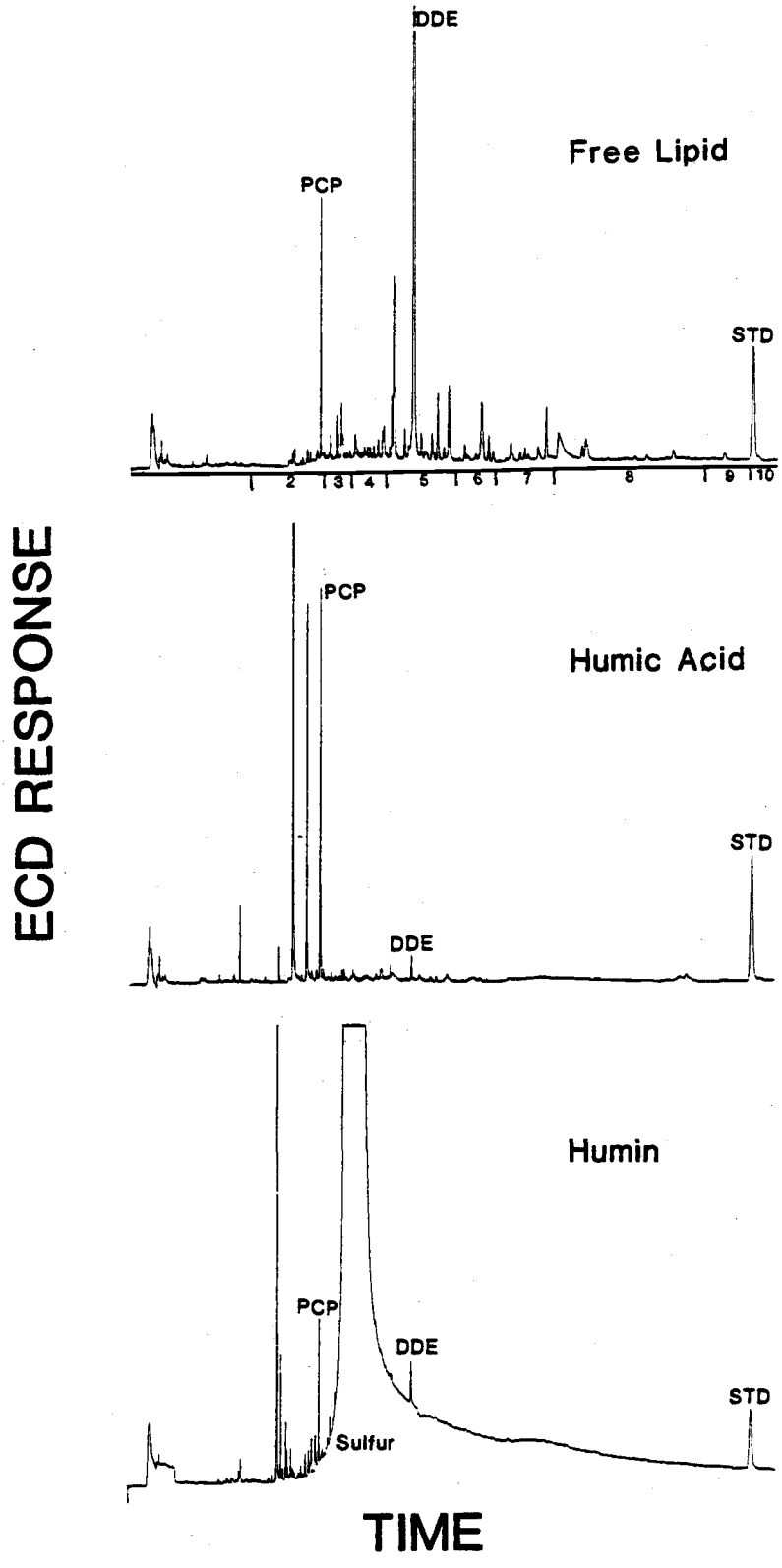

Figure 12. Capillary GC-ECD chromatograms of FL, HA, and HU fractions of sample LA. See legend of Figure 8.

Hydrocarbons

Quantitative Results

Saturated hydrocarbons, like chlorinated hydrocarbons, tended to distribute predominantly in the FL fractions of sediments: over 99% of the hydrocarbons in most samples were associated with this easily extractable fraction (Table 6). Similar results were reported by Van Vleet and Quinn (1978) in a study of estuarine sediments from the northeastern United States and by Cranwell (1981) in a study of lacustrine sediments.

Table 6. Relative Saturated Hydrocarbon Distributions[a]

Sample	FL	HA	HU	Total
NB(0-3)	99.8% (10)[b]	0.11%	0.11% (45)	719 ppm
NB(29-31)	99.8% (10)	0.04%	0.17% (28)	637 ppm
HR	99.5% (18)	0.05%	0.48% (17)	204 ppm
LA	99.9% (10)	0.05%	0.09% (67)	64 ppm
YB	98% (24)	n.a.	2.3% (29)	10 ppm
YB-Q		12% (as % of FL+HU in YB)		

[a] as percent of total sedimentary concentrations

[b] parenthetical values are resolved/total as percent

n.a. - not analyzed

The high total hydrocarbon concentrations of the NB(0-3), NB(29-31), HR and LA samples relative to that of the pristine YB sample indicate the presence of petroleum contamination in these areas. The parenthetical values in Table 6, estimates of the percent of resolved/total hydrocarbons, are also indicative of petroleum contamination and will be discussed in the Qualitative Results section.

The high percentage of humic acid-associated hydrocarbons in YB-

Q (for which the HA was extracted without prior solvent extraction) relative to corresponding distributions from other samples indicates that extraction procedures used in selective extraction studies can affect the results. Nonetheless, the observation that a great majority of the sedimentary hydrocarbons were associated with free lipids would apply for either humic acid extraction procedure. A direct comparison of YB-Q HA to YB HA was impossible because no liquid aliquot of YB HA was saved before freeze drying. As noted in the MATERIALS AND METHODS section, freeze dried humic acids were contaminated with hydrocarbons.

The hydrocarbon content (as wt %) of humic acids for all samples are orders of magnitude lower than the values reported by Khan and Schnitzer (1972) for humic acid extracted from a Canadian Black Chernozem soil (0.34%). Values in this study ranged from ca. 0.0005% (sample LA) to 0.02% (sample YB-Q). The Chernozem soil was not pre-extracted with solvents and is thus best compared to sample YB-Q. The large differences in hydrocarbon content of these humic acids may be attributable to different environments (estuarine vs. terrestrial) and different processes of formation.

Blanks - The procedural blank for the FL fraction was negligible, but the blanks for the bound hydrocarbon fractions were in some cases significant. The procedural blank for the HA fraction corresponds to the following values of percent contamination: NB(0-3) - 11%, NB(29-31) - 25%, HR - 51%, LA - 325% and YB-Q - 3%. The chromatogram of the blank was sufficiently different from the samples that no blank corrections were made (see Appendix Figure 2A). The procedural blank for the HU fraction (Appendix Figure 2A) does not appear to be repre-

sentative of possible sample contamination as it had an unusual, strikingly symmetrical alkane distribution from C_{22} to C_{30} whereas all samples showed moderate to strong odd:even predominance in this region. The HU procedural blank also contained a significant amount of a compound eluting between C_{26} and C_{27} which could not be identified by GC-MS, but which generated a fragmentation pattern much like an n-alkane. This peak was most evident in HA fractions, not HU fractions. The extents of contamination calculated using the procedural blank were: NB(0-3) - 17%, NB(29-31) - 7%, HR - 18%, LA - 136% and YB - 8%.

Significant phthalate contamination was not indicated by procedural blanks, yet these compounds were present in some samples, especially the HA and HU fractions of sample HR. Since phthalates have been used as PCB replacements by capacitor manufacturers (Weaver, 1984), are widespread environmental contaminants (Giam et al., 1978), and have been found in association with humic substances (Ogner et al., 1970), it is possible that the phthalate peak in sample HR and minor phthalate peaks in other samples are true environmental, not laboratory, contaminants.

Precision - The coefficient of variation for gas chromatographic hydrocarbon analysis, determined from response factor values for the co-injection standard (perdeuterated tetracosane) was 13% (n=30).

Qualitative Results

The FL fractions of all samples but YB were dominated by an unresolved mixture of hydrocarbons (UCM) with a broad boiling point range (Figures 13 - 17 and resolved/total values in Table 6). The

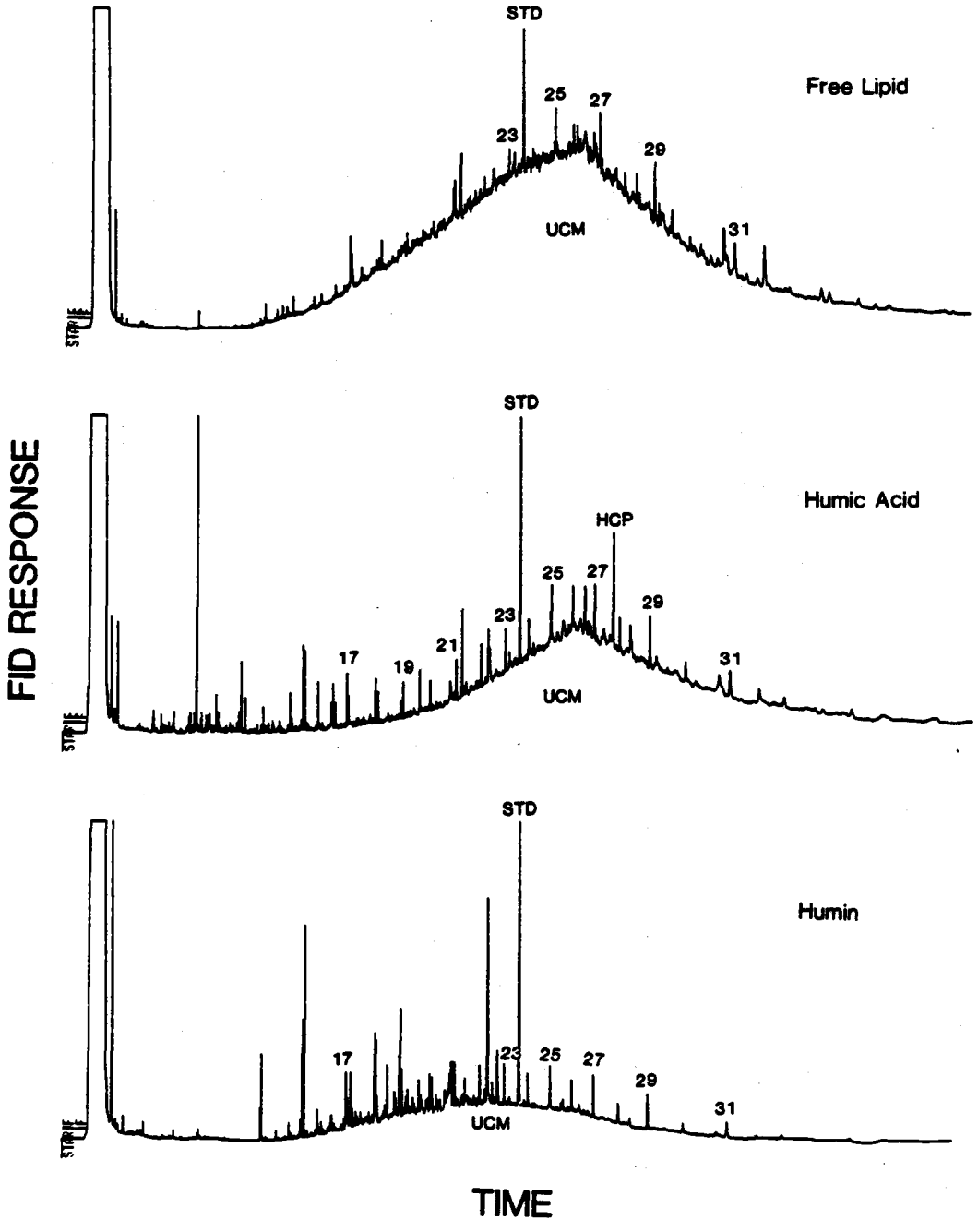

Figure 13. Capillary GC-FID chromatograms of FL, HA, and HU fractions of sample NB(0-3). STD - co-injection standard, perdeuterated tetracosane; UCM - unresolved complex mixture.

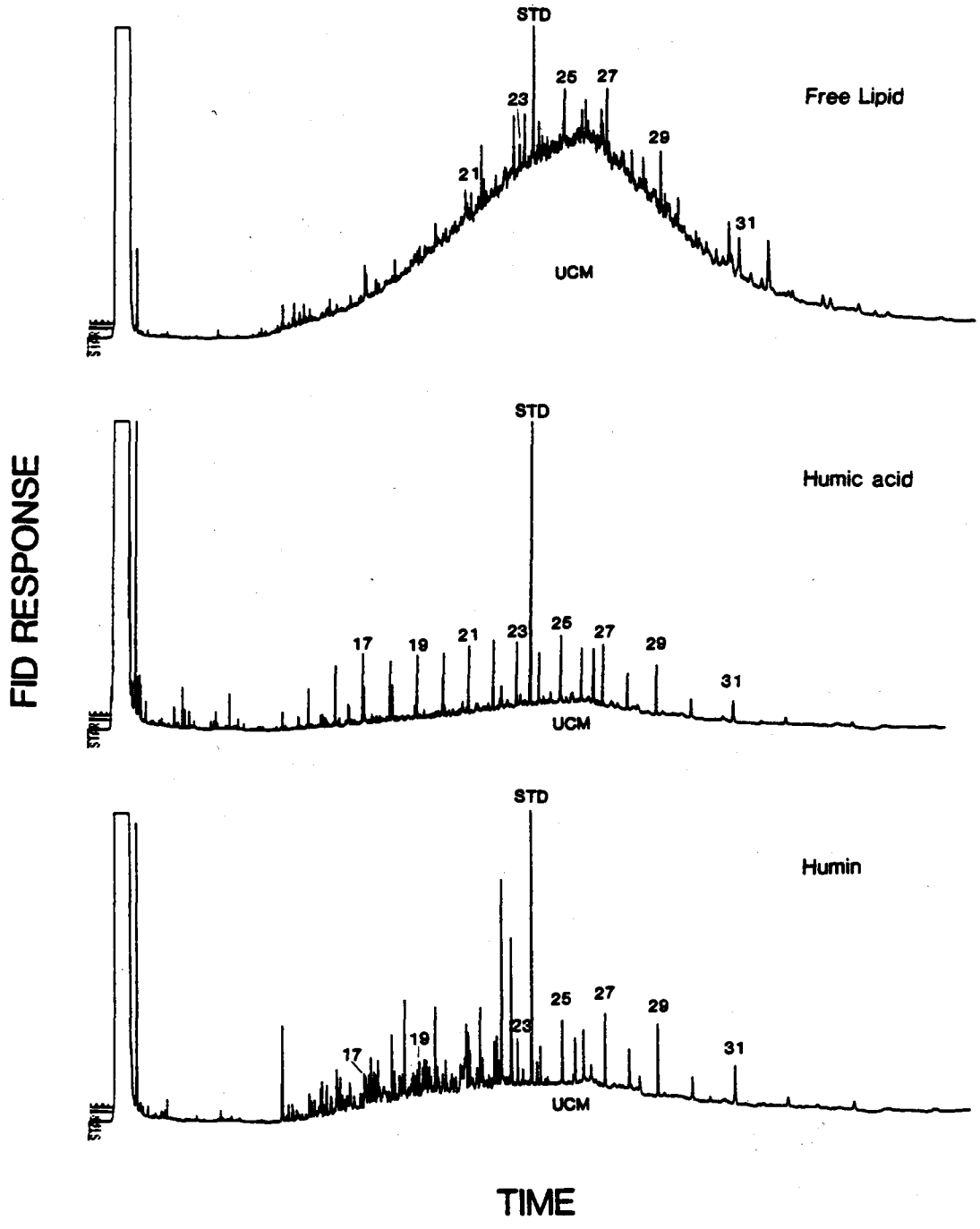

Figure 14. Capillary GC-FID chromatograms of FL, HA, and HU fractions of sample NB(29-31). See legend of Figure 13.

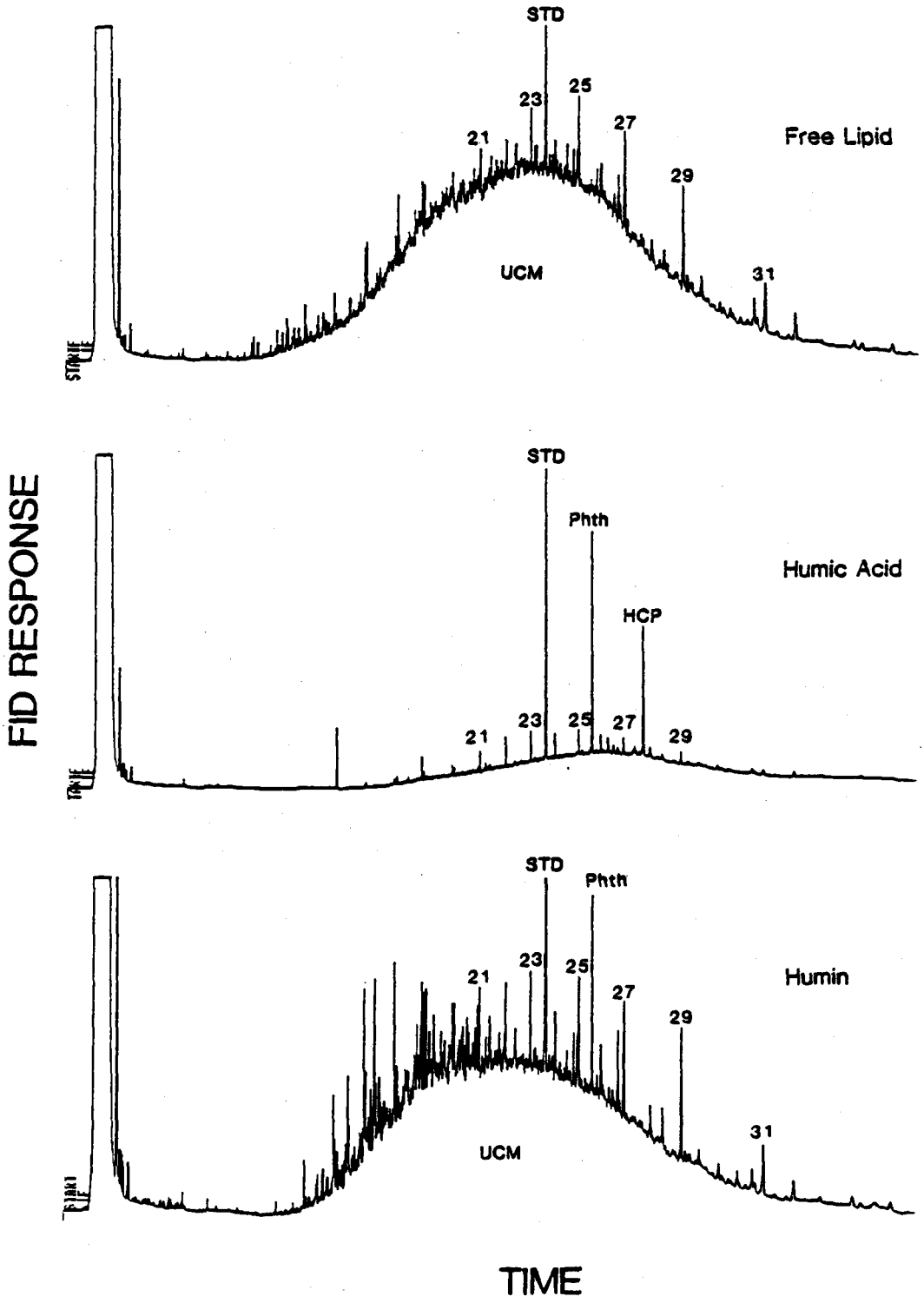

Figure 15. Capillary GC-FID chromatograms of FL, HA, and HU fractions of sample HR. See legend of Figure 13. Phth - C_8-phthalate. Aromatic peaks are prevalent before C_{21} in FL and HU fractions.

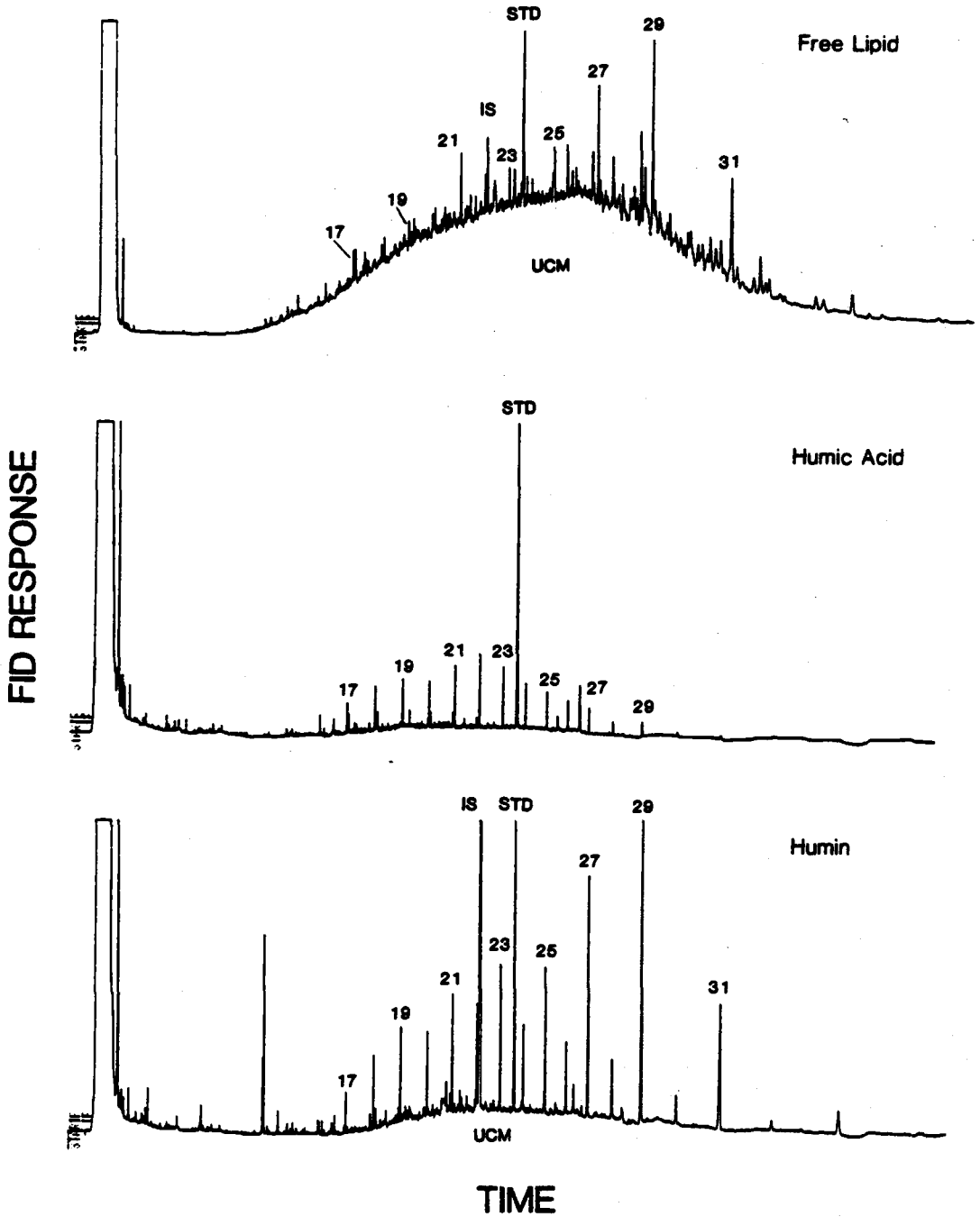

Figure 16. Capillary GC-FID chromatograms of FL, HA, and HU fractions of sample LA. STD - co-injection standard, perdeuterated tetracosane; IS - internal standard, p-terphenyl; UCM - unresolved complex mixture.

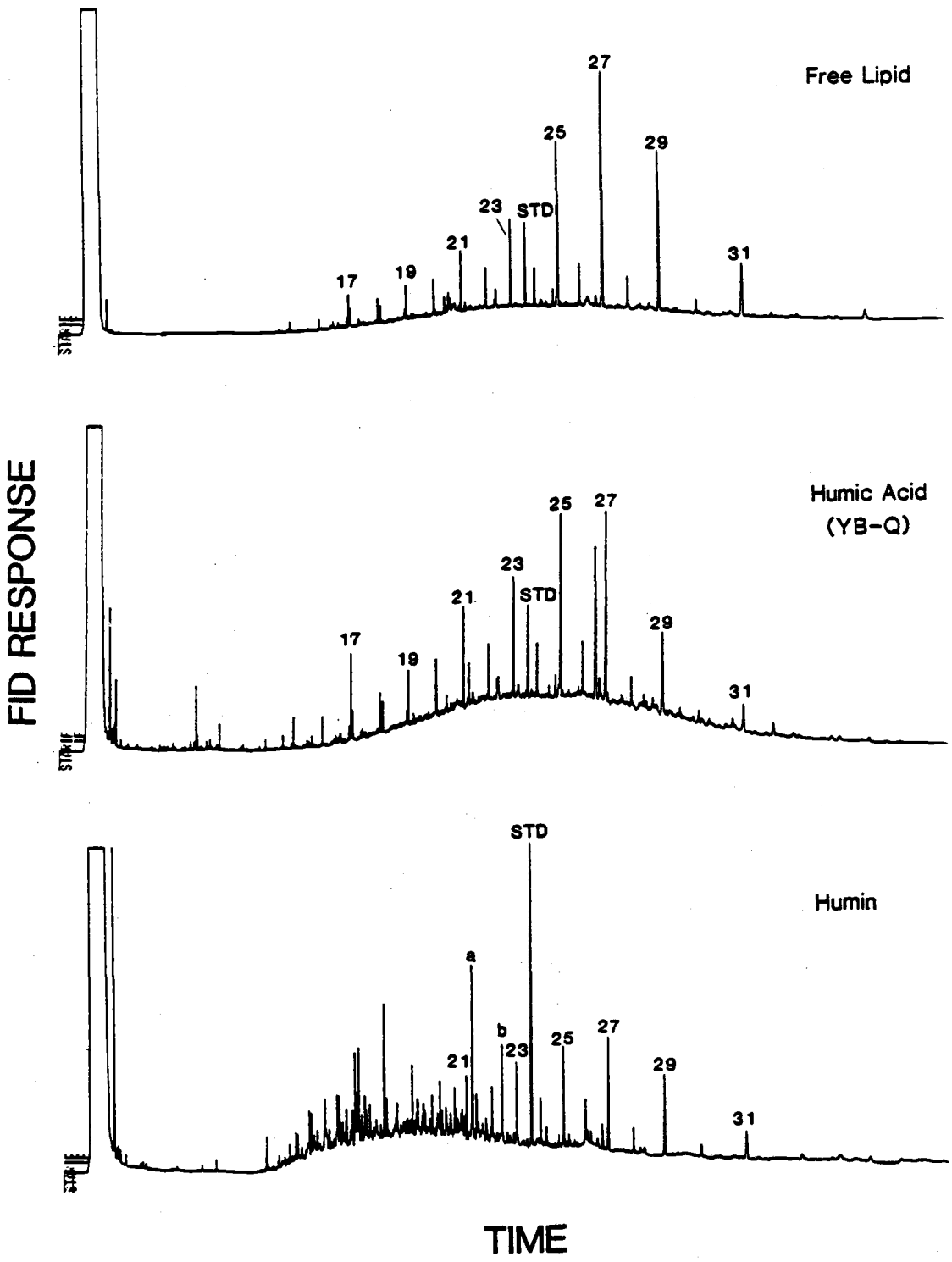

Figure 17. Capillary GC-FID chromatograms of FL, HA, and HU fractions of sample YB, YB-Q. Peaks a and b discussed in text. See legend in Figure 13.

UCM is thought to consist of naphthenic (branched and cyclic), naphtheno-aromatic and aromatic hydrocarbons and was attributed to petroleum hydrocarbons in samples where anthropogenic contamination was likely (Boehm and Quinn, 1978; Farrington and Quinn, 1973; Giger et al., 1980; Venkatesan et al., 1980). Also, a series of (17αH, 21βH)-hopanes, considered to be good markers of petroleum contamination (Simoneit et al., 1980), were the predominant triterpenoids in FL fractions from New Bedford, the Hudson River, and LA Harbor.

Generally, HA fractions of these sediments appear different from both FL and HU fractions but no trends with respect to the FL and HU fractions could be discerned. While the hydrocarbons of the HA fractions of the New Bedford samples (Figures 13 and 14) are not definitive indicators of their sources, they could be derived in part from bacteria. Certain bacteria are known to produce a broad range of n-alkanes (from C_{13} to C_{31}) with virtually no odd:even predominance (Davis, 1968; Han and Calvin, 1969). Unresolved complex mixtures of hydrocarbons have also been observed in bacterial lipids (Han and Calvin, 1969). The hydrocarbons of the HA fraction of sample LA (Figure 16) may also be attributable to bacteria, although this fraction was far below the procedural blank concentration and may have been contaminated. The HA fraction of sample HR (Figure 15) consisted almost entirely of two compounds, a phthalate and methylated hexachlorophene, neither of which is a true hydrocarbon. The YB-Q HA fraction was similar to the FL fraction of sample YB and may reflect a "carryover" of lipids due to a lack of preliminary solvent extraction (Figure 17).

In general, hydrocarbon distributions of HU fractions of petroleum-contaminated sediments appear quite different from those of

the FL fractions. The most noticeable difference is the greatly reduced significance of the UCM in the HU fractions (see values of resolved/ total hydrocarbons in Table 6 and Figures 13,14,16). This pattern is most pronounced in sample LA (Figure 16), whose HU hydrocarbon assemblage is similar to that found in terrestrial plant waxes (predominated by n-alkanes from C_{23} to C_{31} with a maximum at C_{27}, C_{29}, or C_{31} and a high odd:even preference; Eglinton and Hamilton, 1967; Simoneit, 1978; Smith et al., 1983) whereas its FL fraction contains a large UCM indicative of petroleum contamination. The FL fraction also contains terrestrially-derived alkanes.

The HU fractions of samples NB(0-3) and NB(29-31), like the LA HU fraction, have reduced UCM's in relation to the FL fractions (Figures 13 and 14 and Table 6). Comparison of FL and HU hydrocarbon fractions of both NB samples (Figure 18) indicates that the FL fractions of both samples are very similar. The HU fractions of both samples are also similar, and are distinctly different from the FL fractions (although all fractions have a terrestrial plant wax component). Two interesting features that the HU fractions share are 1) the "noisy" area in the chromatogram before C_{22} and 2) peaks a and b (Figure 18), significant resolved components of both samples. The noisy peaks are, at least in part, alkylated aromatic compounds including alkyl fluorenes and phenanthrenes. Spectra of peaks a and b (Figure 19) feature a base peak of 81 and an apparent parent (M+) ion at 362 (corresponding to a possible elemental composition of $C_{26}H_{50}$). While the identities and sources of a and b could not be discerned, they may be cyclic olefins of biogenic, not anthropogenic (petroleum) origin (see Blumer et al., 1970), and are further indica-

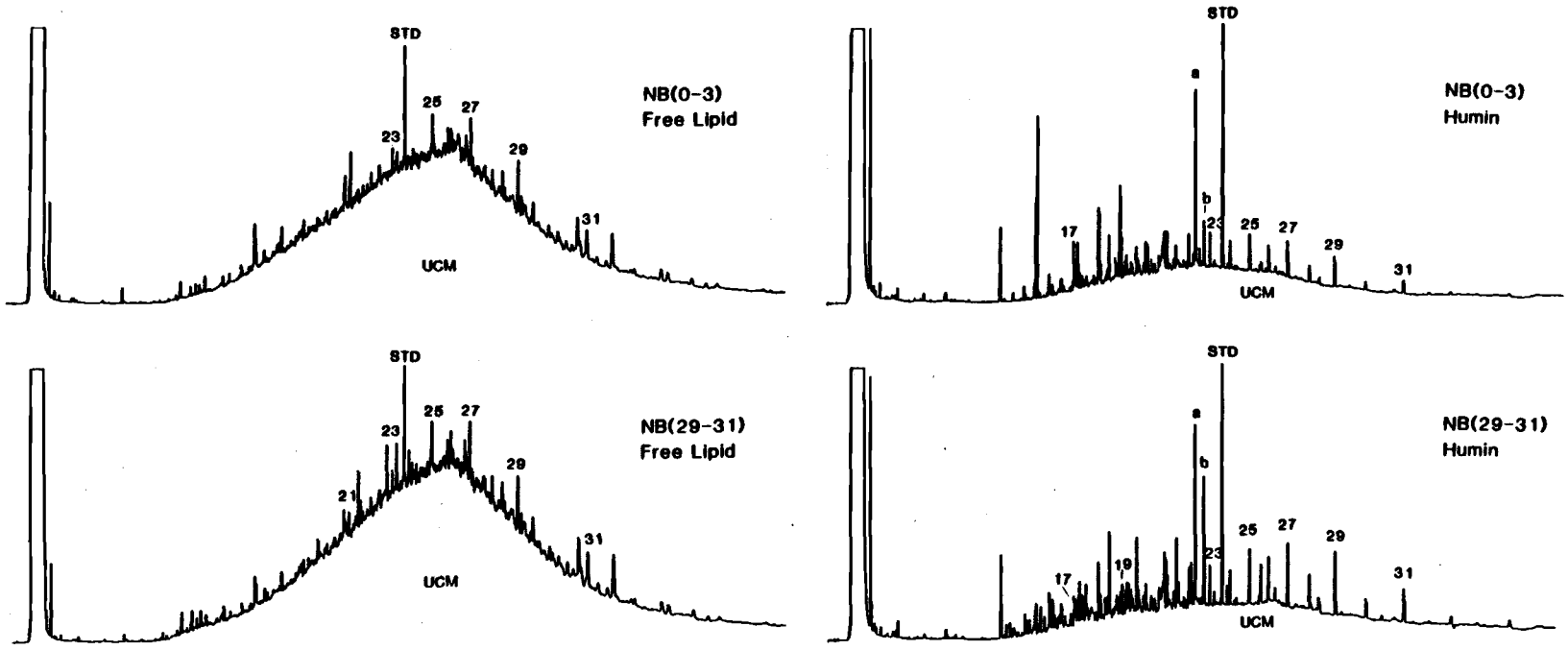

Figure 18. Capillary GC-FID chromatograms of saturated hydrocarbons in FL and HU fractions of samples NB(0-3) and NB(29-31). Peaks a and b discussed in text. See legend in Figure 13.

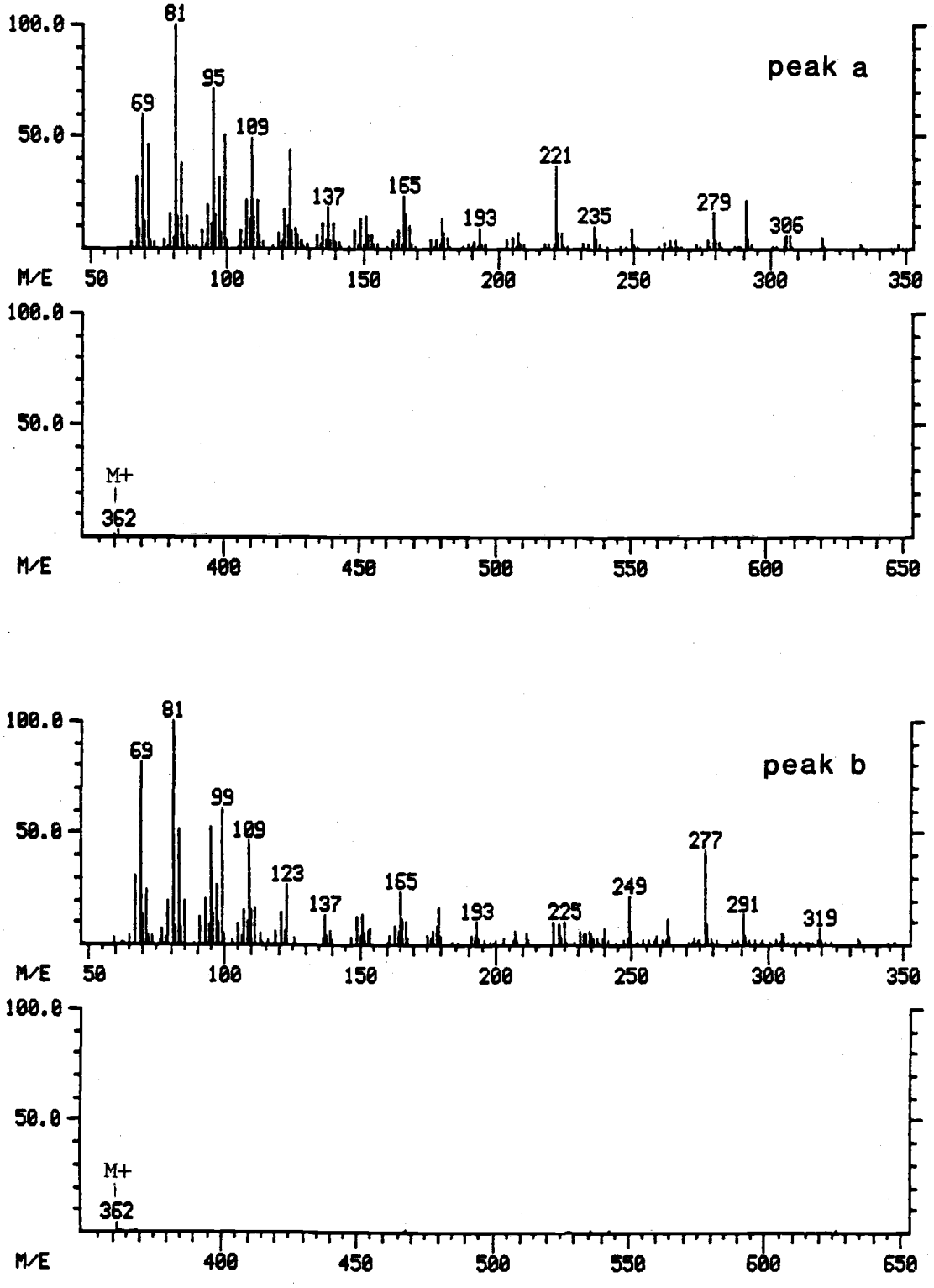

Figure 19. 70 eV mass spectra of peaks a and b in Figure 18, NB(0-3)

tion that HU and FL fractions are not closely related.

Sample HR does not follow the pattern described for the LA and NB samples; the HU fraction has a UCM similar in proportion and boiling point range to that of the FL fraction (see unresolved/total hydrocarbons in Table 6 and Figure 15).

Sample YB, a relatively pristine sample, has a characteristic terrestrial plant wax alkane signature in its FL fraction with a minor UCM (Figure 17). The HU fraction also has a terrestrial plant wax component, but is dominated by two aromatic peaks labelled a and b in Figure 17 and identified as pyrene or fluoranthene (peak a) and retene (peak b) by GC-MS. Fluoranthene and pyrene are thought to be combustion-derived whereas retene is thought to be derived from abietic acid, a resin acid found in conifers (Hites et al., 1980; Prahl et al., 1984; Simoneit, 1977). A number of lower intensity aromatic peaks occur in the region before C_{21}. Selected mass spectra of these peaks had base peaks of 91 (tropylium ion, characteristic of alkylated benzenes), 167 and 181. These compounds could be clearly identified as aromatic due to their simple spectra and intense parent ions and base peaks. A possible source of fluoranthene or pyrene and other aromatic peaks is soot or charred wood particles, which were observed in sediments of this area by Kulm (1965). The occurrence of retene is consistent with the coniferous vegetation in this area.

Qualitative comparisons of FL versus HU hydrocarbon distributions indicate that the sources for unbound and bound hydrocarbons are different in these samples. One possible explanation for these differences is that detrital particles (e.g., vascular plant fragments or soot particles) containing some inextractable hydrocarbons are major contributors to hydrocarbons in the HU fractions, while the

FL hydrocarbons (mostly petroleum hydrocarbons) exist as easily extractable components, perhaps as surface coatings on particles (Van Vleet and Quinn, 1978). A size fractionation study (Thompson and Eglinton, 1978) supports the idea that within a sedimentary matrix, hydrocarbons of different sources can be associated with distinct particle types or surfaces. If a portion of hydrocarbons in plant detritus or soot were entrapped and unavailable to solvents during extraction, this material might be released during saponification.

A similar explanation could pertain to PCB distributions. PCB's, often combined with oils for industrial use, could be components of particle coatings that resulted from the direct discharge of industrial effluents. Untreated, PCB-contaminated effluents were released in large quantities by capacitor manufacturers near the New Bedford site and upriver from the Hudson River site. PCB's associated with atmospheric soot particles might be unavailable to solvent extraction but released during saponification.

The significance of the above discussion is that distributions of bound hydrocarbons (and other bound compound classes) could be determined by particle associations that existed prior to the deposition of particles as bottom sediments. In other words, bound hydrocarbons could be transported to and deposited in sediments in bound or entrapped form. This process is at odds with an equilibrium sorption model, which requires that various substrates all be exposed to the same pool of compounds and that distribution be determined by the affinity of each of these compounds for each substrate. If some compounds enter the sediments in bound form, it is unlikely that they would migrate out of their matrix to attain equilibrium concentra-

tions with other sedimentary organic matter fractions or with an aqueous phase. Thus, the equilibrium sorption model may not apply as well for bound fractions as it does for free fractions.

Fatty Acid Methyl Esters

Quantitative Results

The relative distributions of FAME's among the sedimentary organic matter fractions were more variable from sample to sample than were the corresponding distributions of PCB's or hydrocarbons (Table 7). As presented in Table 7, FL, HA and HU fractions accounted for 53-87%, 5-30% and 2-16% of the total sedimentary FAME, respectively. Van Vleet and Quinn (1979) found even broader ranging distributions for sediments from three estuaries in the northeastern United States: 8-62% of the total FAME's were in the free lipid fraction, 2-22% in the humic acid fraction and 38-86% in the residual organic matter-mineral (HU) fraction. Cranwell, in two separate studies of lacustrine sediments, found that 22-25% (1981) and 32% (1978) of total n-alkanoic acids were in bound sediment fractions. Studies of Narragansett Bay and Buzzards Bay revealed that 32-65% and 65%, respectively, of total FAME's were in bound fractions (Farrington and Quinn, 1971; Farrington et al., 1977).

Table 7. Relative FAME Distributions (as % of total sed. conc.)

Sample	FL	HA	HU	Total
NB(0-3)	53%	30%	16%	59 ppm
NB(29-31)	69%	21%	11%	40 ppm
HR	82%	5.6%	12%	32 ppm
LA	87%	11%	1.9%	11 ppm
YB	79%	5.4%	16%	40 ppm
YB-Q		63% (as % of total FAME in YB)		

The high yield of bound FAME's relative to yields of bound PCB's and hydrocarbons could be explained by the fact that in addition to releasing physically entrapped and sorbed fatty acids, base treatment may release fatty acids that are chemically bound to humic substances

or mineral matter. The importance of fatty acids as structural components of humic substances has been suggested in numerous studies involving NMR, pyrolysis GC-MS, permanganate oxidation and other chemical techniques (Gagosian and Stuermer, 1977; Harvey et al., 1983; Hatcher et al., 1981; Ishiwatari and Machihara, 1982; 1983; Khan and Schnitzer, 1978; Larter and Douglas, 1980; Stuermer and Harvey, 1978; Wilson et al., 1983). Several authors have suggested that fatty acids could be esterified to OH groups in humic acid or to SiOH or AlOH groups in clay minerals (Farrington et al., 1977; Farrington et al., 1971). Fatty acids are also esterified components of bacterial cell walls which may be relatively inextractable with organic solvents but hydrolyzable with base (Brooks et al., 1976; Cranwell, 1978). The suggestion that base treatment is releasing chemically bound fatty acids is supported by a study by Farrington et al. (1977) in which sediments were transesterified in absolute methanol after solvent extraction and a minimum of 14% of the bound fatty acids were determined to have been associated to sediment through ester or amide bonds. In contrast, non-polar, non-ionic species like PCB's and saturated hydrocarbons could only have weak physicochemical associations (London forces) with sedimentary organic matter.

Blanks - Procedural blanks for the FL and HU procedures demonstrated negligible contamination while the HA blank revealed minor contamination. Blank concentrations of $\underline{n}$-C_{14} and $\underline{n}$-C_{16} FAME's, the only significant contaminants in the HA procedural blank, were less than 2% of the corresponding acid concentrations in YB-Q, NB(0-3) and NB(29-31), less than 5% in YB and LA and less than 8% in HR.

Precision - The coefficient of variation, determined for the co-

injection standard as for the hydrocarbons, was 13% (n=30).

Qualitative Results

Histograms of the major components of the FL, HA and HU fractions of each sample are presented in Figures 20 - 24. Similar qualitative trends are readily apparent for all but the YB, YB-Q samples: FL fractions contain a broad chain length distribution from C_{14} to C_{30}, often displaying bimodality with maxima at C_{16} and C_{24} or C_{26}, whereas bound fractions have narrower distributions ranging approximately from C_{14} to C_{18} with maxima at C_{14} or C_{16}. (All fractions had a high even:odd preference typical of biogenic fatty acids.) Another notable and related trend is the tendency for branched (iso- and anteiso-) 15:0 and n-16:1 acids to be far more significant in the bound fractions than in the free fractions. This trend, evident in the histograms, is presented numerically in Table 8. Table 8 presents the weight percentages (as percent of total resolved FAME in a given fraction) of branched 15:0 and n-16:1 in each sedimentary fraction. Samples LA and YB deviate somewhat from this trend.

Table 8. Relative a+i-15:0 and n-16:1 Distributions[a]

Sample	FL	HA	HU
NB(0-3)	0;1	13;12	16;8
NB(29-31)	3;0	15;6	13;5
HR	4;0	29;31	16;3
LA	5;0	7;4	5;1
YB	8;26	22;13	11;7
YB-Q		13;31	

[a] as % of total FAME in fraction (a+i-15:0;n-16:1)

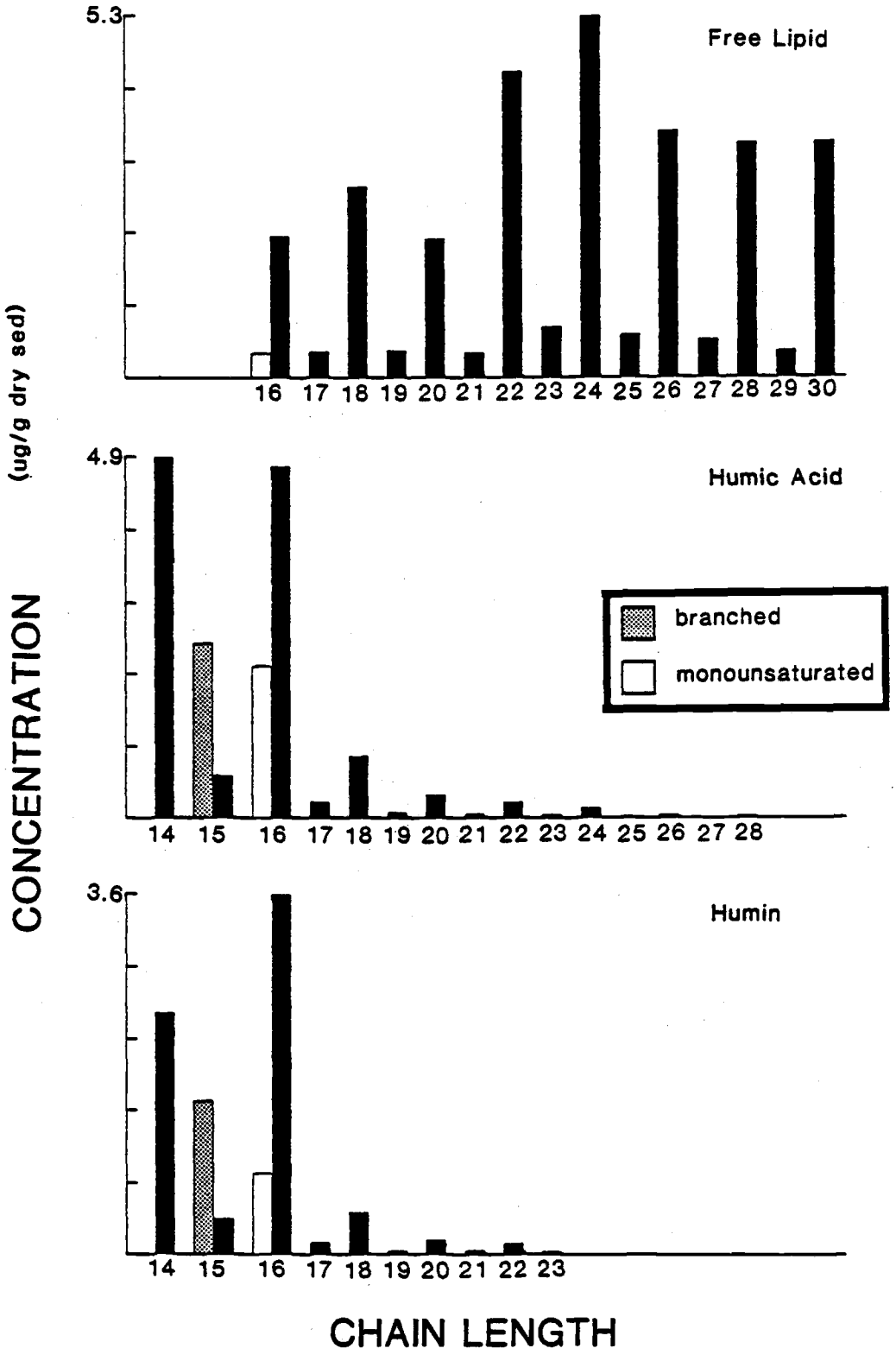

Figure 20. Fatty acid methyl ester distributions in FL, HA, and HU fractions of sample NB(0-3). Branched - iso-+ anteiso-15:0; monounsaturated - n-16:0.

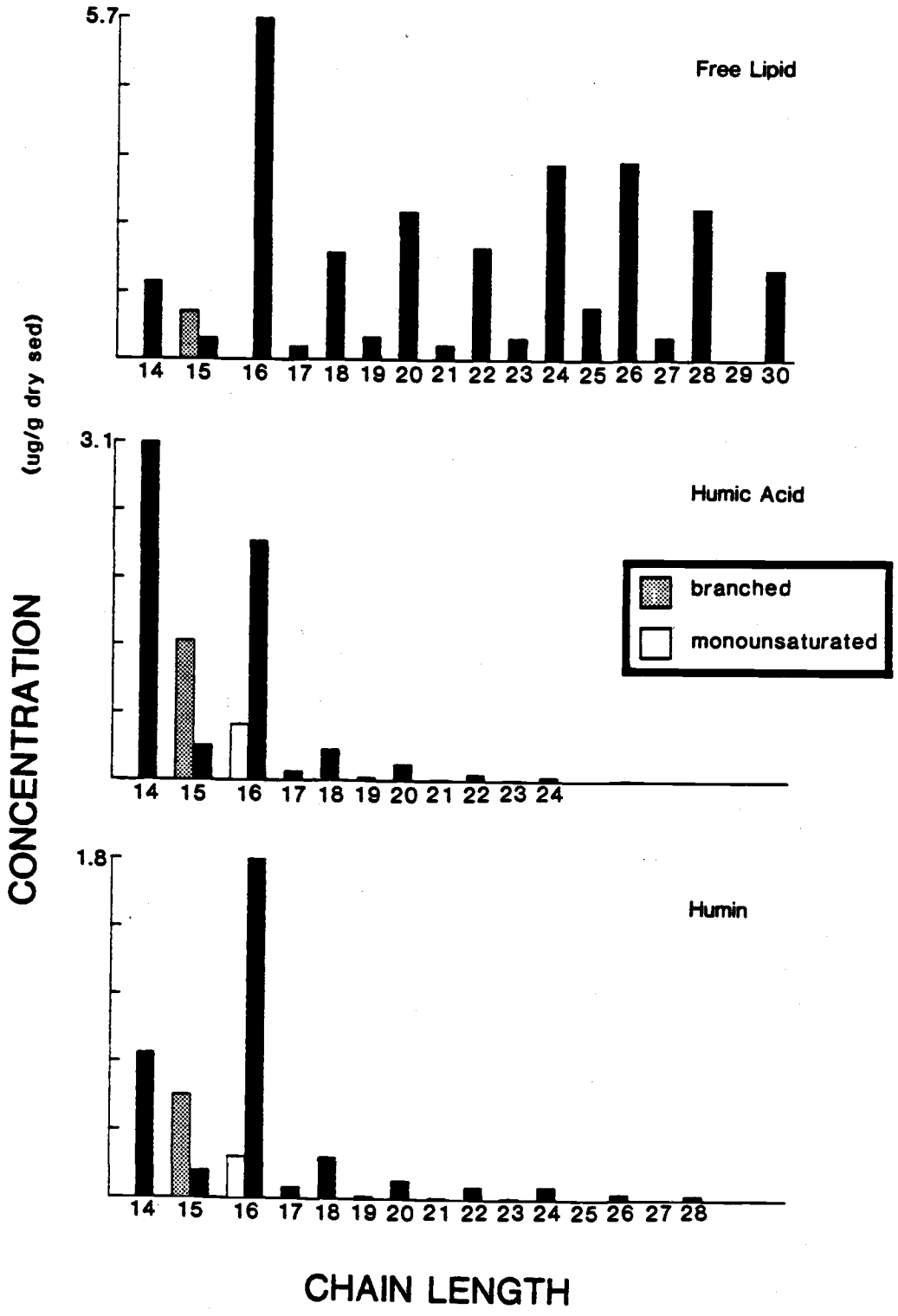

Figure 21. Fatty acid methyl ester distributions in FL, HA, and HU fractions of sample NB(29-31). Legend as in Figure 20.

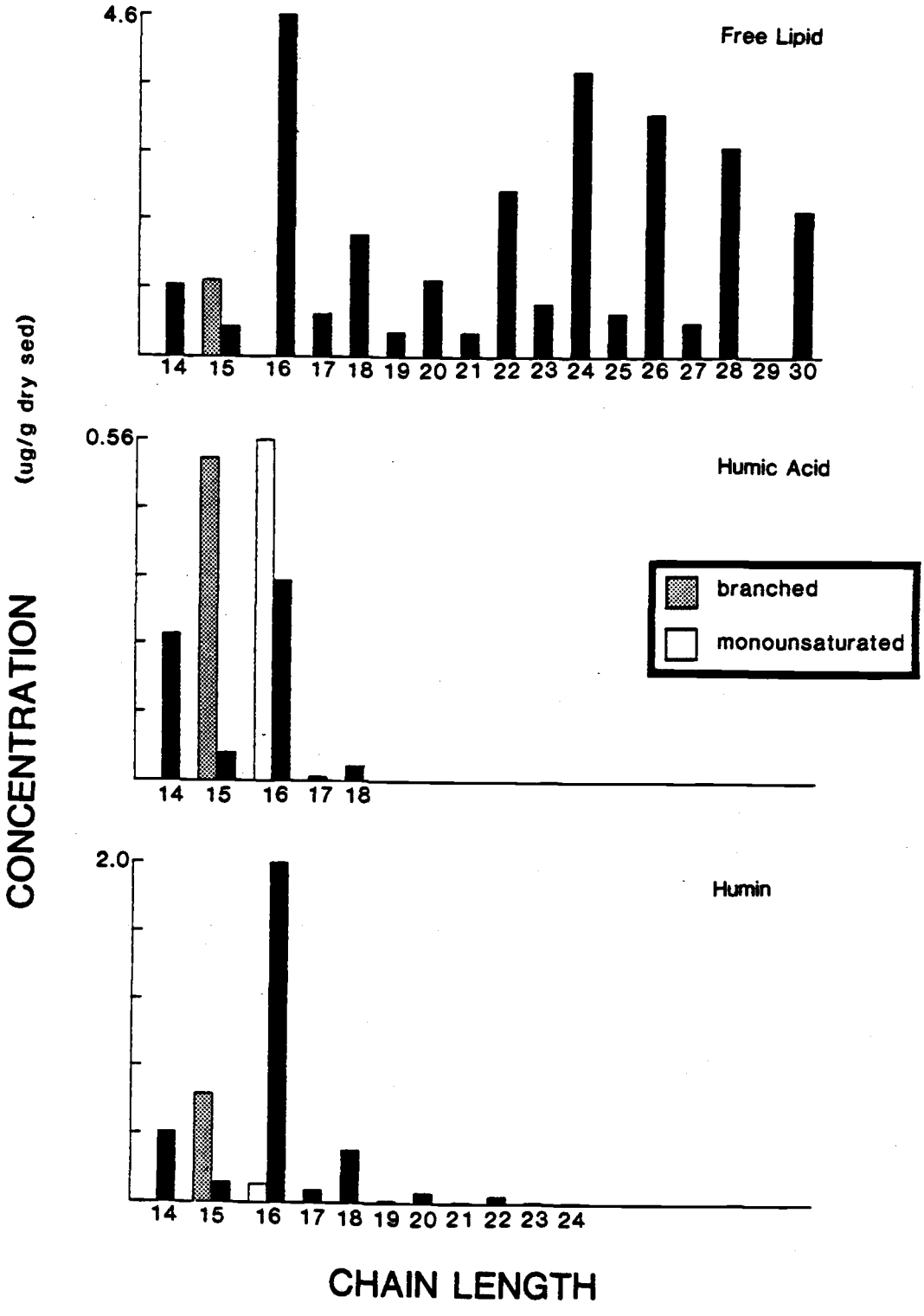

Figure 22. Fatty acid methyl ester distributions in FL, HA, and HU fractions of sample HR. Legend as in Figure 20.

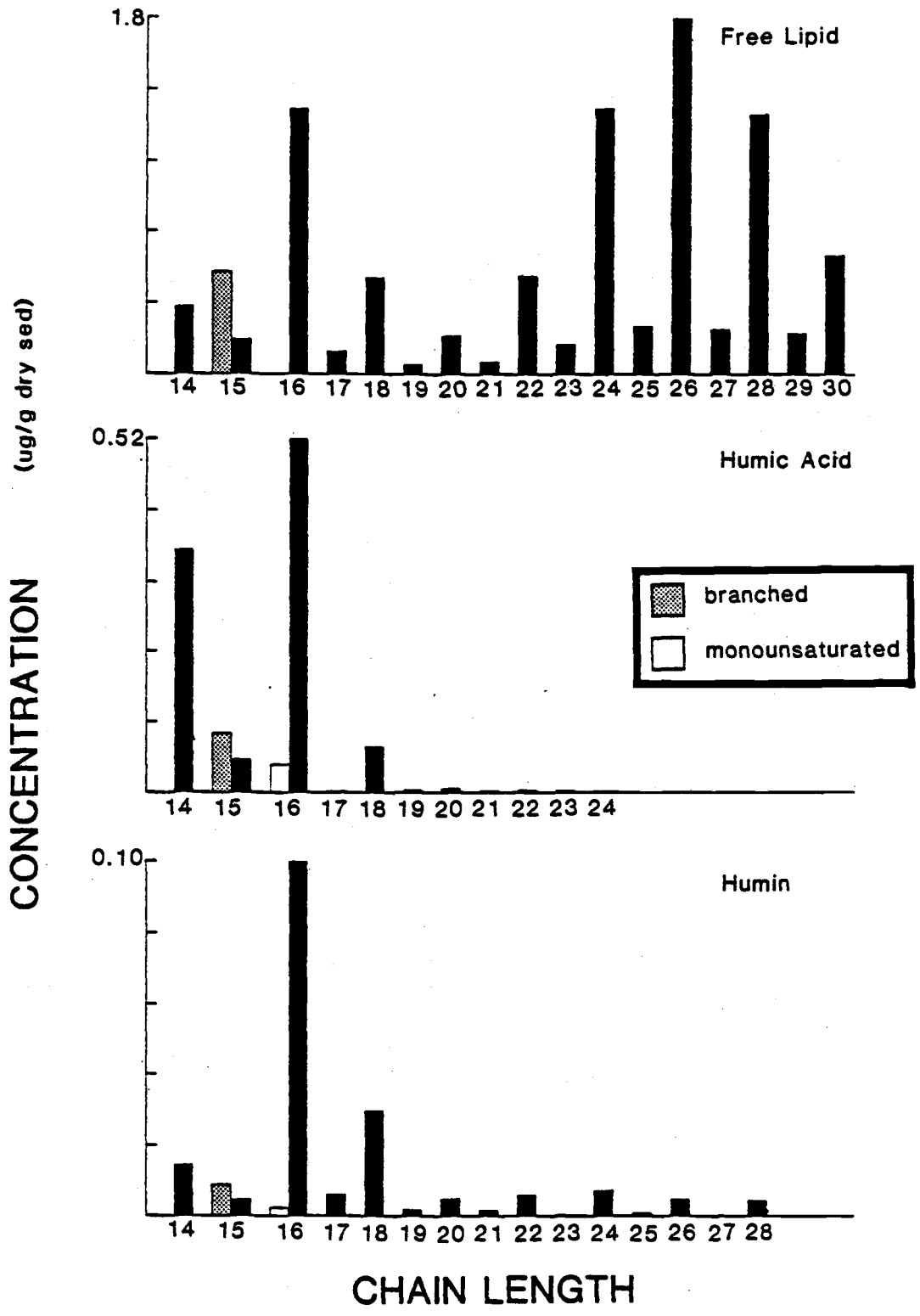

Figure 23. Fatty acid methyl ester distributions in FL, HA, and HU fractions of sample LA. Legend as in Figure 20.

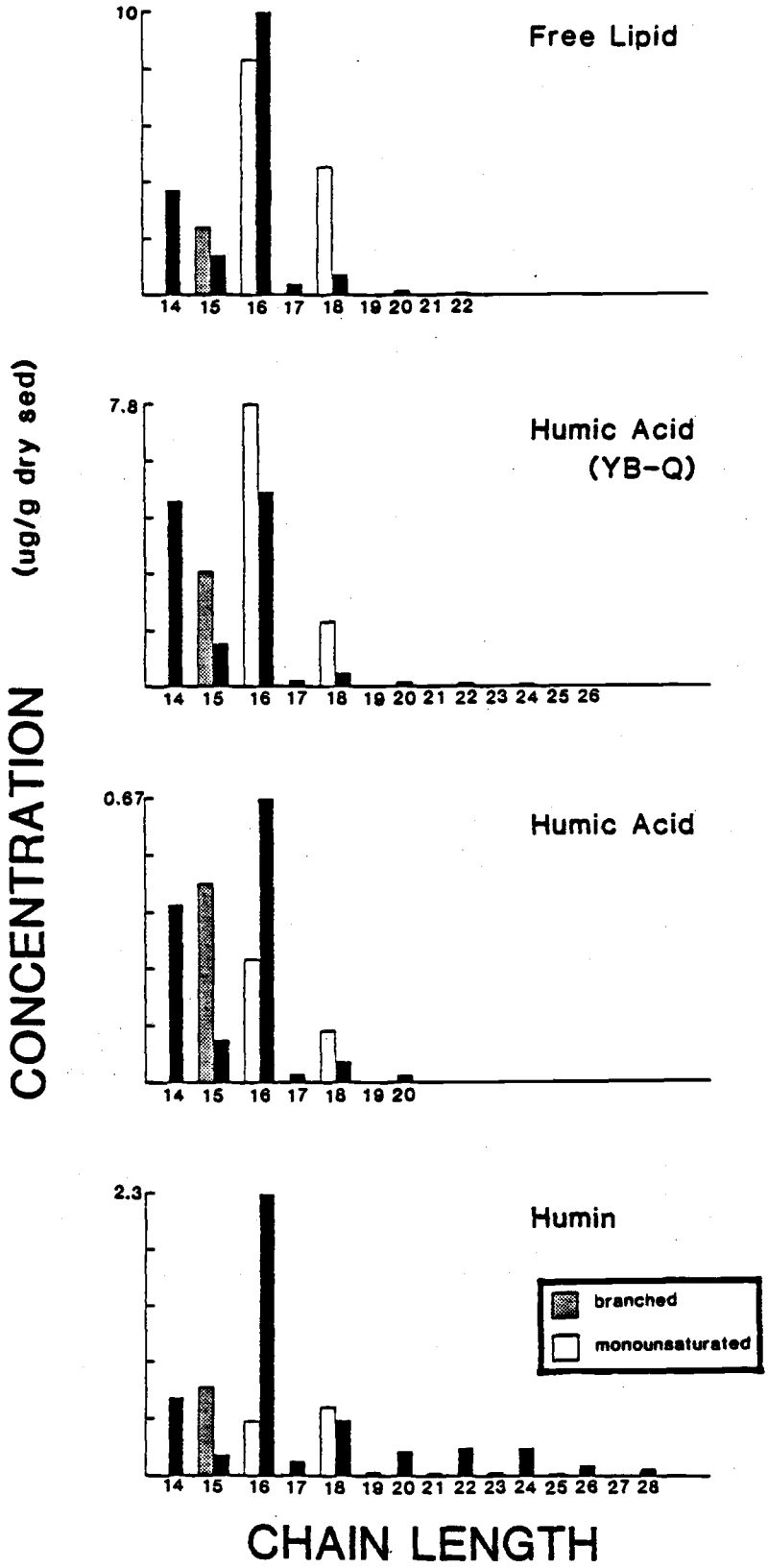

Figure 24. Fatty acid methyl ester distributions in FL, HA, and HU fractions of sample YB, YB-Q. Branched - iso- + anteiso- 15:0; monounsaturated - n-16:0 and n-18:0.

The qualititive distributions of fatty acids in these samples suggest that, regardless of the biogenic source of acids in FL fractions, the fatty acids in bound fractions derive from a microbial source. In all but the YB sample, the long-chained fatty acids, characteristic of higher plants (Eglinton and Hamilton, 1967), predominate in FL fractions. This finding is in accord with the presence of long-chained alkanes with high odd-even predominance in these samples, also suggestive of a terrestrial plant origin. The bound fractions of these samples either contain long-chained acids as minor components or do not contain them at all. Fatty acid distributions of C_{14} to C_{18} with a maximum at C_{16} are characteristic of both algae and bacteria, but the presence of branched components (particularly iso- and anteiso-C_{15}) is considered to be a definitive indicator of bacteria (Johns et al., 1977; Kaneda, 1967; Parkes and Taylor, 1983; Perry et al., 1979; Volkman et al., 1980). n-16:1 is probably a less conclusive indicator of bacteria (Johns et al., 1977; Kaneda, 1967; Parkes and Taylor, 1983; Perry et al., 1979; Volkman et al., 1980), but its presence in conjunction with branched 15:0 in fractions with predominantly short-chained acids is also strongly suggestive of bacteria. Thus, for all but the YB sample, it appears that FL fractions have prevalent terrestrial input with some contribution from algae or bacteria, but the bound fractions are all strongly indicative of bacterial input.

Other researchers have reported similar findings for lacustrine (Cranwell, 1979; 1981; Ishiwatari et al., 1980; Kawamura and Ishiwatari, 1984) and sub-tropical lagoonal/tidal flat (Brooks et al., 1976) sediments. However, Van Vleet and Quinn (1979) found that branched 15:0 acids were more prevalent in free lipid fractions than

in bound fractions in estuarine sediments.

The YB samples deviate somewhat from the other samples in that the YB FL fraction had a FAME signature similar to the bound fractions with no long-chained fatty acids. It is possible that the vegetation in this area, largely coniferous rather than broad-leaved deciduous, does not contain long-chained fatty acid wax components. Indeed, coniferous cuticular waxes are known to contain a narrower n-fatty acid range (C_{12} to C_{18}) than angiosperms but have n-alkane assemblages similar to those of angiosperms (longer-chained alkanes maximizing at C_{27}, C_{29}, of C_{31} with strong odd:even predominance, as observed in sample YB) (Borges Del Castillo et al., 1967; Herbin and Robins, 1968). Regardless, the YB HA and HU fractions are analogous to the corresponding fractions in other samples and the same interpretations apply.

Bound distributions of fatty acids, PCB's, and hydrocarbons were not necessarily consistent in their indications of sources. Fatty acids characteristic of bacteria were prevalent in bound fractions whereas hydrocarbons from vascular plant waxes, and possibly bacteria and combustion sources, were evident in these fractions; bound assemblages of PCB's did not appear to be microbially altered versions of free PCB's despite the predominance of bacterial fatty acids in bound fractions. Such discrepancies can be explained by the fact that bound assemblages of different compound classes may be associated with different sedimentary constituents and have different kinds of association with organic matter. For example, fatty acids are chemically bound components of bacterial cell walls and humic substances whereas hydrocarbons may be entrapped within plant detri-

tus, soot, or some other kind of refractory organic matter. In essence, the selective extraction procedure is of limited selectivity and can yield compounds entrapped in a variety of matrices as well as hydrolyzed compounds all in the same fraction.

Chlorinated Phenols: Hexachlorophene and Pentachlorophenol

Two phenolic pollutants derivatized as methyl ethers, pentachlorophenol (PCP) and hexachlorophene (HCP or 2,2'-methylenebis-(3,4,6-trichlorophenol)), eluted with PCB's during TLC separation. The identities of these compounds in samples were confirmed by comparison of retention times and mass spectra to those of methylated standards. Salient features of these mass spectra are described by Buhler et al. (1973). A spectrum of methylated HCP is presented in Figure 25 because it is virtually inaccessible elsewhere; it is not included in the NBS computer library of mass spectra.

Hexachlorophene is a powerful bacteriostatic agent and germicide patented by the Givaudan Corporation (the sole US producer) in 1941. HCP was widely used in the US until 1972, when the FDA banned over the counter sales of soaps, cosmetics and drugs containing more than 0.1% HCP; products with levels exceeding 0.1% HCP were put on a prescription basis. Because of its effectiveness, HCP is still used in some nurseries (to prevent staphylococcal infections) and in cleaning solutions in some hospitals.

In the two samples in which its presence was confirmed, HR and NB(0-3), HCP occurred only in HA fractions and was a major chlorinated component of these fractions (Figures 8 and 10). Note that the chlorinated phenols, HCP and PCP, were essentially the only chlorinated compounds in the HA fraction of sample HR (Figure 10). HCP may have occurred in the HA fractions of samples LA and NB(29-31) but was not confirmed due to low concentrations. HCP did not show up in any blanks.

The occurrence of HCP in HA fractions and its absence in FL

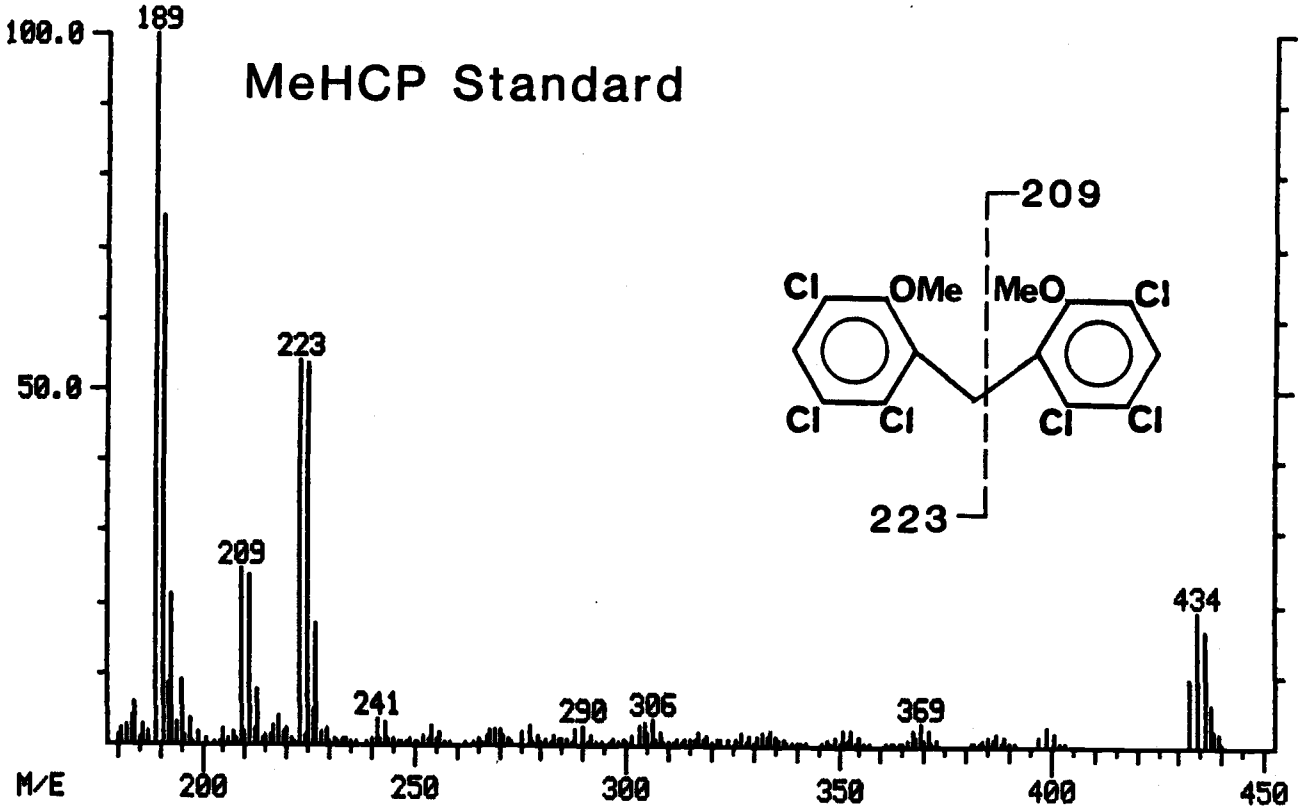

Figure 25. 70 eV mass spectrum of hexachlorophene (dimethyl ether derivative).

fractions suggests that the pollutant was strongly associated with, perhaps covalently bound to, organic matter and was probably deposited in the sediments in bound form. Thus, HCP may have been released hydrolytically from organic matter during base treatment. Laboratory studies support this contention: Miller et al. (1978) demonstrated that HCP covalently binds to rat tissue protein (in vitro) and Mathur and Morley (1978) showed that a structurally similar compound, methoxychlor (2,2'-bis(p-methoxyphenyl)1,1,1-trichloroethane), strongly associated with a synthetic humic acid.

The detection of HCP in environmental samples is noteworthy not only because of its unique distribution, but also because it is seldom reported in environmental literature. Apparently, only two papers document environmental HCP distributions and both were written in the early to mid 1970's. HCP concentrations in the ppb range were reported for municipal sewage effluents (Buhler et al., 1973) and for water and sediments near sewage outfalls (Sims and Pfaender, 1975). The commercial use of HCP has been greatly reduced since the FDA ban was instituted in 1972. However, HCP is very persistent: a laboratory study revealed that HCP was apparently not degraded in river water and had a "half life" of 290 days in estuarine sediments at 22^{o}C (Lee and Ryan, 1979). Furthermore, the environmental release of HCP after 1972 is plausible since some hospitals still use the chemical and may discharge their effluents through municipal sewage treatment plants.

PCP, a general biocide widely used as a wood preservative, may also have been chemically bound to sediments, although the evidence for this is not as strong as that for HCP. Table 9, which presents PCP concentrations for FL, HA and HU fractions of all samples, shows

that PCP was a much more significant component of bound fractions than were the less polar PCB's. Similarly, Murthy et al. (1979) found that PCP and a microbially methylated metabolite, pentachloroanisole, bound to HA and HU fractions of aerobic and anaerobic soils over a 24 day laboratory incubation period.

Table 9. Relative PCP Distributions (as % of total sed. conc.)

Sample	FL	HA[a]	HU
NB(0-3)	38%	17%	45%
NB(29-31)	74%	3%	23%
HR	86%	9%	5%
LA	94%	2%	3%
YB	92%	26%	8%
aerobic loam[b]	15%	15%	9.7%
anaerobic loam[b]	74%	6.5%	7.2%
aerobic loam[c]	38%	38%	24%
anaerobic loam[c]	84%	7.4%	8.2%

[a] HA values have been corrected for blanks

[b] from Murthy et al. (1979); some PCP was recovered in the fulvic acid fraction: 20% - aerobic and 7.4% - anaerobic.

[c] Murthy et al. data standardized such that FL, HA, and HU are reported as percent of FL+HA+HU. This provides a better comparison to the values reported in the present study.

PCP distributions in anaerobic sediments (NB(0-3), NB(29-31), and LA) and aerobic sediments (HR, YB) do not correlate well with the corresponding distributions in incubated loam soils (Table 9). However, sedimentary oxygen content may not be the predominant factor controlling such distributions.

Summary and Conclusions

Quantitative results of this study indicate that "bound" fractions of PCB's and hydrocarbons constituted a relatively minor portion (<10%) of the total sedimentary concentrations of these compounds. Fatty acids and polar pollutants, hexachlorophene and pentachlorophenol, were proportionately more significant in bound fractions than were non-polar compounds.

Assemblages of PCB's, hydrocarbons, and fatty acids in free lipid fractions were generally consistent in their indication of sources and geochemical processes. PCB's and petroleum hydrocarbons were both predominant in free lipid fractions and may have been introduced separately or together by any number of processes (e.g., direct industrial discharge, discharge of treated sewage, surface runoff). The similar chemical characteristics of these non-polar, non-ionic pollutants may contribute to their similar sedimentary organic matter distributions; both compound classes may exist as easily extractable surface coatings on particles. Saturated hydrocarbon and fatty acid distributions both indicated that vascular plant waxes were easily extractable, biogenic sedimentary constituents.

Bound assemblages of each compound class apparently derived from different sources than free assemblages. For hydrocarbons and PCB's, free and bound assemblages may have been associated with particles from different sources and incorporation may have occurred prior to sediment deposition. Both classes of bound compounds may have been entrapped within detrital matrices, e.g., plant detritus or soot. Chemical binding to sedimentary organic matter was probably a con-

trolling factor in distributions of the polar compounds studied. Bound fatty acid distributions, strongly indicative of a microbial source, were probably derived from hydrolyzed bacterial cell walls or humic substances. Hexachlorophene, which occurred in strong associations with humic acid and was not recovered in free lipid or humin fractions, was very indicative of chemical incorporation prior to deposition.

Selective extraction, because it relies on inherantly ambiguous operational definitions, cannot definitively characterize pollutant-organic matter associations. However, it can provide valuable geochemical information, particularly when used to investigate strongly bound pollutants (such as HCP), which would be poorly recovered by solvent extraction techniques conventionally employed in environmental studies.

BIBLIOGRAPHY

Abdullah, M.I., Kveseth, N.J., and Ringstad, O. 1982. PCB's in the sediments of the inner Oslofjord. Water, Air Soil Poll. 18:485-497.

Abelson, P.H. and Hare, P.E. 1971. Reactions of amino acids with natural and artificial humus and kerogens. Carnegie Inst. Wash. Yrbk. 69:327-334.

Albro, P.W., Corbett, J.T., and Schroeder, J.L. 1981. Quantitative characterization of PCB mixtures (Aroclors 1248, 1254, and 1260) by gas chromatography using capillary columns. J. Chromatography 205:103-111.

Albro, P.W. and Parker, C.E. 1979. Comparison of the compositions of Aroclor 1242 and Aroclor 1016. J. Chromatography 169:161-166.

Armour, J.A. 1973. Quantitative perchlorination of PCB's as a method for confirmatory residue measurement and identification. Journal of the A.O.A.C. 56:987-993.

Ballard, T.M. 1971. Role of humic carrier substances in DDT movement through forest soil. Soil Sci. Amer. Proc. 35:145-147.

Ballschmiter, K. and Zell, M. 1980. Analysis of PCB by glass capillary gas chromatography. Fresenius Z. Anal. Chem. 302:20-31.

Bevenue, A., Kelley, T.W., and Hylin, J.W. 1971. Problems in water analysis for pesticide residues. J. Chromatography 54:71-76.

Blumer, M., Souza, G., and Sass, J. 1970. Hydrocarbon pollution of edible shellfish by an oil spill. Marine Biology 5:195-202.

Boehm, P.D. and Quinn, J.G. 1978. Benthic hydrocarbons of Rhode Island Sound. Est. Coastal Mar. Sci. 6:741-794.

Bopp, R.F. 1983. Revised parameters for modeling the transport of PCB components across an air water interface. J. Geophysical Research 88:2521-2529.

Bopp, R.F., Simpson, H.J., Olsen, C.R., and Kostyk, N. 1981. PCB's in sediments of the tidal Hudson River, NY. Envi. Sci. and Tech. 15:210-216.

Bopp, R.F., Simpson, H.J., Olsen, C.R., Trier, R.M., and Kostyk, N. 1982. Chlorinated hydrocarbons and radionuclide chronologies in sediments of the Hudson River and Estuary, New York. Envi. Sci. and Tech. 16:666-676.

Bordovskiy, O.K. 1965. Accumulation and transformation of organic substances in marine sediments. Marine Geology 3:1-114.

Borges Del Castillo, J., Brooks, C.J.W., Cambie, R.C., Eglinton. G., Hamilton, R.J., and Pellitt, P. 1967. The taxonomic distribution of some hydrocarbons in gymnosperms. Phytochemistry 6:391-398.

Briggs, C.G. 1973. A simple relationship between soil adsorption of organic chemicals and their octanol/water partition coefficients. Proc. 7th British Insecticide and Fungicide Conference 11:475-478.

Brooks, P.W., Eglinton, G., Gaskell, S.J., McHugh, D.J., Maxwell, J.R., and Philip, R.P. 1976. Lipids of Recent sediments, part I: Straight-chain hydrocarbons and carboxylic acids of some temperate lacustrine and subtropical lagoonal/tidal flat sediments. Chemical Geology 18:21-38.

Brown, J.F., Jr., Wagner, R.E., Bedard, D.L., Brennan, M.J., Carnahan, J.C., May, R.J., and Tofflemire, T.J. 1984. PCB transformations in upper Hudson sediments. Northeastern Environmental Science 3:167-179.

Buhler, D.R., Rasmusson, M.E., and Nakaue, H.S. 1973. Occurrence of hexachlorophene and pentachlorophenol in sewage and water. Envi. Sci. and Tech. 7:929-934.

Carcich, I.G. and Tofflemire, T.J. 1982. Distribution and concentration of PCB in the Hudson River and associated management problems. Environ. Int. 7:73-85.

Carter, C.W. and Suffet, I.H. 1982. Binding of DDT to dissolved humic materials. Envi. Sci. and Tech. 16:735-740.

Chiou, C.T., Peters, L.J., and Freed, V.H. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science 206:831-832.

Chiou, C.T., Porter, P.E., and Schmedding, D.W. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Envi. Sci. and Tech. 17:227-230.

Choi, W.W. and Chen, K.Y. 1976. Associations of chlorinated hydrocarbons with fine particles and humic substances in nearshore surficial sediments. Envi. Sci. and Tech. 10:782-786.

Clark, R.R., Chian, E.S.K., and Griffin, R.A. 1979. Degradation of PCB's by mixed microbial cultures. Applied and Environ. Microbiology 37:680-685.

Cranwell, P.A. 1981. Diagenesis of free and bound lipids in terrestrial detritus deposited in a lacustrine sediment. Organic Geochemistry 3:79-89.

Cranwell, P.A. 1978. Extractable and bound lipid components in a freshwater sediment. Geochim. Cosmochim. Acta 42:1523-1532.

Davis, J.B. 1968. Paraffinic hydrocarbons in the sulfate-reducing bacterium Desulfovibrio Desulfuricans. Chemical Geology 3:155-160.

Degens, E.T. and Mopper, K. 1975. Early diagenesis of organic matter in marine soils. Soil Science 119:65-72.

Dexter, R.N. and Pavlou, S.P. 1978a. Distribution of stable organic molecules in the marine environment: physical and chemical aspects. Chlorinated hydrocarbons. Marine Chemistry 7:67-84.

Dexter, R.N. and Pavlou, S.P. 1978b. Mass solubility and aqueous activity coefficients of stable organic chemicals in the marine environment: PCB's. Marine Chemistry 6:41-53.

Diachenko, G.W. 1981. Sorptive interactions of selected volatile hydrocarbons with humic acid from different environments. PhD Dissertation, University of Maryland.

Duinker, J.C. and Hillebrand, M.T.J. 1983. Characterization of PCB components in Clophen formulations by capillary GC-MS and GC-ECD techniques. Envi. Sci. and Tech. 17:449-456.

Duinker, J.C., Hillebrand, M.T.J., Palmork, K.H., Wilhelmsen, S. 1980. An evaluation of existing methods for quantitation of PCB's in environmental samples and suggestions for an improved method based on measurement of individual components. Bull. Envi. Contam. Tox. 25:956-964.

Eglinton, G. and Hamilton, R.J. 1967. Leaf epicuticular waxes. Science 156:1322-1335.

Eichelberger, J.W., Harris, L.E., and Budde, W.L. 1974. Analysis of the PCB problem. Anal. Chem. 46:227-232.

Ertel, J.R., Hedges, J.I., and Perdue, E.M. 1984. Lignin signature of aquatic humic substances. Science 223:485-487.

Fales, H.M., Jaouni, T.M., and Babashak, J.F. 1973. Simple device for preparing ethereal diazomethane without resorting to codistillation. Anal. Chem. 45:2302-2303.

Farrington, J.W., Henrichs, S.M., and Anderson, R. 1977. Fatty acids and ^{210}Pb geochronology of a sediment core from Buzzards Bay, MA. Geochim. Cosmochim. Acta 41:289-296.

Farrington, J.W. and Quinn, J.G. 1973. Petroleum hydrocarbons in Narragansett Bay. I. Survey of hydrocarbons in sediments and clams. Est. and Coastal Mar. Sci. 1:71-79.

Farrington, J.W. and Quinn, J.G. 1971. Comparison of sampling and extraction techniques for fatty acids in Recent sediments. Geochim. Cosmochim. Acta 35:735-741.

Flaig, W. 1964. Effects of microorganisms in the transformation of lignin to humic substances. Geochim. Cosmochim. Acta 28:1523-1535.

Fuhrer, G.J. and Rinella, F.A. 1983. Analyses of elutriates, native water and bottom material in selected rivers and estuaries in western Oregon and Washington. USGS Open File Report 82-922. 147p.

Furukawa, K. and Matsumura, F. 1976. Microbial metabolism of PCB's. Studies on the relative degradability of PCB components by Alkaligenes sp. J. Agric. Food Chem. 24:251-256.

Furukawa, K., Tonomura, K., and Kamibayashi, A. 1978. Effect of chlorine substitution on the biodegradability of PCB's. Applied and Environ. Microbiology 35:223-227.

Gagosian, R.B. and Stuermer, D.H. 1977. The cycling of biogenic compounds and their diagenetically transformed products in seawater. Marine Chemistry 5:605-632.

Giam, C.S., Chan, H.S., Neff, G.S., and Atlas, E.L. 1978. Phthalate ester plasticizers: a new class of marine pollutant. Science 199:419-421.

Giger, W., Schaffner, C., and Wakeham, S.G. 1980. Aliphatic and olefinic hydrocarbons in Recent sediments of Greifensee, Switzerland. Geochim. Cosmochim. Acta 44:119-129.

Glooschenko, W.A., Strachan, W.M.J., and Sampson, R.C.J. 1976. Distribution of pesticides and PCB's in water, sediments, and seston of the upper Great Lakes-1974. Pesticide Monitoring Journal 10:61.

Goerlitz, D.F. and Law, L.M. 1974. Distribution of chlorinated hydrocarbons in stream-bottom material. Journal Research USGS 2:541-543.

Goerlitz, D.F. and Law, L.M. 1971. Note on removal of sulfur interferences from sediment extracts for pesticide analysis. Bull. Envi. Contam. Tox. 6:9-10.

Griffin, R.A. and Chou, S.F.J. 1981. Movement of PCB's and other persistent compounds through soil. Water Sci. Tech. 13:1153-1163.

Halcrow, W., Mackay, O.W., and Bogan, J. 1974. PCB levels in Clyde marine sediments and fauna. Marine Pollution Bulletin 5:134-136.

Han, J. and Calvin, M. 1969. Hydrocarbon distribution of algae and bacteria, and microbiological activity in sediments. Proc. Nat. Acad. Sci. 64:436-443.

Hance, R.J. 1969. The adsorption of linuron, atrazine and EPTC by model aliphatic adsorbents and soil organic preparations. Weed Research 9:108-113.

Haque, R. and Schmedding, D. 1976. Studies on the adsorption of selected PCB isomers on selected surfaces. J. Envi. Sci. Health B11:129-137.

Harvey, G.R., Boran, D.A., Chesal, L.A., and Tokar, J.M. 1983. The structure of marine fulvic and humic acids. Marine Chemistry 12:119-132.

Hassett, J.P. and Anderson, M.A. 1979. Association of hydrophobic organic compounds with dissolved organic matter in aquatic systems. Envi. Sci. and Tech. 13:1526-1529.

Hatcher, P.G., Maciel, G.E., and Dennis, L.W. 1981. Aliphatic structure of humic acids; a clue to their origin. Organic Geochemistry 3:43-48.

Hatcher, P.G., Rowan, R., and Mattingly, M.A. 1980. ^{1}H and ^{13}C NMR of marine humic acids. Organic Geochemistry 2:77-85.

Hatcher, P.G., VanderHart, P.L., and Earl, W.L. 1980. Use of solid-state ^{13}C NMR in structural studies of humic acids and humin from Holocene sediments. Organic Geochemistry 2:87-92.

Hayase, K. and Tsubota, H. 1983. Sedimentary humic acid and fulvic acid as surface active substances. Geochim. Cosmochim. Acta 47:947-952.

Hayes, M.H.B., Swift, R.S., Wardle, R.E., and Brown, J.K. 1975. Humic materials from an organic soil: a comparison of extractants and of properties of extracts. Geoderma 13:231-245.

Hedges, J.I. 1978. The formation and clay mineral reactions of melanoidins. Geochim. Cosmochim. Acta 42:69-76.

Herbin, G.A. and Robins, P.A. 1968. Studies on plant cuticular waxes - III. The leaf wax alkanes and w-hydroxy acids of some members of the Cupressaceae and Pinaceae. Phytochemistry 7:1325-1337.

Hetling, L., Horn, E., and Tofflemire, J. 1978. Summary of Hudson River PCB study results. New York State Dept. of Environmental Conservation Technical Paper 51. 88p.

Hiraizumi, Y., Takahashi, M., and Nishimura, H. 1979. Adsorption of PCB onto sea bed sediment, marine plankton and other adsorbing agents. Envi. Sci. and Tech. 13:580-584.

Hites, R.A., LaFlamme, R.E., Windsor, J.G., Jr., Farrington, J.W., and Deuser, W.G. 1980. Polycyclic aromatic hydrocarbons in an anoxic sediment core from the Pettaquamscutt River (Rhode Island, USA). Geochim. Cosmochim. Acta 44:873-878.

Hoering, T.C. 1973. A comparison of melanoidin and humic acid. Carnegie Inst. Wash. Yrbk. 72:682-690.

Horn, E.G., Hetling, L.J., and Tofflemire, T.J. 1979. The Problem of PCB's in the Hudson River system, pp.591-609. In Health Effects of Halogenated Aromatic Hydrocarbons, Annals of NY Academy of Sciences, Vol. 320.

Hutzinger, O., Safe, S., and Zitko, V. 1974. The Chemistry of PCB's. CRC Press: Cleveland, OH. 269p.

Ishiwatari, R. and Machihara, T. 1983. Early stage incorporation of biolipids into kerogen in a lacustrine sediment: evidence from alkaline $KMnO_4$ oxidation of sedimentary lipids and humic matter. Organic Geochemistry 4:179-184.

Ishiwatari, R. and Machihara, T. 1982. Algal lipids as a possible contributor to the polymethylene chains in kerogen. Geochim. Cosmochim. Acta. 46:1459-1464.

Ishiwatari, R., Ogura, K., and Horie, S. 1980. Organic geochemistry of a lacustrine sediment (Lake Haruna, Japan). Chemical Geology 29:261-280.

Jensen, S. 1966. Report of a new chemical hazard. New Scientist 32:612.

Johns, R.B., Perry, G.J., and Jackson, K.S. 1977. Contribution of bacterial lipids to Recent marine sediments. Est. Coastal Mar. Sci. 5:521-529.

Kaneda, T. 1967. Fatty acids in the genus Bacillus. J. Bacteriology 93:894-903.

Karickhoff, S.W., Brown, D.S., and Scott, T.A. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Research 13:241-248.

Kawamura, K. and Ishiwatari, R. 1984. Tightly bound aliphatic acids in Lake Biwa sediments: their origin and stability. Organic Geochemistry 7:121-126.

Kerkhoff, M.A.T., de Vries, A., Wegman, R.C.C., and Hofstee, A.W.M. 1982. Analysis of PCB's in sediments by glass capillary gas chromatography. Chemosphere 11:165-174.

Khan, S.U and Schnitzer, M. 1978. Soil Organic Matter. Elsevier Scientific Pub. Co.: New York. 319p.

Khan, S.U. and Schnitzer, M. 1972. The retention of hydrophobic organic compounds by humic acid. Geochim. Cosmochim. Acta 36:745-754.

Kulm, L.D. 1965. Sediments of Yaquina Bay, Oregon. PhD Dissertation, Oregon State University.

Lambert, S.M. 1968. Omega, a useful index of soil sorption equilibria. J. Agr. Food Chem. 16:340-343.

Lambert, S.M. 1967. Functional relationship between sorption in soil and chemical structure. J. Agr. Food Chem. 15:572-576.

Landrum, P.F., Nihart, S.R., Eadie, B.J., and Gardner, W.S. 1984. Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters. Envi. Sci. and Tech. 18:187-192.

Larter, S.R. and Douglas, A.G. 1980. Melanoidins - kerogen precursors and geochemical lipid sinks: a study using pyrolysis-gas chromatography (PGC). Geochim. Cosmochim. Acta 44:2087-2095.

Lee, R.F. and Ryan, C. 1979. Microbial degradation of organochlorine compounds in estuarine waters and sediments, pp. 443-450. In A.W. Bourquin and P.H. Pritchard (eds.) Proc. Workshop: Microbial Degradation Pollut. Mar. Environ. EPA-600/9-79-012.

Liu, R.H., Ramesh, S., Liu, J.Y., and Kim, S. 1984. Qualitative and quantitative analyses of commercial PCB formulation mixtures by single ion monitoring GLC/MS and multiple regression. Anal. Chem. 56:1808-1812.

Malcolm Pirnie, Inc. 1982. Acushnet River Estuary PCB Study. Prepared for the Commonwealth of Mass. Water Resources Commission, Division of Water Pollution Control, Boston, MA.

Martin, J.P. and Haider, K. 1971. Microbial activity in relation to soil humus formation. Soil Science 111:54-63.

Mathur, S.P. and Morley, H.V. 1978. Incorporation of Methoxychlor-^{14}C in model humic acids prepared from hydroquinone. Bull. Envi. Contam. Tox. 20:268-274.

Matsuda, H. and Koyama, T. 1977. Early diagenesis of fatty acids in lacustrine sediments - I. Identification and distribution of fatty acids in Recent sediment from a freshwater lake. Geochim. Cosmochim. Acta 41:777-783.

Metcalf and Eddy, Inc. 1983. Acushnet Estuary PCBs Data Management Final Report. Prepared for EPA Region I, Boston, MA. 137p.

Miller, A., III, Henderson, M.C., and Buhler, D.R. 1978. Cytochrome p-450-mediated covalent binding of hexachlorophene to rat tissue proteins. Molecular Pharmacology 14:323-336.

Miller, M.M., Ghodbane, S., Wasik, S.P., Tewari, Y.B., and Martine, D.E. 1984. Aqueous solubilities, octanol/water partition coefficients, and entropies of melting of chlorinated benzenes and biphenyls. J. Chem. Eng. Data 29:184-190.

Miller, S. 1982. The persistent PCB problem. Envi. Sci. and Tech. 16:98A-99A.

Mrozek, E. and Leidy, R.B. 1981. Investigation of selective uptake of PCB's by Spartina alterniflora Loisel. Bull. Envi. Contam. Tox. 27:481-488.

Mullin, M.D. and Filkins, J.C. 1981. Analysis of PCB's by glass capillary and packed column chromatography, pp. 187-196. In L.H. Keith (ed.) Advances in the Identification and Analysis of Organic Pollutants in Water, Vol. I. Ann Arbor Science: Ann Arbor, MI. 1170p.

Mullin, M.D., Pochini, C.M., McCrindle, S., Romkes, M., Safe, S.H., and Safe, L.M. 1984. High resolution PCB analysis: synthesis and chromatographic properties of all 209 PCB congeners. Envi. Sci. and Tech. 18:468-476.

Mullin, M.D., Pochini, C.M., Safe, S.H., and Safe, L.M. 1983. Analysis of PCB's using specific isomer high resolution capillary gas chromatography, pp. 165-176. In F. D'Itri and M.A. Kamrin (eds.) PCB's: Human and Environmental Hazards. Ann Arbor Science: Ann Arbor, MI. 443p.

Murthy, N.B.K., Kaufman, D.D., and Fries, G.F. 1979. Degradation of pentachlorophenol (PCP) in aerobic and anaerobic soil. J. Envi. Sci. Health B14:1-14.

National Academy of Sciences (NRC, Committee on Assessment of PCB's in the Environment). 1979. Polychlorinated Biphenyls. NAS: Washington, D.C. 182p.

New England Aquarium. 1973. Site selection and study of ecological effects of disposal of dredged materials in Buzzards Bay, MA. Unpublished report DACW33-77-C-0024. 70p.

Neyroud, J.A. and Schnitzer, M. 1975. The alkaline hydrolysis of humic substances. Geoderma 13:171-188.

Nisbet, I.C.T and Sarofim, A.F. 1972. Rates and routes of transport of PCB's in the environment. Environmental Health Perspectives 2:21-38.

Nissenbaum, A. and Kaplan, I.R. 1972. Chemical and isotopic evidence for the in situ origin of marine humic substances. Limnology and Oceanography 17:570-582.

Ogner, G. and Schnitzer, M. 1970. Humic substances: fulvic acid-dialkyl phthalate complexes and their role in pollution. Science 170:317-318.

Onuska, F.I. and Comba, M. 1980. Identification and quantitative analysis of polychlorinated biphenyls on WCOT glass capillary columns, pp. 282-302. In B.K. Afghan and D. McKay (eds.) Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment. Plenum Press: New York. 588p.

Onuska, F.I., Kominar, R.J., and Terry, K.A. 1983. Identification and determination of PCB's by high-resolution gas chromatography. J. Chromatography 279:111-118.

Parkes, R.J. and Taylor, J. 1983. The relationship between fatty acid distributions and bacterial respiratory types in contemporary marine sediments. Est. Coastal Shelf Sci. 11:173-189.

Pavlou, S.P. and Dexter, R.N. 1979. Distribution of PCB in estuarine ecosystems. Testing of the concept of equilibrium partitioning in the marine environment. Envi. Sci. and Tech. 13:65-71.

Perry, G.J., Volkman, J.K., and Johns, R.B. 1979. Fatty acids of bacterial origin in contemporary marine sediments. Geochim. Cosmochim. Acta 43:1715-1725.

Pierce, R.H., Jr., Olney, C.E., and Felbeck, G.T., Jr. 1974. p,p'-DDT adsorption to suspended particulate matter in sea water. Geochim. Cosmochim. Acta 38:1061-1073.

Povoledo, D. and Pitze, M. 1979. Preparation of low-ash humic acids, and the accompanying losses of organic material, from Canadian lake sediments and a gleysol. Soil Science 128:1-8.

Prahl, F.G., Crecelius, E., and Carpenter, R. 1984. Polycyclic aromatic hydrocarbons in Washington coastal sediments: an evaluation of atmospheric and riverine routes of introduction. Envi. Sci. and Tech. 18:687-693.

Rohrback, B.G. and Reed, W.E. 1975. Evaluation of extraction techniques for hydrocarbons in marine sediments. Institute of Geophysics and Planetary Physics, UCLA. 23p. (Unpublished)

Rote, J.W. and Morris, W.J. 1973. Use of isotopic abundance ratios in identification of PCB's by mass spectrometry. Journal of the AOAC 56:188-199.

Rote, J.W. and Murphy, P.G. 1971. A method for the quantitation of PCB isomers. Bull. Envi. Contam. Tox. 6:377-384.

Safe, S., Mullin, M., Safe, L., Pochini, C., McCrindle, S., and Romkes, M. 1983. High resolution PCB analysis, pp. 1-13. In D. Mackay, S. Patterson, S.J. Eisenreich, and M.S. Simmons (eds.), Physical Behavior of PCB's in the Great Lakes. Ann Arbor Science: Ann Arbor, MI. 442p.

Sawhney, B.L., Frink, C.R., and Glowa, W. 1981. PCB's in the Housatonic River: Determination and distribution. J. Envi. Qual. 10:444-448.

Schnitzer, M. and Neyroud, J.A. 1975. Alkanes and fatty acids in humic substances. Fuel 54:17-19.

Schwarzenbach, R.P. and Westall, J. 1981. Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. Envi. Sci. and Tech. 15:1360-1367.

Simmons, M.S., Bialosky, D.I., and Rossmann, R. 1980. PCB contamination in surficial sediments of northeastern Lake Michigan. J. Great Lakes Research 6:167-171.

Simmons, M.S. and Kotz, K.T. 1982. Association studies of PBB's in aquatic systems. Bull. Envi. Contam. Tox. 29:58-63.

Simoneit, B.R.T. 1978. The organic chemistry of marine sediments, pp. 233-311. In J.P. Riley and R. Chester (eds.) Chemical Oceanography, Volume 7. 2nd Edition. Academic Press: New York. 508p.

Simoneit, B.R.T. 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acta 41:463-476.

Simoneit, B.R.T and Kaplan, I.R. 1980. Triterpenoids as molecular indicators of paleoseepage in Recent sediments of the southern California Bight. Marine Environmental Research 3:113-128.

Sims, J.L. and Pfaender, F.K. 1975. Distribution and biomagnification of hexachlorophene in urban drainage areas. Bull. Envi. Contam. Tox. 14:214-220.

Sissons, D. and Welti, D. 1971. Structural identification of PCB's in commercial mixtures by GLC, NMR and MS. J. Chromatography 60:15-32.

Sloan, R.J., Simpson, K.W., Schroeder, R.A., and Barnes, C.R. 1983. Temporal trends toward stability of Hudson River PCB contamination. Bull. Envi. Contam. Tox. 31:377-385.

Smith, D.J., Eglinton, G., and Morris, R.J. 1983. The lipid chemistry of an interfacial sediment from the Peru Continental Shelf: fatty acids, alcohols, aliphatic ketones and hydrocarbons. Geochim. Cosmochim. Acta 47:2225-2232.

Snyder, D. and Reinert, R. 1971. Rapid separation of PCB's from DDT and its analogues on silica gel. Bull. Envi. Contam. Tox. 6:385-390.

Steen, W.C., Paris, D.F., and Baughman, G.L.. 1978. Partitioning of selected PCB's to natural sediments. Water Research 12:655-657.

Strek, H.J. and Weber, J.B. 1982. Adsorption and reduction in bioactivity of PCB (Aroclor 1254) to Redroot Pigweed by soil organic matter and montmorillonite clay. Soil Sci. Soc. Amer. J. 46:318-322.

Stuermer, D.H. and Harvey, G.R. 1978. Structural studies on marine humus: a new reduction sequence for carbon skeleton determination. Marine Chemistry 6:55-70.

Stuermer, D.H., Peters, K.E., and Kaplan, I.R. 1978. Source indicators of humic substances and protokerogen. Stable isotope ratios, elemental compositions and electron spin resonance spectra. Geochim. Cosmochim. Acta 42:989-997.

Summerhayes, C.P., Ellis, J.P., Stoffers, P., Briggs, S.R., and Fitzgerald, M.G. 1977. Fine-grained sediment and industrial waste distribution and dispersal in New Bedford Harbor and western Buzzards Bay, MA. WHOI Technical Report, WHOI-76-115. 110p.

Swift, R.S. and Posner, A.M. 1972. Autoxidation of humic acid under alkaline conditions. Journal of Soil Science 23:381-393.

Thompson, S. and Eglinton, G. 1978. The fractionation of a Recent sediment for organic geochemical analysis. Geochim. Cosmochim. Acta 42:199-207.

Tipping, E. and Ohnstad, M. 1984. Aggregation of aquatic humic substances. Chem. Geol. 44:349-357.

Tucker, E.S., Saeger, V.W., and Hicks, O. 1975. Activated sludge primary biodegradation of PCB's. Bull. Envi. Contam. Tox. 14:705-713.

Van Vleet, E.S. and Quinn, J.G. 1979. Early diagenesis of fatty acids and isoprenoid alcohols in estuarine and coastal sediments. Geochim. Cosmochim. Acta 43:289-303.

Van Vleet, E.S. and Quinn, J.G. 1978. Contribution of chronic petroleum inputs to Narragansett Bay and Rhode Island Sound sediments. J. Fish. Res. Board Can. 35:536-543.

Van Vleet, E.S. and Quinn, J.G. 1977. Input and fate of petroleum hydrocarbons entering the Providence River and upper Narragansett Bay from wastewater effluents. Envi. Sci. and Tech. 11:1086-1092.

Venkatesan, M.I., Brenner, S., Ruth, E., Bonilla, J., and Kaplan, I.R. 1980. Hydrocarbons in age-dated sediment cores from two basins in the southern California Bight. Geochim. Cosmochim. Acta 44:789-802.

Voice,T.C., Rice, C.P, and Weber, W.J., Jr. 1983. Effects of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. Envi. Sci. and Tech. 17:513-518.

Volkman, J.K., Johns, R.B., Gillan, F.T., and Perry, G.J. 1980. Microbial lipids of an intertidal sediment - I. Fatty acids and hydrocarbons. Geochim. Cosmochim. Acta 44:1133-1143.

Weaver, G. 1984. PCB contamination in and around New Bedford, MA. Envi. Sci. and Tech. 18:22A-27A.

Weaver, G. 1982. PCB Pollution in the New Bedford Mass. area: A status report. Mass. Coastal Zone Management. Boston, MA. 62p.

Webb, R.G. and McCall, A.C. 1973. Quantitative PCB standards for electron capture-gas chromatography. J. Chromat. Sci. 11:366-373.

Weliky, K., Suess, E., Ungerer, C.A., Muller, P.J., and Fischer, K. 1983. Problems with accurate carbon measurements in marine sediments and particulate matter in seawater: A new approach. Limnology and Oceanography 28:1252-1259.

Wershaw, R.L., Burcar, P.J., and Goldberg, M.C. 1969. Interaction of pesticides with natural organic material. Envi. Sci. and Tech. 3:271-273.

Wershaw, R.L., Pinckney, D.J., and Booker, S.E. 1977. Chemical structure of humic acids - part 1, a generalized structural model. Journal Research USGS 5:565-569.

West, R.H. and Hatcher, P.G. 1980. PCB's in sewage sludge and sediments of the New York Bight. Marine Pollution Bulletin 11:126-129.

Wildish, D.J., Metcalfe, C.D., Akagi, H.M., and McLeese, D.W. 1980. Flux of Aroclor 1254 between estuarine sediments and water. Bull. Envi. Contam. Tox. 24:20-26.

Wilson, M.A., Philip, R.P., Gillam, A.H., Gilbert, T.D., and Tate, K.R. 1983. Comparison of the structures of humic substances from aquatic and terrestrial sources by pyrolysis-gas chromatography-mass spectrometry. Geochim. Cosmochim. Acta 47:497-502.

Young, D.R., Heesen, T.C. and McDermott, D. 1980. Inputs and distributions of PCB's and DDT in three southern California harbors. (Unpublished manuscript).

Young, S.J.V. and Burke, J.A. 1972. Micro scale alkali treatment for use in pesticide residue confirmation and sample cleanup. Bull. Envi. Contam. Tox. 7:160-167.

Zitko, V., Hutzinger, O., and Safe, S. 1971. Retention times and ECD responses of some individual chlorobiphenyls. Bull. Envi. Contam. Tox. 6:160-163.

APPENDIX

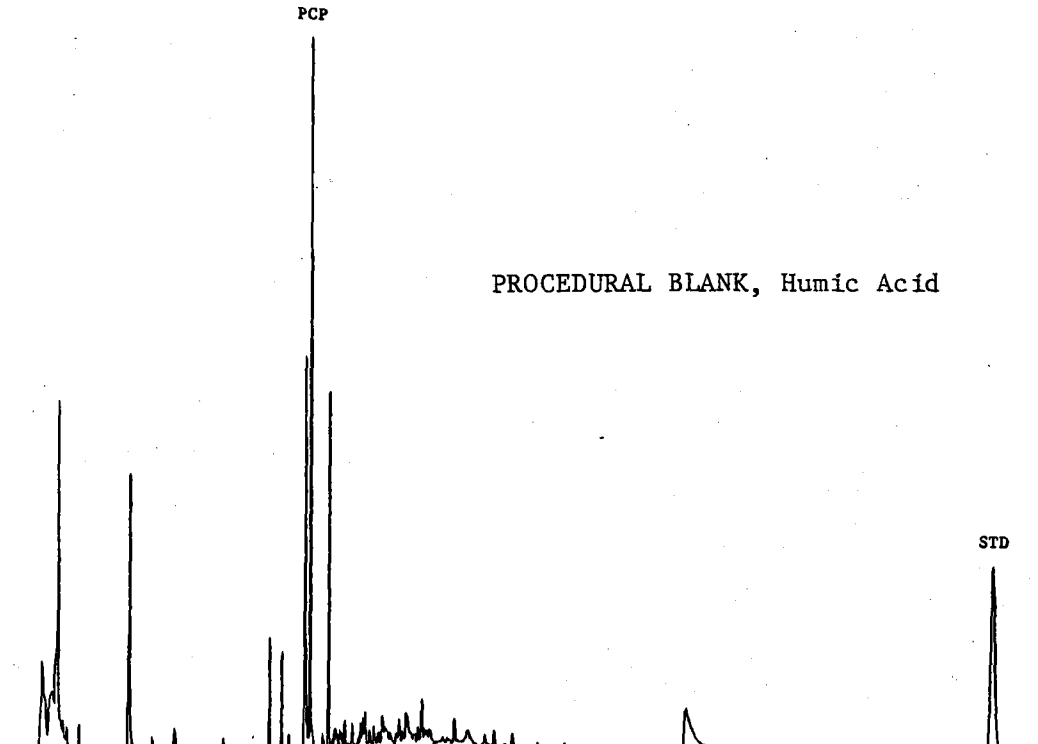

Figure 1A. GC-ECD chromatogram of procedural blank, Humic Acid

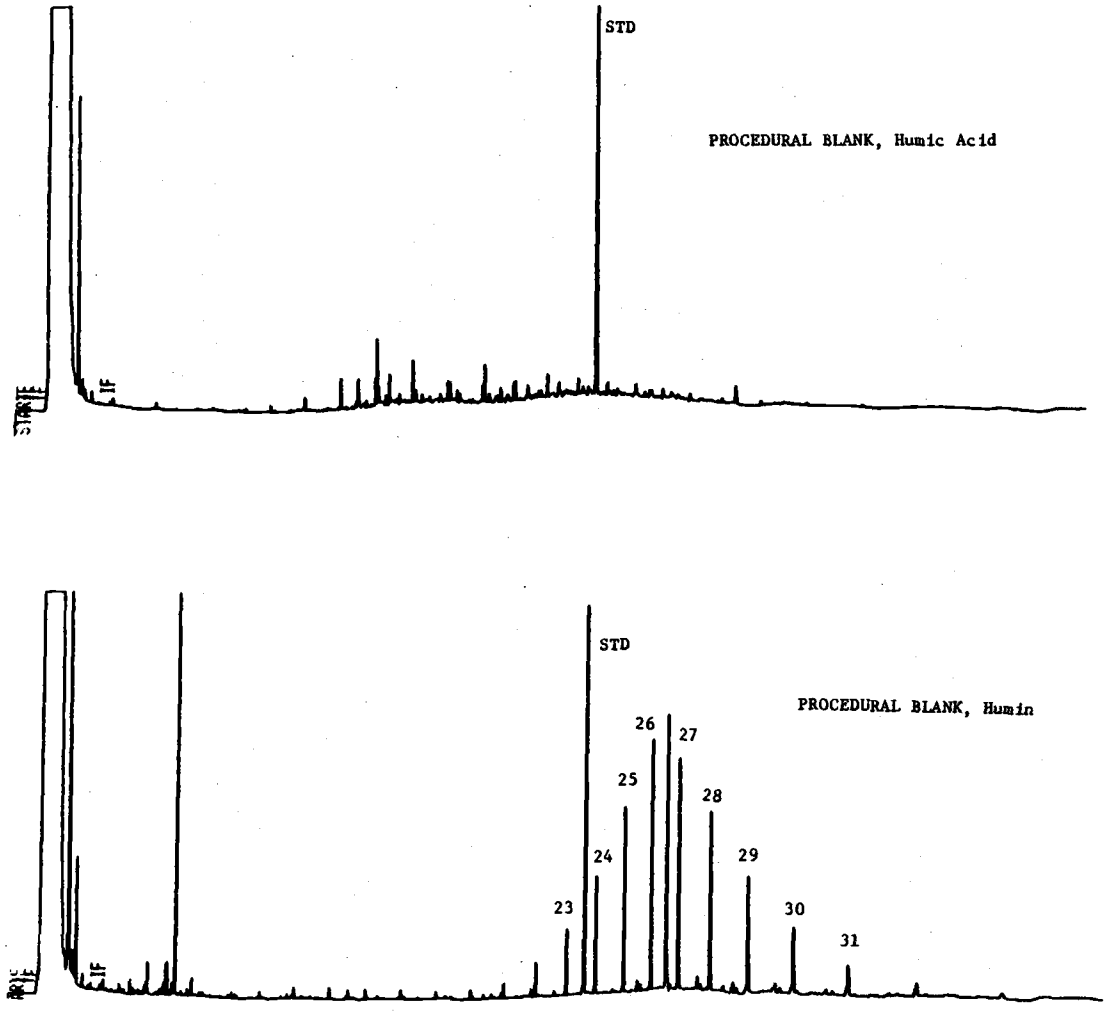

Figure 2A. GC-FID chromatograms of procedural blanks, Humic Acid and Humin (hydrocarbon fractions)