

61746

ATTACHMENT O
PART 1 OF 2

PCB BIOTRANSFORMATION IN
AQUATIC SEDIMENTS:
NEW BEDFORD HARBOR AND
OTHER SITES



SDMS DocID **61746**

New Bedford

61746

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NEW BEDFORD HARBOR AND
OTHER SITES

Prepared for:

AVX Corporation
750 Lexington Avenue
New York, New York 10022-1208

Prepared by:

YOAKUM & ASSOCIATES, INC.
Lenoir City, Tennessee 37771

and

BALSAM ENVIRONMENTAL CONSULTANTS, INC.
59 Stiles Road
Salem, New Hampshire 03079

October 16, 1989
Balsam Project 6292.07/2455

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TERMS

"Additive Effect": To heighten or increase the intensity of a peak in a chromatogram (enhancement).

Anaerobe: A microorganism that flourishes without free oxygen.

Anaerobic microbial (bio)degradation: The reduction of a chemical component from a higher to a lower type by the action of anaerobic microbes.

Anaerobic biotransformations: Changes brought about as the result of the action of anaerobic bacteria.

Anaerobic dechlorination: A specific PCB microbial degradation process whereby chlorine is selectively removed from a congener as the result of anaerobic microbial actions.

Aroclor: Trade name (Monsanto) for a series of commercial polychlorinated biphenyl (PCB) and polychlorinated terphenyl mixtures marketed in the United States.

Aroclor degradation: A reductive modification with respect to the proportions of the individual PCB congeners present in the specific Aroclor.

Aroclor transformation: Any change (either reduction or enhancement) in the unique characteristic of the composition of a specific Aroclor.

Chromatogram: A tracing of the detector output from a chromatograph which consists of a series of peaks over time.

Chromatographic pattern alteration: Any change or modification which occurs in the chromatogram produced by a known reference material (e.g., a specific Aroclor).

Congener: One of the 209 PCBs or other group of compounds, not necessarily the same homolog.

Congener selectivity pattern: The sequence whereby specific PCB congeners undergo anaerobic dechlorination.

Degrade: To reduce from a higher to a lower type.

Enhance: To heighten or increase in intensity.

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TERMS (continued)

Environmental aging (weathering): The process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. True molecular solution in water is shown (on chromatograms) as the non-selective loss of the more volatile and more water-soluble congeners from the Aroclors in the sediments.

"High-end drop-off": The pattern alteration observed when higher chlorinated PCB congeners (usually penta- and hexa-) undergo anaerobic dechlorination.

High resolution gas-liquid chromatography: Gas chromatography with a capillary column.

Homolog: One of the 10 degrees of chlorination of PCBs ($C_{12}H_9Cl$ through $C_{12}Cl_{10}$) or other group of compounds varying by systematic addition of a substituent.

Isomer: Any PCB or other compound which has the same molecular formula, but with different positional substitutions. 2,2'-dichlorobiphenyl and 2,3-dichlorobiphenyl are isomeric; 4-chlorobiphenyl and 2,3,4-trichlorobiphenyl are not.

"Low-end drop-off": The pattern alteration observed when lower chlorinated PCB congeners are removed from samples, e.g., by weathering.

Part per million (ppm): One part in 10^6 .

Pattern alterations: Changes in a characteristic chromatographic pattern. The effect of the changes will be reflected by peak enhancements, reductions, or both. (See chromatographic pattern alterations.)

Polychlorinated biphenyl (PCB): One of 209 individual compounds having the molecular formula $C_{12}H_nCl_{10-n}$, where $n = 0-9$. This definition includes monochlorobiphenyls, but not biphenyl.

PCB degradation: A conversion whereby a PCB congener of a higher chlorine content is reduced (converted) to one of a lower chlorine content.

PCB transformation: Any change whereby a PCB congener is converted into another compound.

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TERMS (continued)

Reductive dechlorination: Selective removal of chlorine from PCB congeners in an atmosphere without free oxygen.

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, typically expressed in seconds or minutes.

Transformation: Any change which gives a different appearance.

Weathering: A process which gives a compositional change in an Aroclor residue (see environmental aging).

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ABBREVIATIONS

ACOE	(U.S.) Army Corps of Engineers
EPA	(U.S.) Environmental Protection Agency
GC	Gas-liquid chromatography (column type unspecified)
GC/EC	Gas chromatography/electron capture (detector)
GC/MS	Gas-liquid chromatography/mass spectrometry (ionization mode unspecified)
NBH	New Bedford Harbor
PCB	Polychlorinated biphenyl
ppm	Parts per million (10^{-6})
RIC	Reconstructed ion chromatogram (in GC/MS)
RT	Retention time
YAI	Yoakum & Associates, Inc.

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EXECUTIVE SUMMARY

Polychlorinated biphenyls (PCBs) have been present in aquatic sediments at numerous sites throughout the United States for several decades. PCBs were widely used commercially because of properties which made them relatively resistant to physical and chemical decomposition. It was in part due to this fact that environmental degradation of PCBs was not considered as a significant, viable process until the early to mid-1970s when it was first discussed in the scientific literature. At that time, PCBs were shown to undergo transformations in the environment by several physical processes and by bacterial oxidation. Later, in 1980, it was first observed that PCBs were being extensively degraded in anaerobic aquatic sediments. It was determined that these transformations were mediated by anaerobic bacteria and the process was termed reductive dechlorination. This discovery was of great significance since much of the PCB contaminated aquatic sediments at known sites across the U.S. existed in anaerobic zones where degradation processes were not known to be operating to a great extent.

During this decade, research has been performed to determine the occurrence and extent of anaerobic transformations, primarily reductive dechlorination, of PCBs in aquatic sediments at various sites. It has become apparent that significant changes in environmentally deposited PCBs can be effected by this process. These changes, when present, are evident in analytical chromatograms of environmental samples contaminated by PCBs. Each PCB Aroclor or formulation yields a characteristic pattern of peaks when analyzed by gas chromatography and this pattern is compared to that of an environmental sample to evaluate transformations that may have occurred. It requires a highly specialized analyst to recognize these patterns and identify the governing transformation processes. It is for this reason that, historically, many transformed Aroclor peak patterns have been misinterpreted or unnoticed.

PCB biotransformation in aquatic sediments has been shown to occur at numerous sites across the country with two sites being studied extensively: the upper Hudson River and the Acushnet River Estuary region of the New Bedford Harbor Superfund site. Hundreds of analytical chromatograms of samples collected at both of these sites have been reviewed by several researchers and distinctive, recurring transformed Aroclor patterns have been classified. The different patterns result from congener-selectivity and the stage of the anaerobic reductive dechlorination process represented in a particular chromatogram. Reductive dechlorination has been found to remove preferentially chlorine atoms located at the meta and para positions on the biphenyl ring and thus to eliminate preferentially PCB congeners associated with toxic effects. Removal of chlorine atoms in the ortho positions has also been shown to occur in selected samples.

The New Bedford Harbor data evaluations performed for purposes of this paper encompass many of EPA's sediment sampling programs. Ninety-seven percent (97%) of the sediment sampling sites examined exhibited biotransformations in the form of reductive dechlorination. A qualitative system for classifying the extent of dechlorination at these sites was developed, and a majority of the sites were found to have undergone moderate or advanced Aroclor 1254 transformations and moderate Aroclor 1016/1242 transformations. It thus appears that significant detoxification of PCBs present in Acushnet River Estuary sediments already has occurred and will continue to occur if anaerobic conditions in these sediments are left undisturbed.

**PCB BIOTRANSFORMATION IN
AQUATIC SEDIMENTS:
NEW BEDFORD HARBOR AND
OTHER SITES**

1.0 INTRODUCTION

Since the early to mid-1970s, it has been established that polychlorinated biphenyls (PCBs) can undergo transformation in the environment and in the laboratory as a result of several different processes, including oxidation by certain bacteria, volatilization, solubilization and photolysis (Furukawa, 1982). Until recently, however, the consensus among much of the scientific community was that PCBs were generally resistant to a significant degree of degradation by these processes in the environment.

The first reported observation of anaerobic transformations of Aroclors came in 1980, when Yoakum (1982) found substantial pattern alterations in PCB residues detected in the sediments of Silver Lake in Pittsfield, Massachusetts. The Silver Lake sediment chromatograms indicated that extensive alteration of the original Aroclor PCB congener distribution had occurred. About the same time, Suflita (1982) demonstrated a novel pathway for the anaerobic biodegradation of halo-aromatic compounds that suggested reductive dehalogenation of aromatics could be important in removal of some chlorinated xenobiotic compounds from the environment. Following these initial observations, additional research has been performed to determine the occurrence and extent of anaerobic transformations of PCBs in aquatic sediments at various sites, and it has become apparent that anaerobic reductive dechlorination can effect significant changes in environmentally deposited Aroclors.

In view of the relatively short history of awareness regarding reductive dechlorination of PCBs, this paper has been prepared to collect and organize the

existing knowledge on the subject, and to discuss the now extensive body of evidence indicating that this process has been and is occurring at several sites under investigation, including the New Bedford Harbor (NBH) Superfund site. A brief review of selected references discussing aerobic PCB biotransformation, a potentially complementary process, also is provided.

The appendices to this paper comprise a series of reports prepared by Yoakum and Associates, Inc. (YAI) as part of an ongoing research project designed to determine the extent to which reductive microbial PCB dechlorination is occurring in New Bedford Harbor sediments. Appendix I (YAI Task 11 Report, 1989) contains background information on the chemistry, properties and analysis of PCBs. Appendices II through VII (YAI Task 2, 3, 7, 8, 10 and 12 Reports, 1989, respectively) review and discuss PCB analytical data from several EPA-sponsored NBH sediment sampling programs and one special NBH sediment sampling program sponsored by AVX Corporation, providing a classification and evaluation of the Aroclor transformations evident in each of these data sets.

2.0 PCB BIOTRANSFORMATION AT SITES OTHER THAN NEW BEDFORD HARBOR

In this decade, papers have appeared in the scientific literature presenting and discussing evidence of PCB biotransformation occurring at several locations in the U.S. where aquatic sediments have been contaminated by PCBs. Initially, this evidence was observed by environmental analytical chemists in the course of routine examination of sediment sampling analytical data (Yoakum, 1980, 1981 and 1982). These observations suggested that PCB biotransformations were occurring under anaerobic conditions. Subsequently, analysis of aquatic sediment samples from selected sites was performed by several independent research groups in order to further evaluate the occurrence and mechanisms of PCB biotransformation.

As a result of these efforts, a substantial database has been developed which documents the occurrence of PCB biotransformation at aquatic sites. The emerging consensus among researchers is that PCB biotransformation is occurring to a significant degree at numerous sites and that the primary mechanism responsible for the observed biotransformation is reductive dechlorination mediated by indigenous anaerobic bacteria.

Note: Throughout this document, the positions of chlorine atoms on the biphenyl ring system will be designated according to the conventions employed by Brown et al. (1987 a & b). Using this practice, the congeners 2,2'-dichlorobiphenyl and 2,2',3,4,5'-pentachlorobiphenyl would appear as 2-2 CB and 234-25 CB (or simply 2-2 and 234-25), respectively.

2.1 OCCURRENCE OF ENVIRONMENTAL PCB BIOTRANSFORMATIONS IN AQUATIC SEDIMENTS

The information presented in this section has been derived from three sources:

- o review of published literature,
- o personal communications as noted, and
- o experience of YAI investigators.

2.1.1 Background

Prior to 1984, the transformation and consequent detoxification of Aroclors in aquatic sediments (resulting from both aerobic and anaerobic microbiological actions) was seldom recognized and even less often understood. The explanation for this situation lies primarily in the historical perception of the behavior of PCBs in the environment and in the basic nature of the Aroclors. Until the early 1980s, PCBs were assumed to be persistent in all environmental compartments; little attention was given to the specific question of their biodegradability in aquatic sediments. Although considerable evidence demonstrating aerobic biodegradation of single PCB congeners and selected components of commercial Aroclors under laboratory conditions was available (Section 2.3), the nature and extent of PCB biodegradation occurring in aquatic sediments was unknown.

The first in-depth investigation designed to characterize the fate of PCBs in aquatic sediments was conducted in 1982 by Brown and co-workers (1984). Evidence of PCB degradation in Hudson River sediments by both aerobic oxidation and anaerobic reductive dechlorination reactions was observed. The findings of this study and subsequent investigations by the same group (Brown et al., 1987 a & b) have had a profound influence on the development of the current understanding of PCB biotransformations occurring in aquatic sediments, especially of the phenomenon of anaerobic reductive dechlorination.

The existence of microbial PCB dechlorination in Hudson River sediments has been questioned by investigators from the New York State Departments of Health and Environmental Conservation (Mark P. Brown et al., 1988). There exists, however, substantial evidence to support the position that the pattern alterations observed in the chromatograms resulted from microbial biotransformations rather than external physical and chemical processes. Not only has the phenomenon of anaerobic reductive dechlorination been observed at a number of sites throughout the country, Quensen, Tiedje, and Boyd (1988) have successfully demonstrated PCB dechlorination by anaerobic bacteria in their laboratory at Michigan State University. In this experiment, using microorganisms from Hudson River sediments, Aroclor 1242 was reductively dechlorinated under anaerobic conditions.

Based upon historical records afforded by sample chromatograms, anaerobic reductive dechlorination in aquatic sediments apparently is widespread and has been occurring for a considerable period of time. However, as noted, the chromatographic pattern alterations indicative of the transformations were not recognized until recently. The failure on the part of many analysts to recognize PCB transformations is related to analytical difficulties: Aroclors are complex mixtures of chlorobiphenyl congeners rather than single compounds, requiring highly skilled data interpretation, and subtle variations in chromatograms often are overlooked.

The various Aroclor formulations produced by Monsanto Corporation from 1929 to 1977 are unique because they were synthesized by chlorinating biphenyl to a fixed weight gain for each product blend. As a consequence, the composition of Aroclors had little, if any, variation in their congener distributions. This consistency of composition resulted in a unique, reproducible "fingerprint" chromatogram for each Aroclor. Because each PCB congener reacts independently to the environmental factors to which it is subjected, the origin of

the PCBs present in an environmental sample and a complete history of compositional changes can be ascertained from its chromatogram. Therefore, any force that results in a compositional change causes an alteration in the standard Aroclor chromatographic pattern. Differing environmental processes will alter the distribution of PCBs in a given Aroclor according to a particular congener selectivity pattern. A more detailed discussion of the various types of alterations in the chromatographic patterns of Aroclors can be found in Appendix I (Yoakum Task 11 Report, 1989).

2.1.2 Recognition of Environmental PCB Alteration Patterns

There are both advantages and disadvantages associated with the complex chromatograms produced by Aroclors. As historical records, they provide valuable insight into the environmental fate of individual PCB congeners. The complex chromatograms, however, give rise to a number of interpretive problems.

Although the chromatographic patterns produced by the different Aroclor formulations are distinctive, environmental transformations generally result in chromatograms that do not match Aroclor standards because of modifications with respect to the relative proportions of individual PCB congeners present in the sample. As a result, the most serious problem in accurately identifying PCB residues in environmental samples is the inability on the part of the analyst to directly correlate sample results with a known reference standard. Current analytical methodology requires that PCB concentrations be reported in terms of the commercial Aroclor(s) whose chromatogram is most similar to that of the sample. Unfortunately, this approach is not conducive to the recognition of PCB biotransformations and other environmental alterations. In addition, the indiscriminate comparison of the chromatogram of a transformed sample with that of an Aroclor standard chromatogram frequently provides results that essentially represent a compromise with respect to the identity of the Aroclor(s)

originally present. For biotransformed samples, the analytical results may be both inaccurate and misleading if the analyst fails to recognize transformation alterations in the chromatographic patterns. According to Brown (1987a), this practice has left concealed not only the extent of PCB degradation in nature, but also the diversity of the microbiological processes that are involved.

Frequently, PCB alteration processes produce chromatographic pattern changes that are subtle and difficult to detect unless the sample chromatogram is of high quality. Also, it is extremely important that the full pattern be displayed and that all peaks remain "on scale," with the most intense peaks giving between 90 and 95 percent full-scale deflection. The automated data reduction techniques employed by most laboratories during the past decade frequently produce chromatograms that do not meet these criteria. When Aroclor quantitations are performed by total area integrations within established retention time windows, it is common practice in many laboratories to allow the major peaks of the sample chromatograms to be "off-scale." When this occurs, the entire congener peak pattern cannot be viewed and evaluated by the analyst. As a consequence, pattern alterations associated with PCB biotransformations in sediments are usually unnoticed.

2.1.3 Mechanisms of PCB Biotransformations in Aquatic Sediments

Much of the research efforts directed at understanding PCB biotransformations in the environment have been conducted as part of an ongoing research and development program on the destruction of PCBs initiated in 1982 by Corporate Research and Development of the General Electric Company (GE Reports, 1983-1989). Until recently (GE Report, 1989), the GE investigations have indicated that aerobic microbial attack on PCBs proceeded via oxidation, followed by ring fission; whereas anaerobic microbial attack appeared to be limited to reductive dechlorination without alteration of the biphenyl ring system. It now appears that an anaerobic biodegradation process has been observed both in the

laboratory and in Hudson River Estuary sediments which is removing lower chlorinated PCB congeners (mostly di- and trichlorobiphenyls) including many congeners originally considered to be terminal dechlorination products. The implications of these observations are significant because anaerobic reductive dechlorination coupled with anaerobic biodegradation could lead to the ultimate mineralization (conversion to CH_4 and CO_2) of PCBs in sediments.

Both aerobic and anaerobic microbial attacks on PCBs in sediments are known to exist. However, the most significant and widely observed PCB biotransformations occurring in aquatic sediments appear to be those arising from anaerobic reductive dechlorination. Laboratory studies, as well as investigations involving analysis of environmental sediment samples, indicate that anaerobic dechlorinations are enzyme-mediated processes, which exhibit wide ranges of congener selectivity. Although the entire process is not clearly understood, it appears to proceed in a stepwise fashion. In a recent laboratory study (Abramowicz et al., 1989) involving the single PCB congener, 234-34 pentachlorobiphenyl, stepwise dechlorination from penta- to monochlorobiphenyl was observed. The major metabolites were 24-34, 24-3, 2-3, and 2-chlorobiphenyl.

In environmental sediment samples, different sampling sites exhibit distributional differences of partially dechlorinated PCBs. Nonetheless, in virtually all of the dechlorination systems studied to date, selective removal of meta and para chlorine atoms has been observed. The only exception found to date is the process in Silver Lake, which appears to remove all chlorine substituents and is considered an ortho, meta, para- selective dechlorination system. Some sample patterns give the appearance that degradation ceases at certain dechlorination levels. At this time it is not known whether actual terminal products exist or whether these metabolites represent preferred intermediate steps in the dechlorination process. At sites that have been studied in detail (Upper Acushnet Estuary and Hudson River Estuary) certain

PCB congeners (chromatographic peaks) appear to be formed in some samples and then disappear from other samples through subsequent extraction into the water phase and/or biodegradation.

In a recent laboratory study, Chen et al. (1988) demonstrated complete anaerobic degradation of ¹⁴C-labeled monochlorobiphenyl congeners using a mixed culture of PCB-degrading bacteria isolated from Hudson River sediments. Significant amounts of radioactivity were recovered as CO₂ and in cell material, indicating mineralization and cellular incorporation. A significant amount of radioactivity also was found in the aqueous fraction. The highly hydrophilic compounds unextractable by hexane from the culture supernatant are also evidence of anaerobic transformation. Anaerobic biodegradation of mono-, di-, and trichlorobiphenyl congeners of Aroclor 1221, as well as PCB biodegradation in sediments, were also observed during the study.

2.1.4 Characteristics of PCB Biotransformation Patterns in Aquatic Sediments

As discussed in Section 2.1.1, each environmental force (physical, chemical, or biological) has a preferred set of activities relating to interaction with individual PCB congeners. Therefore, the PCB congener alteration patterns observed at different sites are unique and can be distinguished from each other.

In aquatic sediment systems, the pattern alterations observed result primarily from the reductive dechlorination of Aroclor(s) after their release into the environment. The chromatograms of samples undergoing anaerobic reductive dechlorination are characterized by a decrease in the highly chlorinated (penta-, hexa-, and hepta-) region of the pattern and corresponding increases in the tri- and tetrachlorinated areas. Consequently, the chromatograms frequently demonstrate the presence of new peaks in the pattern, as compared to the Aroclor standard, as well as "high-end" drop-off due to the dechlorination of

higher chlorinated PCBs. Further dechlorination yields increases in mono- and dichlorobiphenyls and decreases in certain tri- and tetrachlorobiphenyls.

Therefore, peak enhancements, reductions, and even disappearances occur.

Anaerobic reductive dechlorination patterns in sediment samples are distinctively different from those found in "weathered" soil samples (volatilization and adsorption alterations) and river and ground water samples (solubilization, volatilization, and aerobic microbial degradation alterations). Brown and his colleagues (GE Report, 1989) have assembled an extensive library of chromatograms from numerous PCB spill sites illustrating altered Aroclor patterns to aid in the identification of PCB alteration processes occurring in specific environmental compartments. During his investigations (Brown et al., 1984, 1987a & b; GE Reports, 1984-1989) of anaerobic PCB alterations in sediments, Brown has assigned letter designations to those patterns seen frequently enough to suggest their independent significance.

2.1.5 Aquatic Sediment Sites Exhibiting Aerobic PCB Biotransformations

The presence of in-situ aerobic microbial PCB degradation in aquatic sediments has been reported at two major PCB spill sites (Brown et al., 1984; GE Report, 1989), the upper Hudson River and the Sheboygan River. These observations indicate that aerobic biodegradation of PCBs generally involves lower chlorinated congeners such as those produced by anaerobic reductive dechlorination processes.

2.1.5.1 Upper Hudson River (New York)

Investigations involving PCB biodegradation in the Hudson River have been ongoing since 1982. Evidence of congener-selective oxidative biodegradation in the water column and at the sediment surface has been reported. In addition,

aerobic bacteria capable of biodegrading PCBs were isolated from the sediments. The aerobic biotransformation pattern observed in Hudson River sediments was designated Pattern A (GE Reports, 1983-1989).

2.1.5.2 Sheboygan River (Wisconsin)

Initial evaluations of Sheboygan River chromatograms showed evidence that at least two dechlorination processes were occurring. One process resulted in a chromatogram similar to a pattern observed in upper Hudson River sample chromatograms and the other resembled the predominant pattern observed in samples from the Acushnet River Estuary. In addition to these similarities, many river bottom samples showed varying degrees of removal of various mono-, di-, and trichlorobiphenyls except for 26-2, 26-3, and 26-4, and 25-4 CB. This transformation process produced a unique alteration pattern dominated by the 26-4 peak that has been provisionally designated Pattern X*. It appears that Pattern X* is an aerobic microbial process. There are indications that aerobic microbial biodegradation of PCBs is occurring more extensively in the Sheboygan River system than in the Hudson River, and that substantial PCB degradation can occur in undisturbed bottom sediments during a 12-month period (GE Report, 1989).

2.1.6 Aquatic Sediment Sites Exhibiting Anaerobic PCB Biotransformations

The phenomenon of anaerobic PCB biotransformation in aquatic sediments appears to be widespread, but its occurrence is not widely reported in the literature. The dominant anaerobic biotransformation process is believed to be reductive dechlorination, although Brown (GE Report, 1989) has reported a new environmental alteration process, Pattern Y, which appears to involve anaerobic biodegradation. This new transformation process was observed in Hudson Estuary sediments.

2.1.6.1 Upper Hudson River (New York)

Brown et al. (1984) noted that chromatograms of PCBs in environmental specimens taken from the upper Hudson River differed greatly from those of the Aroclor originally discharged. As a result, a project was undertaken to determine whether these divergent patterns could be characterized and related to a specific physical or biological transformation process. Accordingly, a number of sediment samples were collected from areas in the upper Hudson River previously found to contain high levels of PCBs. The samples were subjected to detailed microbiological and gas chromatographic examination.

At the time the work was published in 1984, Brown et al. had examined 148 PCB chromatograms from upper Hudson River sediments. The majority of chromatograms were grouped according to one of three major peak patterns based upon the distribution of the lower congener peaks. Most of the remaining chromatograms fit into one of four minor classification groups, which differed slightly from the major patterns.

Pattern A appeared alone or in combination with other patterns in 34 of the 148 chromatograms. This pattern was described as 1242 +/- because it resembled Aroclor 1242 with minor differences. The pattern appeared in the surface sediments where levels of PCB contamination were low relative to those in the deeper sediments. Characteristics of Pattern A included slight relative enhancement of penta- and hexachlorinated PCB congeners, traces of more highly chlorinated congeners not normally present in Aroclor 1242, and diminished portions of mono-, di-, tri-, and tetrachlorinated PCB congeners. The traces of more highly chlorinated congeners not normally present in Aroclor 1242 were later attributed to the presence of trace levels of Aroclors 1254, 1260 and 1268 in the sediments studied (Brown et al., 1987b). Pattern A has been attributed to aerobic biodegradation (see Section 2.1.5.1) and to environmental aging.

Pattern B appeared alone or in combination with other patterns in 101 of the 148 sediment samples. It differed from Pattern A in that all later eluting peaks (later eluting primarily due to higher chlorine content) of the chromatogram had diminished, indicating reductions in hexa-, penta-, and tetrachlorobiphenyls. Certain trichlorobiphenyl peaks were also reduced as compared to Pattern A. Pattern B demonstrated relative increases in mono-, di-, and some trichlorobiphenyls indicating degradation of more highly chlorinated congeners to the less chlorinated congeners.

Pattern C appeared alone or in combination with other patterns (usually Pattern B) in the chromatograms of 68 of the 148 samples. Pattern C exhibited slightly less removal of the more highly chlorinated congeners than Pattern B; however, there were more significant reductions in certain hexa-, penta-, tetra-, and trichlorobiphenyls and a corresponding increase in certain mono-, and dichlorobiphenyls as compared to Pattern B. Figure 2-1 presents chromatograms exhibiting Patterns A, B and C in reference to Aroclor 1242.

Four other patterns were seen in the sediment samples with less frequency than those described above; these were labeled as Patterns B', B'', D and X. These patterns displayed minor variations from the three major patterns described above.

In one sediment core sample taken from the Hudson River (Brown et al., 1984), Patterns A and B were observed in each of the 1-inch increment samples within the top 8 inches of sediment, while only Pattern B was observed in samples between 8 and 21 inches below the sediment surface. Those samples exhibiting only Pattern B contained higher levels of PCBs as compared to those samples exhibiting both Pattern A and B. Accordingly, it was concluded that the more highly PCB-contaminated zones exhibited the most active anaerobic dechlorination and extensive loss of the higher chlorinated congeners.

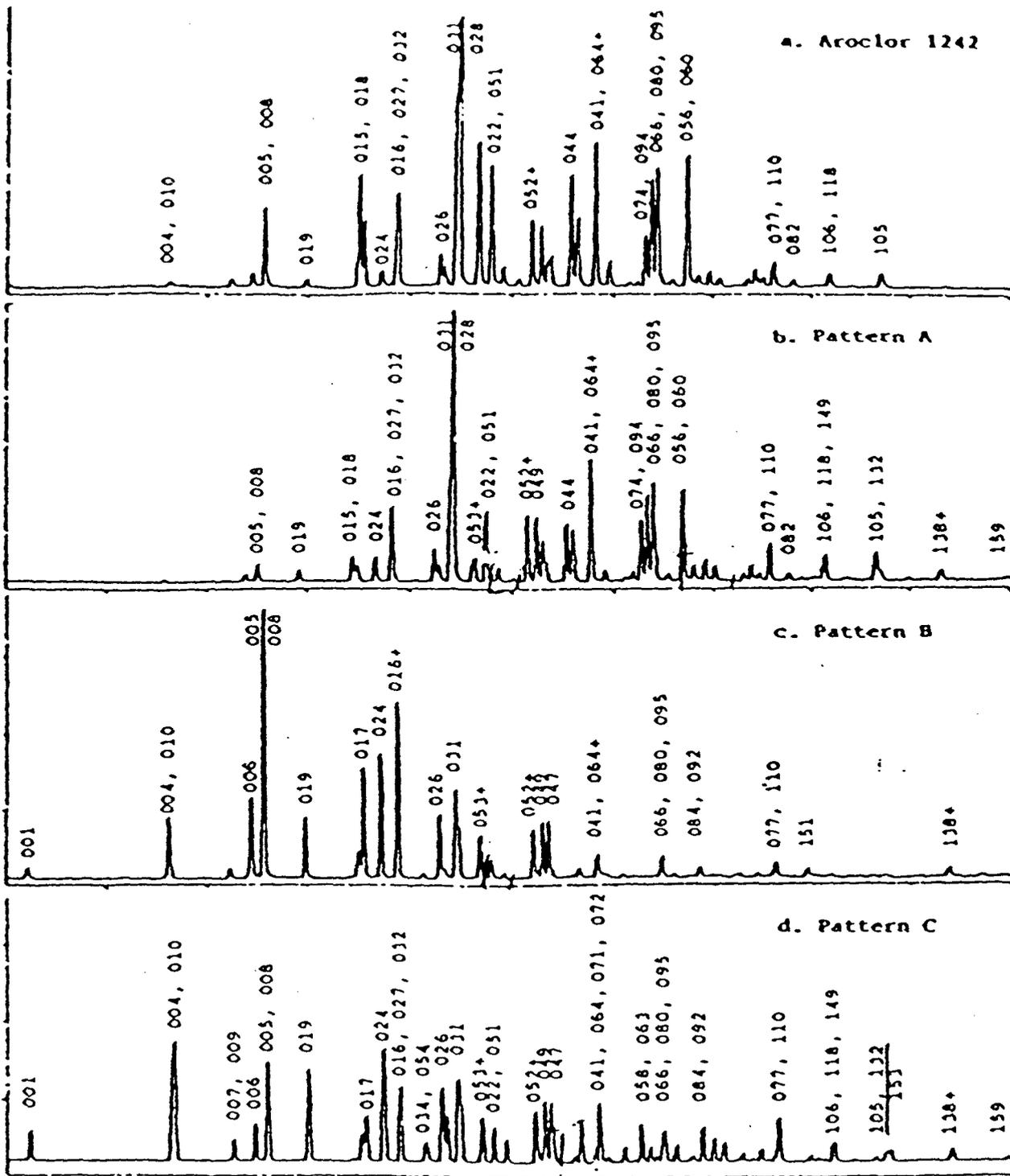


Figure 2-1. Chromatograms of Typical PCB Patterns in Samples from Upper Hudson River Sediments and Aroclor 1242 Standard.

The conclusion that reductive dechlorination of PCBs is occurring in Hudson River sediments was further supported by several additional observations made by Brown et al. (1984). First, sediment samples collected from the upper Hudson River that were found to contain in excess of 50 parts per million (ppm) of PCBs ("hot spot samples") also displayed marked changes in PCB congener distribution. The changes observed corresponded to losses of up to one third of the chlorine originally present. Second, these hot spot samples (50 to 2600 ppm) were found to contain levels of mono-, di-, and trichlorobiphenyls that could not be explained by processes other than reductive dechlorination of higher congeners. The concentration of 2-chlorobiphenyl observed in sediment samples was generally 20 times higher than the levels normally present in Aroclor 1242, while other lower chlorinated congeners were found to have increased to levels 2 to 8 times higher than those present in commercial Aroclor 1242. Brown also concluded that chromatographic pattern alterations observed in these Hudson River samples indicated that reductive dechlorination was occurring in a stepwise fashion to the point where reduction potentials or microbial communities were no longer favorable for reduction to continue. However, more recent literature, discussed in following sections, suggests that degradation may proceed to complete destruction of PCBs under proper conditions.

The selectivity of the reductive dechlorination process seemed to be indicative of an enzyme-mediated process since the presence of a chemical agent capable of such activity under the given conditions could not be conceived. The several chromatographic pattern types observed were attributed to different populations of PCB dechlorinating organisms present in the sediment. The overall conclusion by Brown and his co-workers (1984) was that "every significant congeneric constituent of the Aroclor 1242 discharged into the upper Hudson was found to be degradable by one or more of the oxidative or reductive bacterial agents detected in the Hudson environment."

2.1.6.2 Silver Lake (Pittsfield, Massachusetts)

Anaerobic transformations of Aroclors in the sediments of Silver Lake were first observed in 1980 by Yoakum (1982). Many of the chromatograms generated in support of a study to determine the occurrence and distribution of PCBs in the bottom sediment of Silver Lake showed extensive pattern alterations. Three samples that showed representative pattern alterations were analyzed by packed column GC/MS. The presence of Aroclors 1254 and 1260 was confirmed for all samples. In addition, many di-, tri, and tetrachlorobiphenyls were present that are not found in the patterns of standards for Aroclors 1254 or 1260.

Brown and his co-workers subsequently confirmed the occurrence of anaerobic reductive dechlorination in Silver Lake sediments. Chromatograms which exhibited the most extensive alterations were classified according to two major patterns referred to as Pattern F and Pattern G. These two patterns were distinct and unlike the alteration patterns observed in the Hudson River samples. The major feature of Pattern F is the formation of only two trichlorobiphenyls, 25-3 and 24-3, both of which are not present at more than trace levels in any commercial product (Brown et. al., 1987a). In Pattern G, these two plus three additional trichlorobiphenyls were observed, the new isomers being 26-2, 26-3, and 24-2 trichlorobiphenyls.

A more in-depth study of Silver Lake sediments was conducted by Yoakum in 1982. An examination of chromatograms for lake perimeter samples showed that some samples were mixtures of Aroclor 1254 and 1260 (Figure 2-2a) and others were essentially all Aroclor 1254 (Figure 2-2b). As can be seen from comparing the chromatograms for Samples 4953 (Figure 2-2a) and a standard containing a 50/50 mixture of Aroclor 1254 and Aroclor 1260 (Figure 2-2c), Sample 4953 shows no apparent dechlorination. Early stages of Aroclor 1254 transformations are apparent when the chromatogram of Sample 4972 (Figure 2-

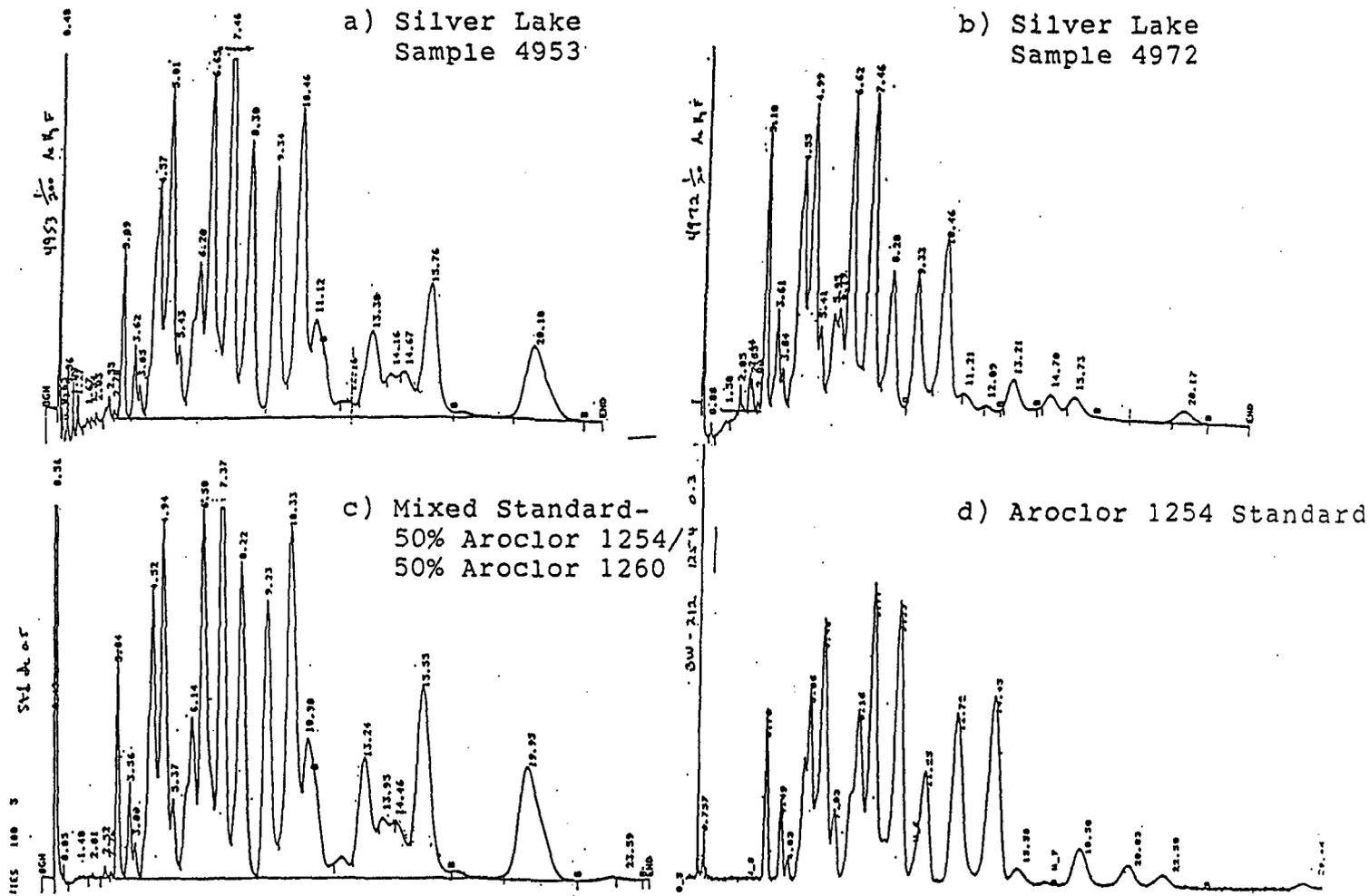


Figure 2-2. Chromatograms for Silver Lake Samples and Aroclor Standards

2b) is compared to Figure 2-2d which is a 100% Aroclor 1254 standard. A comparison of the chromatograms in Figure 2-3 demonstrates the differences between a sample (4953) with no apparent transformation and two samples (4938 and 4914) where significant dechlorination by Pattern G has occurred. Progressive dechlorination is shown in the chromatograms for four deep-water cores in Figure 2-4. Different stages of Pattern G are shown by samples 6019 (Figure 2-4a) and 6007 (Figure 2-4b) while two stages of Pattern F are illustrated by samples 6050 (Figure 2-4c) and 6003 (Figure 2-4d).

Capillary column GC/MS analysis of two deep-water cores was also performed (Figure 2-5). Sample SL 6003 (Figure 2-5a) closely matched Brown's capillary column chromatogram for Pattern F (+G), which is a slight variation of Pattern F that contains some Pattern G characteristics. The second sample, sample SL 6020 (Figure 2-5b), contained many more dechlorination products including small amounts of 2, 24, 2-3, and 23-2 mono, di and trichlorobiphenyls and appreciable formation of 2-2/26, 2-4, 26-2, 25-2/24-2, 26-3, 25-3, 24-3, 26-25 and 26-24 di, tri and tetrachlorobiphenyls. In addition, significant reductions had occurred in 23-25 and 23-24 tetrachlorobiphenyl.

2.1.6.3 Sites Undergoing Reductive Dechlorination by Pattern H/H'

In 1986, Brown conducted an investigation of PCB transformations in the Acushnet River Estuary (New Bedford, Massachusetts). Based upon this study, he concluded that the dominant PCB biotransformation process observed in the sediment samples was anaerobic reductive dechlorination. The transformation pattern observed in the Acushnet River Estuary was somewhat intermediate between, but clearly distinct from, those seen in sediments from the upper Hudson River (Pattern B) and from Silver Lake (Pattern F). Brown concluded that the New Bedford process was a new type of alteration and designated it Pattern H. A second, slightly different pattern was designated Pattern H' (GE Report, 1987). Since the characterization of Acushnet River Estuary

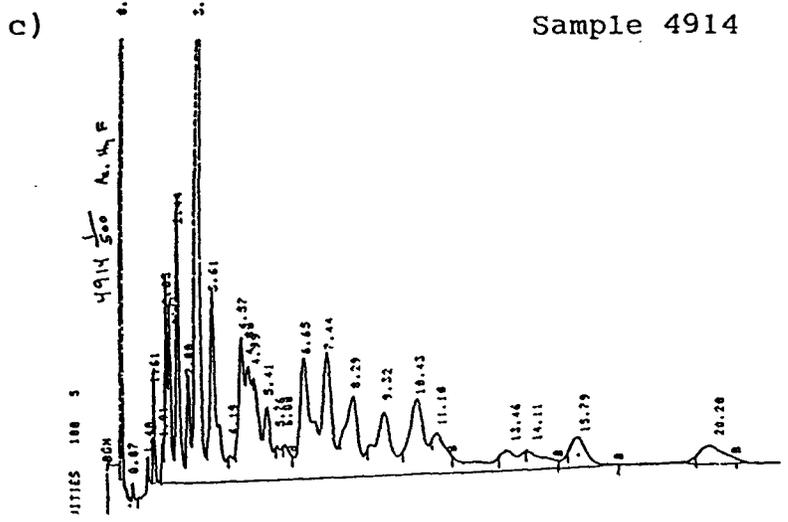
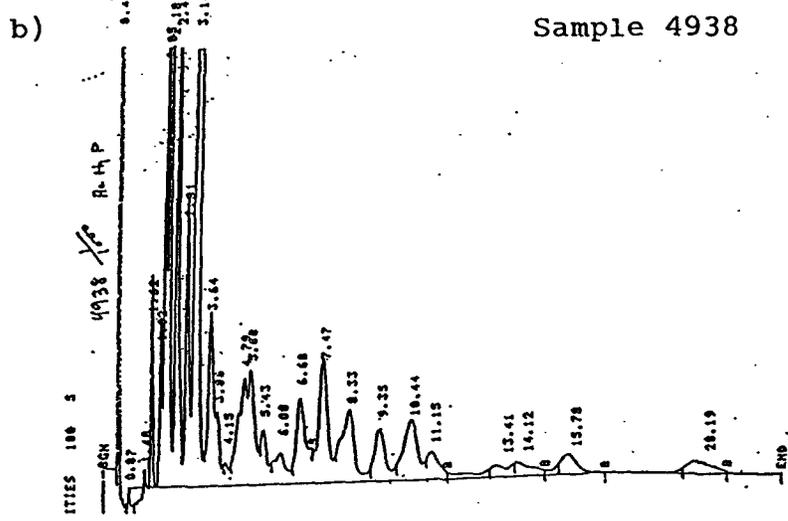
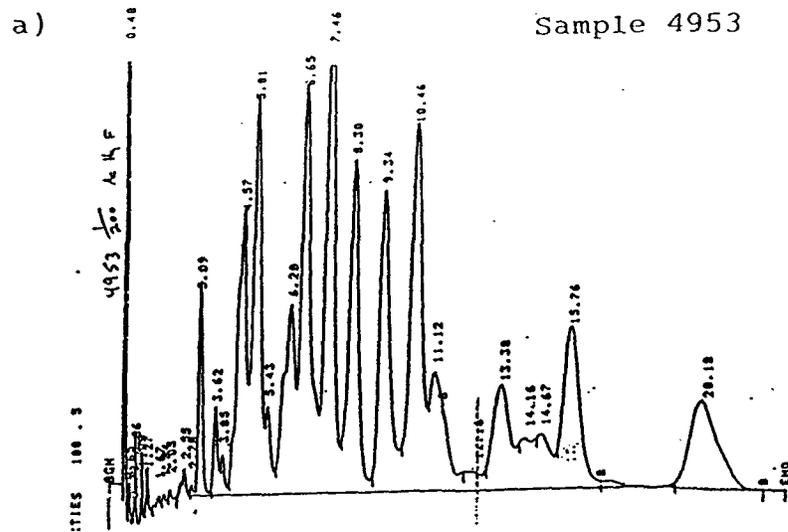


Figure 2-3. Chromatograms Illustrating No Apparent Transformation (a) and Dechlorination by Pattern G (b and c)

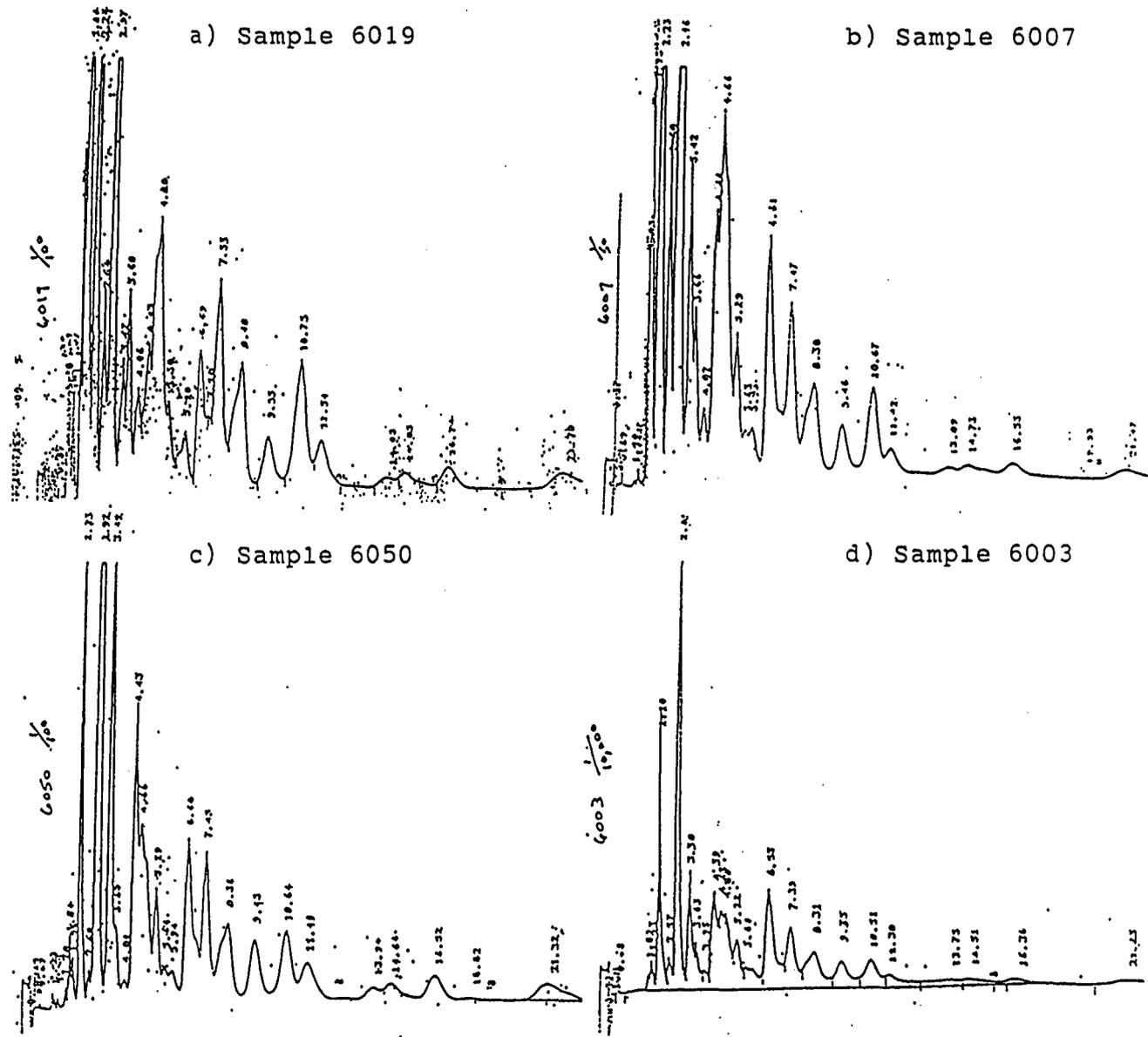


Figure 2-4. Examples of Pattern G Dechlorination (a and b) and Pattern F Dechlorination (c and d) in Deep-water Sediment Samples

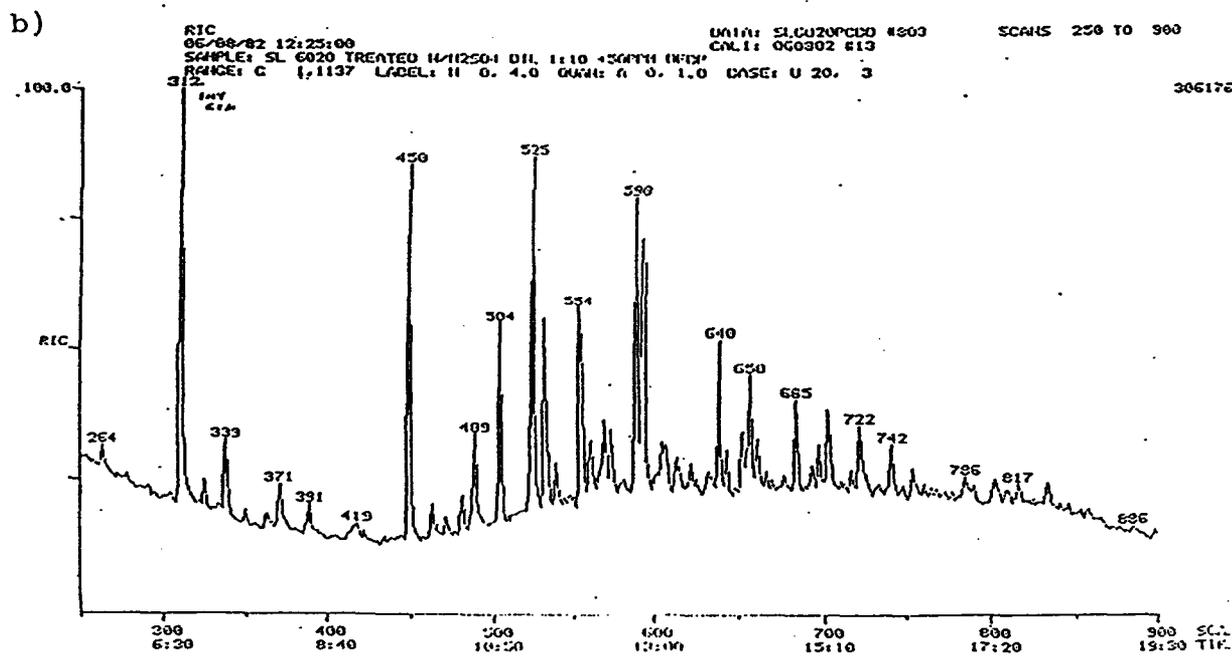
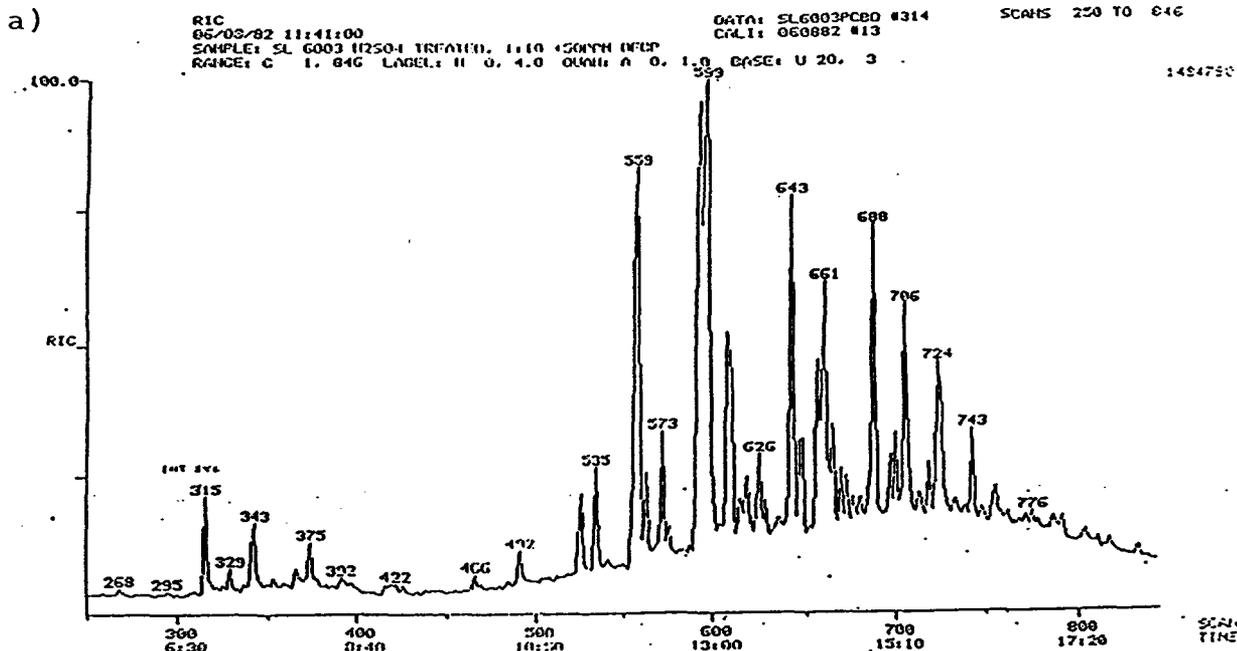


Figure 2-5. Reconstructed Ion Chromatograms for Sample SL 6003 (a) and Sample SL 6020 (b)

Pattern H, identical (or quite similar) dechlorination patterns have been observed at a number of sites throughout the country, including:

- o Escambia Bay near the mouth of the Pensacola River in Florida;
- o Hudson River Estuary in the vicinity of Troy, Albany, Poughkeepsie, Catskill, and Kingston, New York;
- o Woods Pond near Lenox, Massachusetts;
- o Housatonic River in Connecticut; and
- o Sheboygan River and Harbor in Wisconsin.

2.1.6.4 Waukegan Harbor (Waukegan, Illinois)

Based on capillary column GC patterns for five Waukegan Harbor sediment samples from the study by Stalling (1982), Brown and his co-workers (1987a&b) observed various degrees of removal for most of the tri-, tetra-, and pentachlorobiphenyls originally present in the Aroclor 1248 released at that site. Increases, corresponding to dechlorination enhancements, were seen in the levels of several di- and trichlorobiphenyls, as well as 2,4-dichlorobiphenyl. These alterations, which appeared to occur in only one congener selection pattern, were designated Pattern W.

2.1.6.5 Hoosic River (North Adams, Massachusetts)

Chromatograms of sediments from the Hoosic River showed enhanced levels of the trichlorobiphenyl congeners 2,4,6-trichlorobiphenyl and 2,4,5-trichlorobiphenyl, each of which are not present at appreciable levels in commercial Aroclors. The presence of these congeners was considered indicative of PCB dechlorination (Brown et al., 1987a).

2.1.6.6 Settling Pond (Municipal Landfill, Waynesboro, Tennessee)

Significant chromatographic pattern alterations were observed by Yoakum (1981) in sediment samples collected from a settling pond at the municipal landfill in Waynesboro, Tennessee. Packed column GC/MS was used to confirm anaerobic biotransformation in the samples. The reconstructed ion chromatograms (RICs) in Figure 2-6 illustrate the biotransformed sediment sample (Figure 2-6b) as well as a slightly weathered Aroclor 1242 core (Figure 2-6c) and an extensively weathered soil sample (Figure 2-6d). An Aroclor 1242 standard (Figure 2-6a) is included for reference.

2.1.6.7 Housatonic River (New Lenox, Massachusetts)

Two samples of Housatonic River sediment collected at SLI Station S16E (River Mile 48.25) showed signs of early anaerobic biotransformation, but the transformation had not progressed sufficiently to determine the transformation pattern (Figure 2-7). Significant peak enhancements were observed for 25-25 and 24-25 tetrachlorobiphenyl at retention time (RT) 3.16. Smaller enhancements occurred at RT 3.49 (23-25 and 23-24 tetrachlorobiphenyl) and new peaks were present at RT 2.84 (25-26 and 24-26 tetrachlorobiphenyl), as well as at RT 2.56 (25-4 and 24-4 trichlorobiphenyl and possibly 246-2 tetrachlorobiphenyl). There is a possibility that the peak enhancement at RT 10.22 in Sample 4832 (Figure 2-7a) was due to the formation of an intermediate dechlorination product. A sample chromatogram representative of that typically observed for samples of Housatonic River sediments in this reach of the river is shown in Figure 2-8a. As can be seen by comparing the sample chromatogram with that of a standard of Aroclor 1260 (Figure 2-8b), the PCB contamination present in the river at this location is primarily Aroclor 1260.

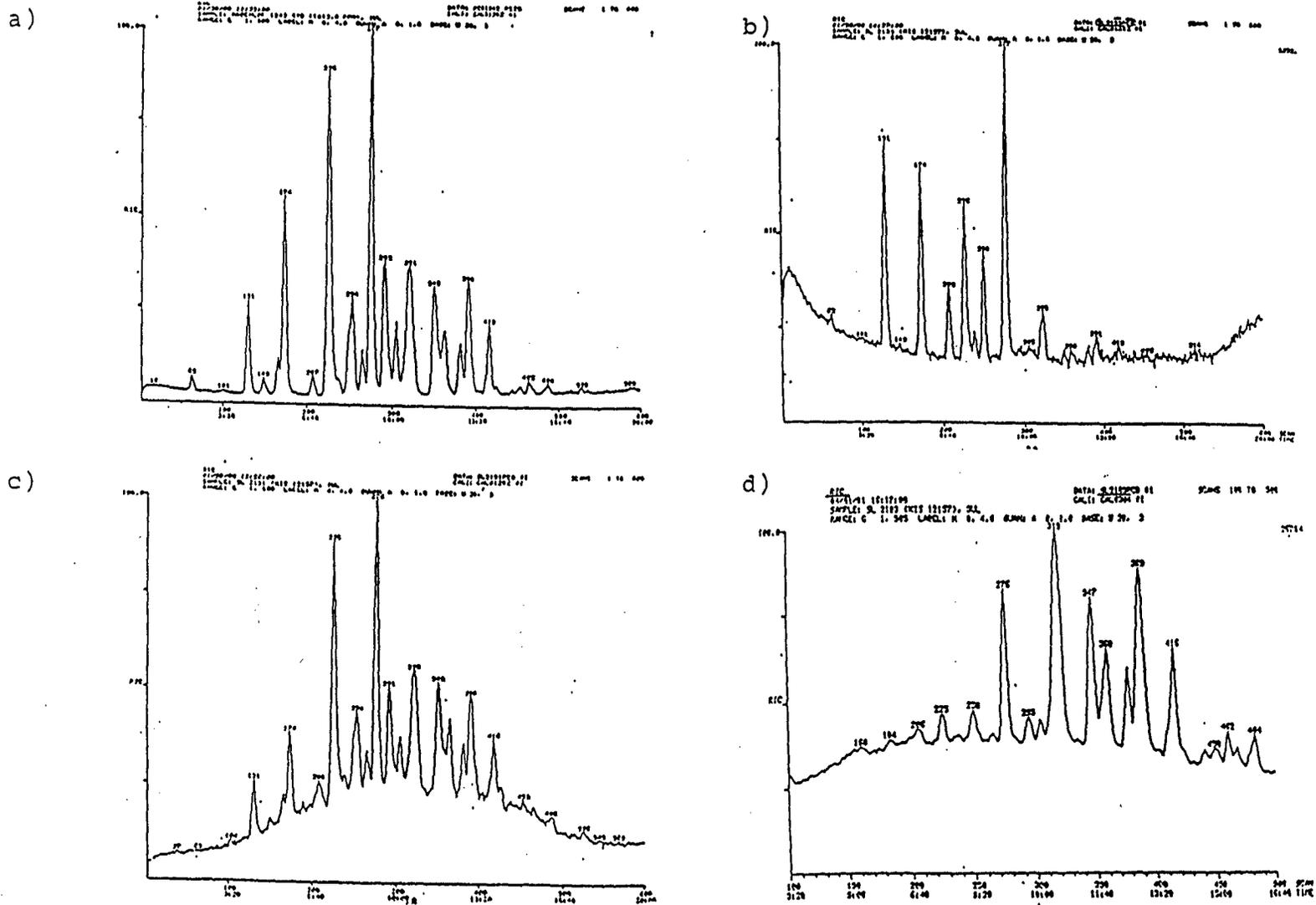


Figure 2-6. Reconstructed Ion Chromatograms Illustrating Biotransformation (b), Slight Weathering (c), and Extensive Weathering (d), of Aroclor 1242 (a)

2 METH 222 FILE 18

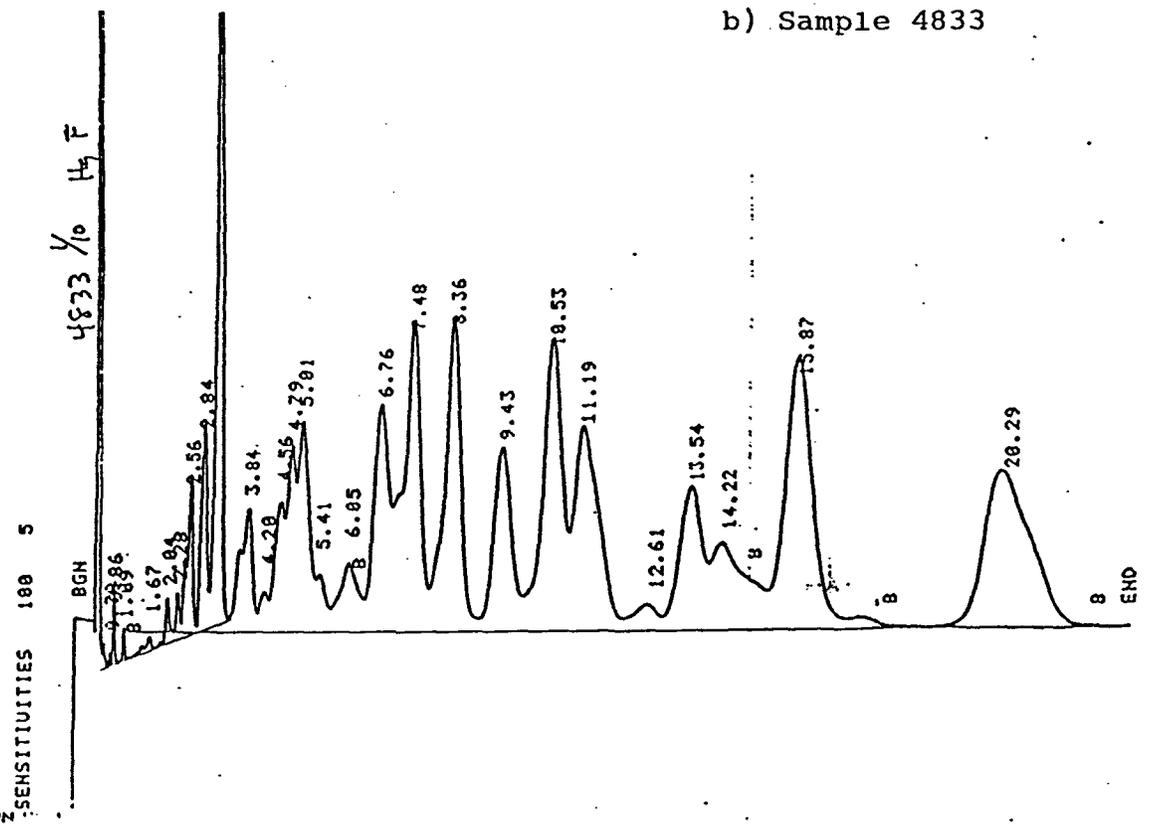
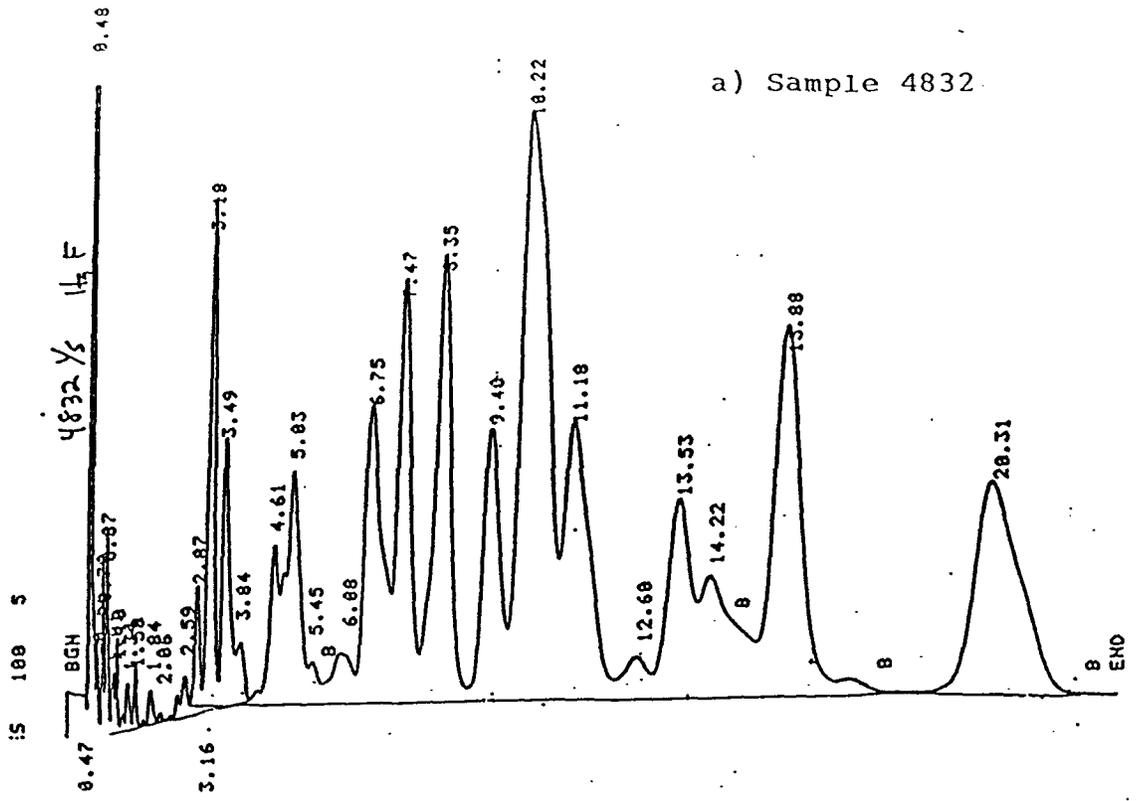


Figure 2-7. Illustrations of Anaerobic Biotransformation in Housatonic River Sediments

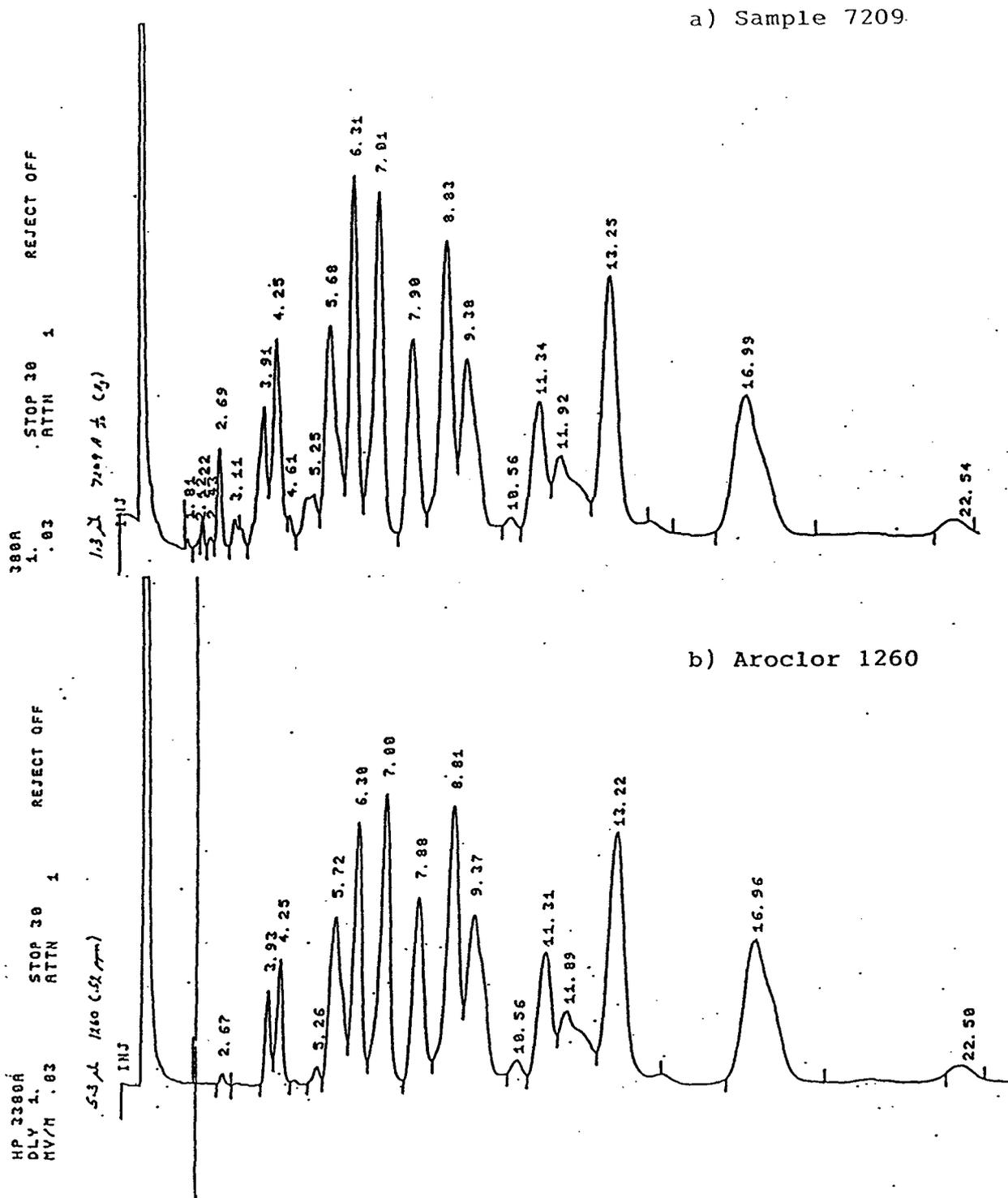


Figure 2-8. Chromatograms for Typical Housatonic River Sediment (a) and Aroclor 1260 Standard (b)

2.1.6.8 Wastewater Lagoon (Huntsville, Alabama)

Sediment samples collected from a wastewater holding lagoon at a government installation in Huntsville, Alabama showed pattern alterations (Figure 2-9b) indicative of anaerobic reductive PCB dechlorination (Yoakum, 1980). Subsequent analysis using packed column GS/MS confirmed the presence of numerous PCB congeners that were not present in the original PCB source (Aroclor 1260). In addition to the new peaks, numerous congener enhancements and reductions also were observed. Comparison of the chromatogram for a composite lagoon sample with a Pattern G dechlorinated sample from Silver Lake is shown in Figure 2-10. Several significant differences were immediately apparent and were confirmed by GC/MS data. The most obvious differences were the presence of significant enhancement of the tetrachlorobiphenyls 25-26 and 24-26 at RT 2.15 in the lagoon sample, and the complete absence, in the lagoon sample, of the unusual trichlorobiphenyl congeners (25-3 and 24-3) present in the Silver Lake sample (6019). Both samples contained significantly enhanced levels of the tetrachlorobiphenyls 25-25, 25-24, and probably 24-24. In addition, a number of new penta- and hexachlorobiphenyl congeners were found in the lagoon sample. Evaluation of GC/MS data indicated that a trace level of 2-chlorobiphenyl, as well as fairly substantial levels of 26 and 2-2 dichlorobiphenyl and 26-2, 25-2 and 24-2 trichlorobiphenyls were present.

Samples of water and sediments from the lagoon site were examined by Dr. G. S. Sayler at the University of Tennessee. Five Pseudomonas cultures, including Pseudomonas aeruginosa, were isolated and determined by laboratory experiment to be capable of PCB biodegradation.

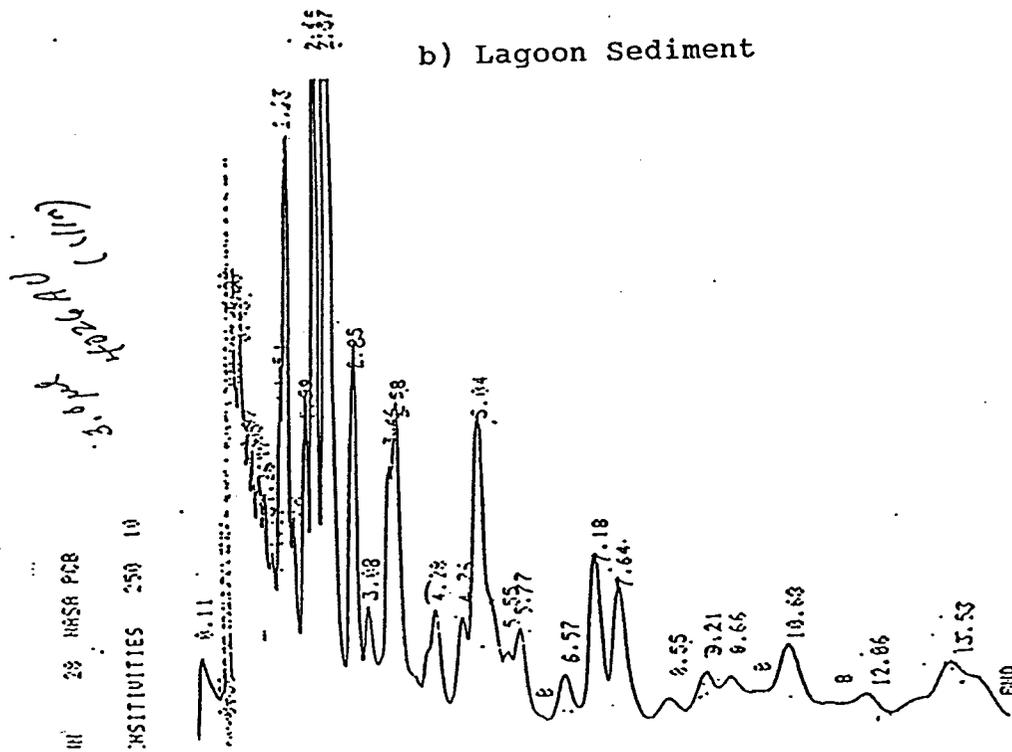
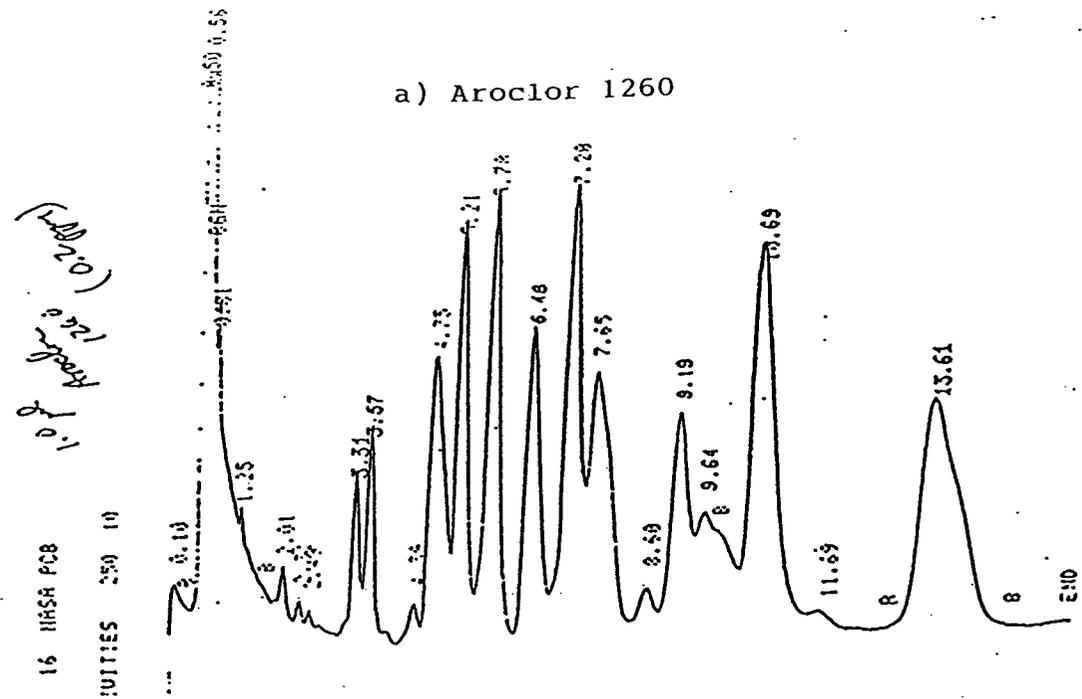


Figure 2-9. Comparison of Chromatograms for Aroclor 1260 Standard and Lagoon Sediment Exhibiting Anaerobic Biotransformation

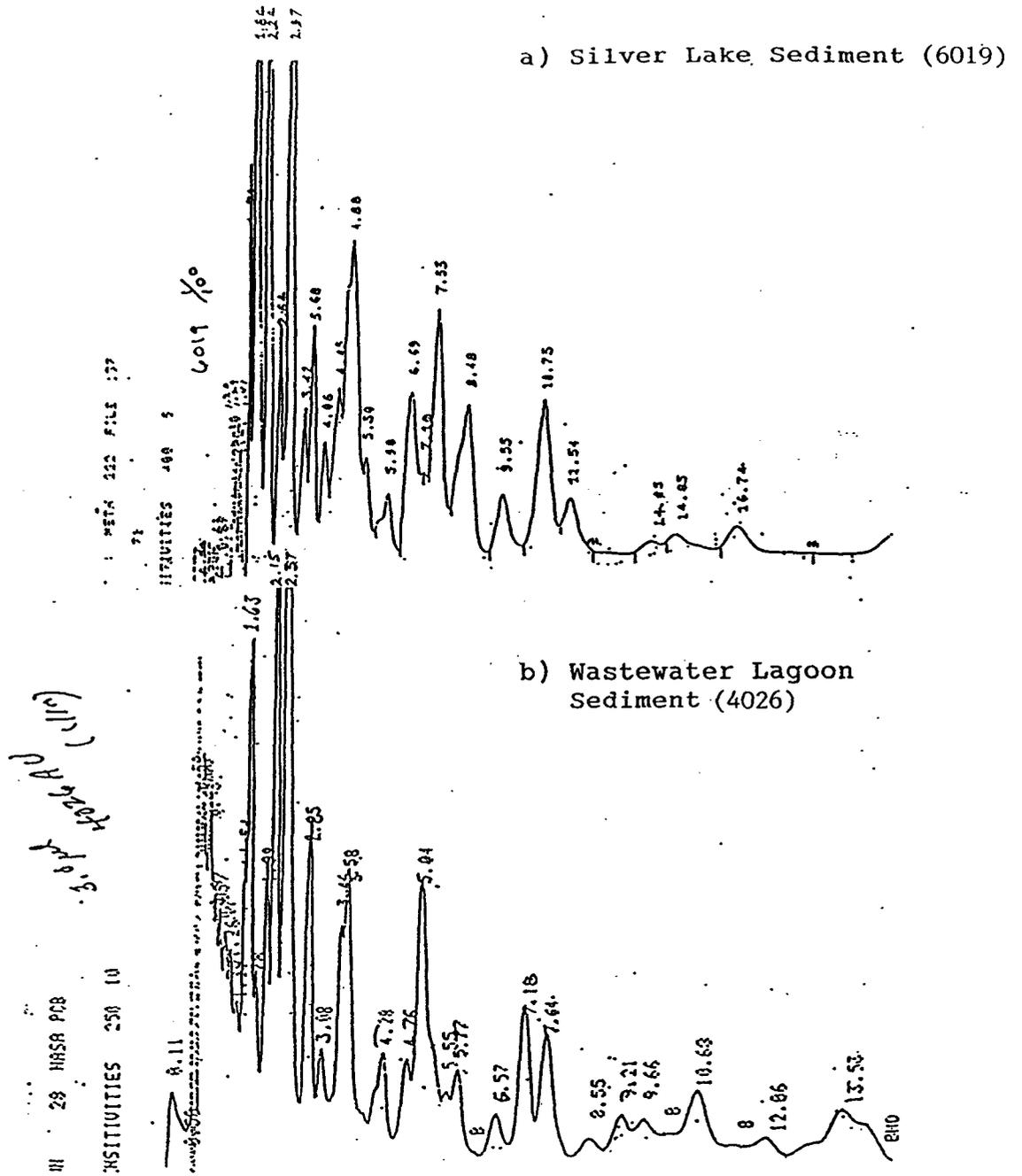


Figure 2-10. Comparison of Anaerobic Biotransformation Patterns in Silver Lake Sediment (a) and Wastewater Lagoon Sediment (b)

2.2 LITERATURE REVIEW: ANAEROBIC PCB BIOTRANSFORMATIONS (REDUCTIVE DECHLORINATION AND BIODEGRADATION)

Observations of Aroclor biotransformations at the sites discussed above have spawned a rapidly growing body of scientific literature discussing and classifying microbial PCB dechlorination and degradation. In the following discussion, that literature is canvassed, with particular focus upon reductive dechlorination of PCBs in anaerobic sediments.

The most extensively studied PCB spill site in the country is the upper Hudson River between Ft. Edward and Troy, New York (GE Reports 1984-1988; Brown et al., 1984, 1987 a & b). In the initial study, conducted in 1982, the investigators found evidence indicative of the reductive dechlorination of PCBs in sub-surface sediments. These samples, collected from PCB "hot spots," showed marked changes in congener distributions corresponding to losses of up to one-third of the chlorine originally present. The classification system adopted to describe the observed Aroclor transformations is discussed in Section 2.1.6.1, above.

Since the original paper released by Brown et al. (1984), further work has been performed in this area by several researchers. Bopp et al. (1984) independently confirmed some of Brown's observations, specifically with respect to the presence of altered PCB homolog distributions in sediment samples from the Hudson.

Brown and others (1987a) conducted a review of several hundred chromatograms from various sites in the U.S. where PCB contamination was detected in aquatic sediments; 100 of these were archive chromatograms from a 1977 survey of Hudson River sediments. In all classes of sediment samples from the Hudson River, the levels of most tri- and tetrachlorobiphenyls had been reduced relative to their original concentration in Aroclor 1242 with the exception of 26-2 and 26-

3 trichlorobiphenyl, which, along with all dichlorobiphenyls, had increased to levels 2 to 6 times the concentration in commercial Aroclor 1242. The levels of 2-chlorobiphenyl had increased 7 to 70 times in the samples reviewed. The most significant changes in congener distributions were observed in those samples with Patterns B, B' and C, which generally corresponded to deeper, more highly PCB-contaminated sediments. This observation indicated that anaerobic reductive dechlorination in the Hudson River was most active under oxygen deficient and elevated PCB concentration conditions. The paper (Brown, 1987a) concluded that "in the upper Hudson River as a whole, a massive (40 to 70 metric tons) conversion of tri-, tetra-, and higher chlorobiphenyls to mono-, di-, and 26-X-trichlorobiphenyls (X = 2, 3, or 4) had occurred, particularly in the subsurface (15- to 30-year-old) portion of the sediment."

Selected chromatograms of sediment samples collected from Silver Lake in Pittsfield, Massachusetts were reviewed by Brown and his co-workers (1987a and b). Based on their evaluations of these chromatograms and the subsequent characterization of a Silver Lake sediment composite sample using capillary column GC/EC, they concluded that anaerobic dechlorination was occurring in Silver Lake sediments. Losses of 90 to 98% of the hexa- and heptachlorobiphenyls originally present in Aroclor 1260 were observed with a corresponding increase in the tetra-, tri- and lower chlorinated chlorobiphenyls which comprise less than 1% of commercial Aroclor 1260. The authors concluded that massive conversions of higher to lower chlorinated PCB congeners had occurred in Silver Lake sediments.

The various dechlorination patterns observed in samples from the Hudson River, Silver Lake and Waukegan Harbor (see Section 2.1.6.4, above) are attributed to separate, unidentified strains of anaerobic bacteria (Brown et al., 1987a). The PCB residues present in sediment samples from these areas indicated preferential loss of 34-34, 234-34, 24-34, and other higher chlorobiphenyls that have chlorine atoms in the 4-4 positions. This group of PCB congeners includes

all those that are known to be either persistent in man, inducers of P-448-type cytochromes or thyrotoxic in rats (Brown et al., 1987a).

Further work performed by Brown and others (1987b) indicated that the patterns of congener reactivity in reductive dechlorination fall into two broad categories: those that remove chlorine atoms from ortho, meta, and para positions, which are driven by reduction potentials, and a system of meta and para dechlorinators, which are controlled by molecular shape. Both of these systems reportedly degrade the more toxic PCB congeners and produce residues that are amenable to aerobic degradation, as well as further anaerobic dechlorination. Patterns B, B', C, and W appear to be the result of meta and para position dechlorination, while Patterns F and G seem to arise from the loss of meta, para and ortho chlorine atoms.

Brown and his co-workers (1987b) concluded that the PCB dechlorination agents must be enzymes associated with environmental bacteria, and that, since the biphenyl ring backbone was not destroyed, it appeared that the microbes used the PCB molecule as an electron acceptor rather than a carbon source. An assessment of the thermodynamic feasibility of this reaction indicated that microbes with PCB-dechlorinase enzymes should be at a competitive advantage among other bacteria unable to use PCB as an electron acceptor.

A laboratory experiment on reductive dechlorination conducted by Quensen, Tiedje and Boyd (1988) indicated that indigenous anaerobic microorganisms from Hudson River sediments were able to reductively dechlorinate most PCBs in Aroclor 1242 under laboratory conditions. During the first 15 weeks of the experiment, 53% of the total chlorine present was removed and the proportion of mono- and dichlorobiphenyls present in Aroclor 1242 increased from 9 to 88%. The authors concluded that the dechlorination products are both less toxic and more readily degraded by aerobic bacteria than the original Aroclor components, suggesting that reductive dechlorination may be an important environmental

fate of PCBs and that sequential anaerobic-aerobic biological treatment for PCBs may be feasible.

In general, the experiment referenced above involved eluting microorganisms from PCB-contaminated Hudson River sediments and placing them into reaction vessels under controlled anaerobic conditions along with PCB-free sediment from the Hudson River, nutrients, and Aroclor 1242. After 16 weeks the PCBs were extracted from the reaction vessel and analyzed for total PCB homolog content. Results indicated that dechlorination occurred primarily from the meta and para positions yielding a Pattern C similar to the one described by Brown et al. (1984).

Removal of meta and para chlorine atoms can reduce the mammalian toxicity of PCBs because the PCBs with the greatest toxicity are those with a para and at least one meta chlorine atom on each ring and no more than one ortho chlorine atom (Quensen et al., 1988).

Quensen has conducted an experiment that parallels the one described above using microorganisms eluted from NBH sediment rather than the Hudson River. Preliminary results are similar to those obtained from the Hudson River sediment experiment (Quensen personal communication, 1989). That is, indigenous microorganisms eluted from highly PCB-contaminated NBH sediments are capable of extensively degrading components of Aroclor 1248. A 78% removal of meta and para chlorine atoms was observed in one set of samples after 12 weeks, and all penta- and hexachlorobiphenyl congeners were dechlorinated to lower congeners. Two of the congeners reported to be most acutely toxic, 34-34 tetrachlorobiphenyl and 234-34 pentachlorobiphenyl (Quensen personal communication, 1989), were readily dechlorinated by NBH microbes during the experiment.

Chen and others (1988) also conducted a laboratory experiment on anaerobic degradation of PCBs using Hudson River bacterial populations, Aroclor 1221, ¹⁴C-labeled monochlorobiphenyls, and 2,4,6-trichlorobiphenyl. Results of this experiment indicated that a mixed microbial population, when inoculated into PCB-contaminated sediments under laboratory conditions, had the ability to anaerobically biodegrade PCBs.

2.3 AEROBIC PCB BIODEGRADATION: SELECTED TOPICS

The aerobic biodegradation of PCBs by natural strains of bacteria has been well established in the scientific literature. Numerous advances have been made during this decade and extensive research is continuing to further understand this mechanism. For the purposes of this paper, aerobic biodegradation of PCBs will not be discussed in detail because the majority of the PCB contamination present in aquatic sediments at sites such as NBH exists in subsurface layers where anaerobic conditions exist.

Aerobic biodegradation of PCBs is generally catalyzed by the enzyme dioxygenase, which requires the availability of two adjacent unsubstituted carbon atoms. If the two adjacent carbons are at ortho and meta positions, the operating enzyme will be 2,3-dioxygenase (Furukawa et al., 1979), if the reaction occurs at meta and para positions, 3,4-dioxygenase will mediate (Bedard et al., 1987). Since reductive dechlorination preferentially removes meta and para chlorine atoms, resultant PCB rings with no more than one ortho chlorine atom should be subject to 2,3-dioxygenase attack. Unsubstituted biphenyl rings should be subject to 3,4-dioxygenase attack (Quensen et al., 1988).

Bedard et al. (1986) developed a method for screening and characterizing bacteria with the ability to aerobically biodegrade PCBs. Recently, it was demonstrated that two strains of aerobic bacteria have the ability to biodegrade 2,4,6-trichlorobiphenyl to a single ring product, 2,4,6-trichloroacetophenone

(GE Report 1985, Bedard et al., 1987a,b). This observation is significant in that 2,4,5-trichlorobiphenyl has no unchlorinated 2,3- or 3,4-site available for dioxygenase attack. Further evaluation of this phenomenon indicated that a 2,3-dioxygenase with the capability of attacking a chlorinated carbon at position 2 might be involved in this process (GE Report 1989). Research is also continuing in the area of characterizing the genes responsible for producing the enzymes that mediate biodegradation of PCBs by aerobic bacteria (Furukawa 1988).

Recent research in the area of PCB biotransformation has indicated that the reductive dechlorination occurring in anaerobic sediments produces less chlorinated PCB congeners that are readily biodegradable by aerobic bacteria because the positions of the biphenyl rings that are occupied by chlorine atoms favor an aerobic degradation pathway (Bedard et.al.,1986, Unterman et al., 1985). Quensen et al. (1988) concluded from their experiment that it is likely that most PCBs can be biodegraded by a suitable sequential anaerobic-aerobic process.

3.0 EVALUATION OF PCB BIOTRANSFORMATION IN NEW BEDFORD HARBOR SEDIMENTS

During the past four years, three independent investigations have been conducted to evaluate the presence and extent of PCB biotransformations in Acushnet River Estuary sediments. The initial study, in 1986, was done by Brown and Wagner of the General Electric Company. Twelve (12) sample pairs, six from the east side and six from the west side of the estuary were characterized by capillary gas chromatography and mass spectrometry. The investigations determined that the dominant transformation process was a reductive dechlorination which substantially removes meta and para chlorines from many of the higher PCB congeners, including all those associated with toxic effects. The resulting congener distribution observed by Brown and Wagner, designated Pattern H, is different from those of previously reported anaerobic microbial dechlorinations, but has since been observed at several other aquatic PCB spill sites (see Section 2.1.6.3).

The second study, a joint effort of Yoakum and Associates, Inc. and Balsam Environmental Consultants, Inc. commenced in 1988. Full details of the first phase of this investigation are contained in Appendix IV. The investigation involved the characterization of fourteen (14) samples from ten (10) estuary sites using both packed-column and capillary column GC/EC. As was the case in the Brown and Wagner study, the dominant PCB transformation observed was anaerobic reductive dechlorination. A reductive dechlorination pattern corresponding to Pattern H as defined by Brown and Wagner was observed in several samples. In addition, a more advanced transformation pattern showing new peaks and additional transformations not seen in Pattern H was observed.

The most recent investigation involving Acushnet Estuary samples was conducted in 1989 by Lake, Pruell and Osterman of the EPA Environmental Research Laboratory in Narragansett, Rhode Island. Sediment samples from five (5) sites were characterized using capillary column GC/EC. The

investigators observed substantial changes in the relative distributions of PCB congeners in many of the samples, thereby confirming the observations reported in the two previous investigations.

The significant finding of all three studies was the verification of extensive anaerobic reductive dechlorination of PCBs present in the sediments of the Upper Estuary of New Bedford Harbor.

3.1 IN-SITU PCB BIOTRANSFORMATION IN NEW BEDFORD HARBOR SEDIMENTS

Yoakum and Associates, Inc. (YAI) have been involved in an evaluation of PCB transformations in New Bedford Harbor sediments since 1987. The effort has included the following:

- o a review of analytical data from a NBH sampling program conducted by Balsam (Task 7);
- o a review of PCB analytical data from the U. S. Army Corps of Engineers (USACE) Field Investigation Team (FIT) Sampling Program (Tasks 2, 3, and 8);
- o the classification of Aroclor transformations observed in USACE FIT Sampling Program samples (Task 10); and
- o a review of PCB analytical data and classification of Aroclor transformations from selected NUS/GZA Drilling sampling stations (Task 12).

The discussion that follows is based primarily on information derived from these research tasks. The reports for each of these task are appended to this paper.

3.1.1 Background and Overview

During the review by YAI of reports and analytical data pertaining to NBH, it became apparent that PCB transformations were occurring in the NBH sediments. This hypothesis was based on YAI experience with Aroclor transformations in PCB-contaminated sediments at a number of sites throughout the United States. Initially, two information sources indicated probable PCB transformations at NBH:

- 1) reports by a number of laboratories of the presence of Aroclor 1248 in NBH sediment samples, and
- 2) personal communication with Dr. John Brown of General Electric concerning NBH sediments.

Because of PCB and heavy metals contamination, the NBH area was designated by EPA as a Superfund site. In the 10-year period prior to 1983, approximately 3700 PCB analyses were performed by more than 20 different analytical laboratories on NBH samples including sediment, water and biota. The analysis of estuarine sediments accounted for more than 50% of these data. According to Alford-Stevens, Budde, and Bellar (1985) of EPA, standardized procedures were not used for these PCB determinations. Instead, each laboratory produced data acquired using its favored procedures for PCB extraction, enrichment, detection and measurement. As a consequence, the results for many samples were highly variable and inconsistent, especially with regard to identification of the Aroclor(s) present in the samples.

A review of purchasing and inventory records indicated that the PCBs used by electrical capacitor manufacturing facilities located adjacent to NBH were Aroclors 1254, 1242, and 1016. There was no documentary evidence nor

reported use of Aroclor 1248 at these facilities. However, Aroclor 1248 was reported to be present in approximately 25% of the inner harbor sediment samples contained in the Acushnet River Estuary data base (Metcalf & Eddy, 1983). When Aroclor 1248 is reported to be present in samples, but cannot be implicated as a primary PCB contamination source, chromatographic pattern alterations due to transformations of PCBs in other Aroclor mixtures are usually indicated.

Three sediment samples from New Bedford Harbor (one inner harbor and two outer harbor) were analyzed for PCBs in a collaborative study sponsored by EPA (Alford-Stevens, 1985). Six laboratories analyzed the samples using packed column GC/EC, and four used capillary column GC/MS. All 10 laboratories identified the Aroclors present in the samples as mixtures of either 1016 and/or 1242 and 1254. It is significant that the presence of Aroclor 1248 in the samples was not reported by any of the participants. For this reason, it appears that a number of the laboratories involved in earlier analyses of NBH samples misidentified the Aroclors responsible for PCB contamination at New Bedford Harbor. In sediment samples, anaerobic microbial degradation of Aroclor 1254, in conjunction with environmental aging of Aroclor 1016/1242, can produce chromatographic pattern alterations that resemble Aroclor 1248.

3.1.2 Pattern Alterations Observed in Chromatograms of New Bedford Harbor Sediments

Chromatograms of Acushnet River Upper Estuary sediments reviewed by YAI typically showed significant and, frequently, extensive Aroclor peak pattern alterations. A detailed evaluation of the chromatograms indicated that three factors were principally responsible for the wide variety of patterns observed, namely:

- o variable ratios of Aroclors 1016/1242 to Aroclor 1254;

- o environmental "weathering," and
- o changes in compositional distribution of the PCB congeners present due to anaerobic dechlorination transformations.

The impacts of these pattern altering factors are different and operate independently of one another. As a consequence, a single, so-called "standard" pattern alteration was not observed in NBH sediment samples, although characteristic patterns associated with each of these factors can be identified.

3.1.2.1 Aroclor Mixtures in Samples

Aroclor 1016 and/or Aroclor 1242, as well as Aroclor 1254, were detected in all of the samples examined by YAI. Because of the compositional similarities between Aroclor 1242 and Aroclor 1016, it is difficult, if not impossible to distinguish between Aroclor 1016 and/or Aroclor 1242 in a sample if Aroclor 1254 is also present in that sample. Packed column GC/EC chromatograms of Aroclor 1016, Aroclor 1242, and Aroclor 1254 standards are shown in Figure 3-1. The differences in the chromatograms of Aroclor 1016 and Aroclor 1242 all occur beyond peak retention time 4.82 minutes. Since peak overlap from Aroclor 1254 begins to occur at retention time 3.76 minutes, the pattern difference between Aroclor 1016 and Aroclor 1242 is obscured by the "additive effect" of the peaks from Aroclor 1254 when it is present in a sample that also contains Aroclor 1016 and/or Aroclor 1242.

A comparison of the chromatograms in Figure 3-2 clearly shows that, even without the complication of environmental aging or Aroclor degradation, it is impossible to distinguish between an Aroclor 1242/Aroclor 1254 standards mixture and an Aroclor 1016/Aroclor 1254 standards mixture based only on packed column GC/EC patterns, which comprise the majority of the NBH database. Therefore, this report will identify the sediment Aroclors as 1016/1242 and 1254 based on the packed column GC/EC data.

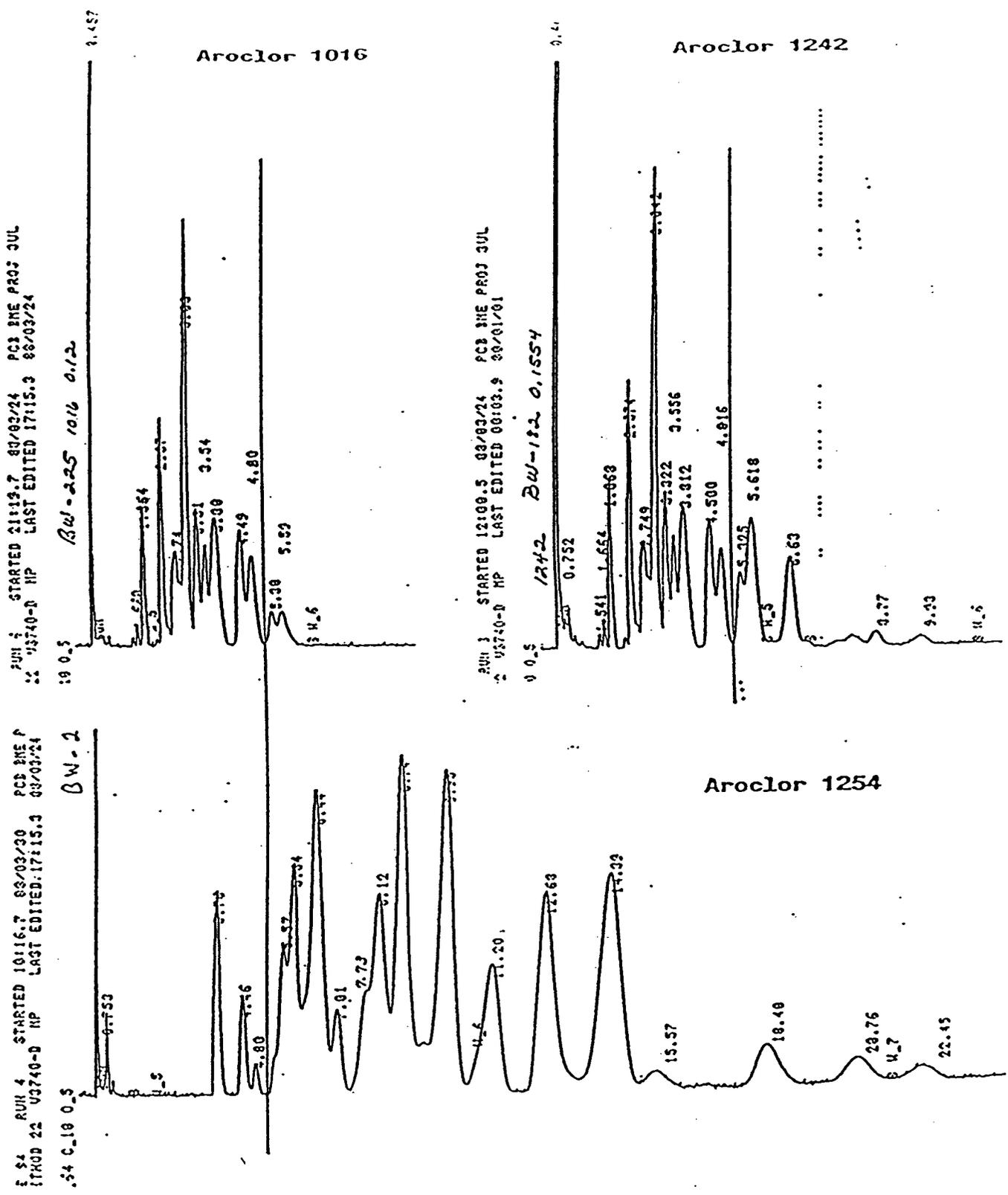
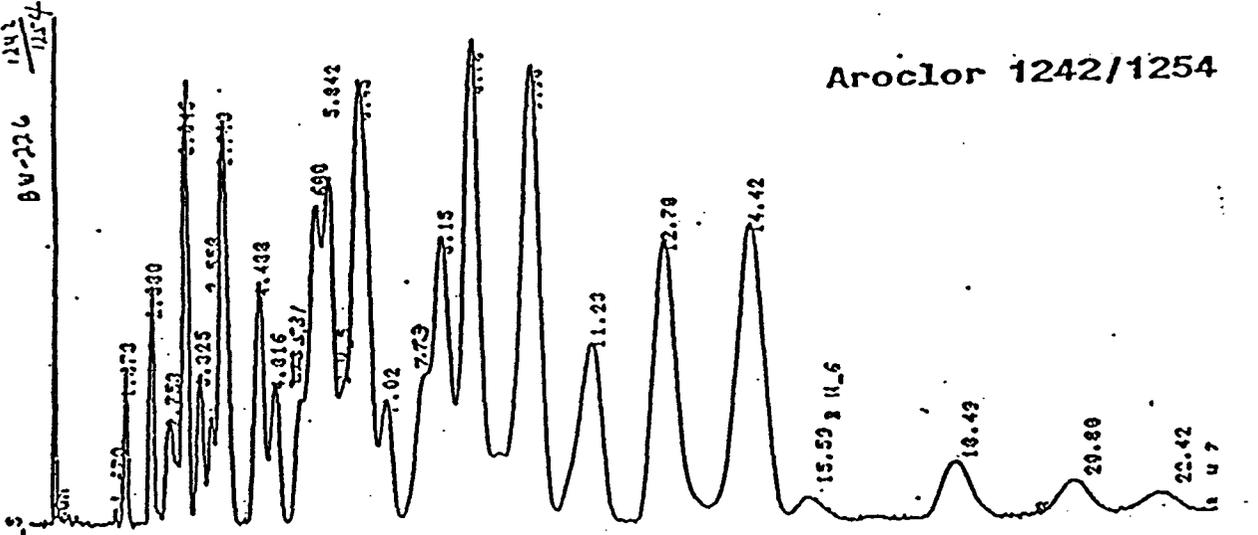


Figure 3-1. Standard Chromatograms - Aroclor 1016, Aroclor 1242, and Aroclor 1254

III 13 STARTED 20102.9 08/03/23 FCS DNE FF
 U3740-B HP LAST EDITED 17:15.3 08/03/24
 15.00 22 U3740-B HP LAST EDITED 17:15.3 08/03/24
 14 C.10 0.5



III 13 STARTED 20102.9 08/03/23 FCS DNE FF
 U3740-B HP LAST EDITED 17:15.3 08/03/24
 15.00 22 U3740-B HP LAST EDITED 17:15.3 08/03/24
 14 C.10 0.5

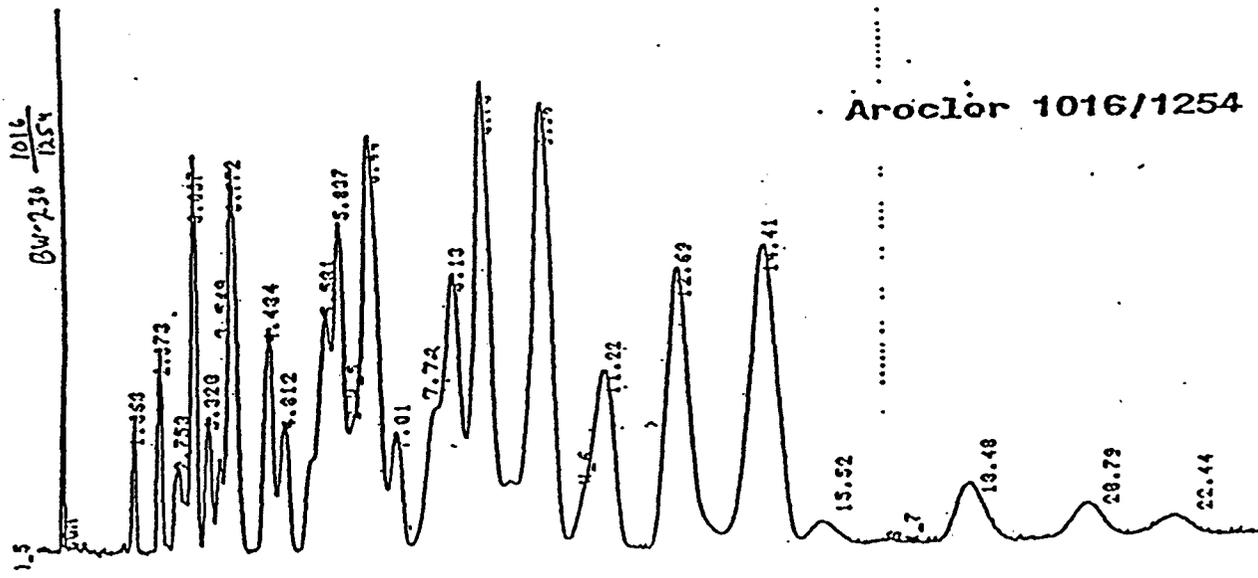


Figure 3-2. Comparison of Chromatograms for Aroclor 1242/1254 and Aroclor 1016/1254 Mixtures

When two or more Aroclors are mixed together, the alteration to a GC pattern is an additive or enhancement effect on chromatogram peaks (Figure 3-3). For the most part, this alteration is recognizable, although strikingly different patterns can result simply from varying the ratio of Aroclors in the mixture (Figure 3-4).

3.1.2.2 Environmental Aging or "Weathering"

Weathering of environmental samples results in chromatogram patterns different than those exhibited by Aroclor standards. Aroclors do not behave as homogeneous substances; the individual congeners have varying properties. The lower molecular weight (less chlorinated) congeners generally evaporate more rapidly, are more soluble in water, are more reactive and degrade more readily. Furthermore, the physical and chemical properties of two isomers in a homolog series can vary significantly, depending on the positions of chlorine atom substitutions. Even among the more highly chlorinated compounds, individual congeners do not behave and react uniformly. A "weathered" sample has undergone modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and extraction into water. Congener losses due to weathering yield a residue which demonstrates "low-end" drop-off (due to the partial loss of lower chlorinated congeners) and, usually, an apparent "high-end" enhancement of chromatogram peaks.

Non-selective losses of mono-, di-, and trichlorobiphenyl congeners associated with the weathering of Aroclor 1016/1242 were observed in chromatograms for a series of soil samples collected from saltmarsh wetlands (see Appendix III). The PCB transformation process most commonly associated with soils (as compared to aquatic sediments) is that of simple evaporation from the soil surface (Tatsukawa, 1976).

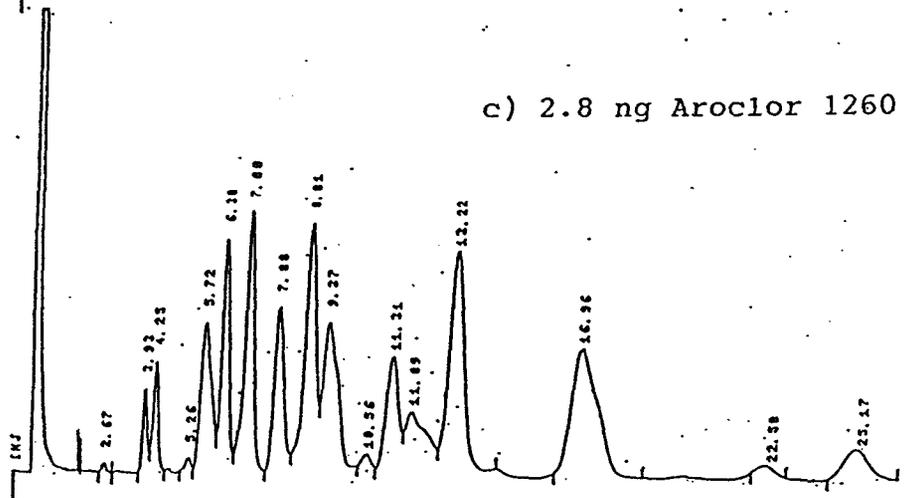
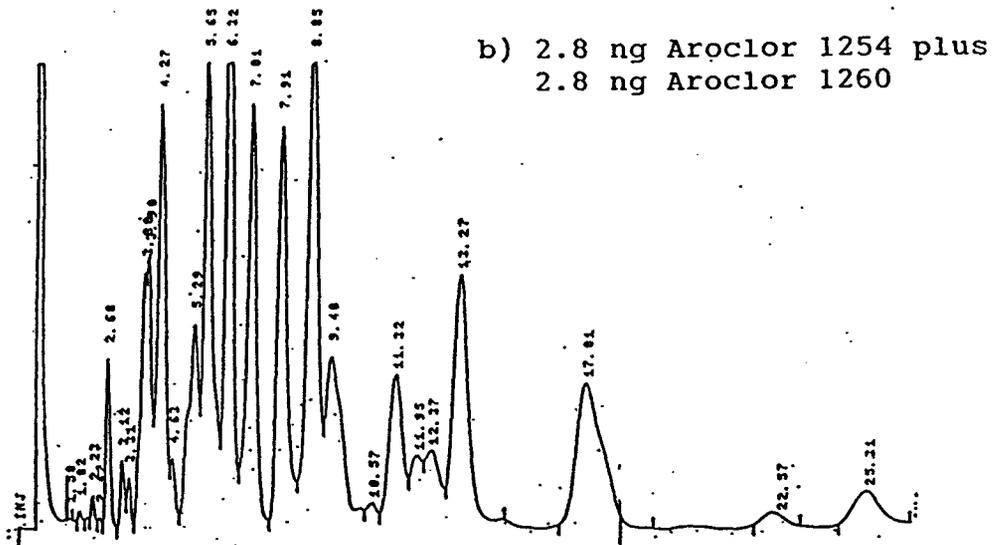
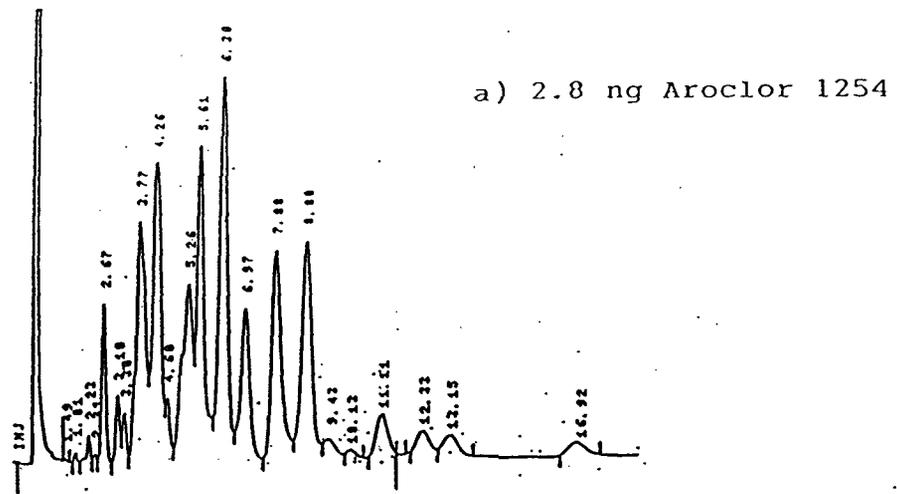


Figure 3-3. Illustration of Pattern Enhancement that occurs when Aroclor Standards are mixed.

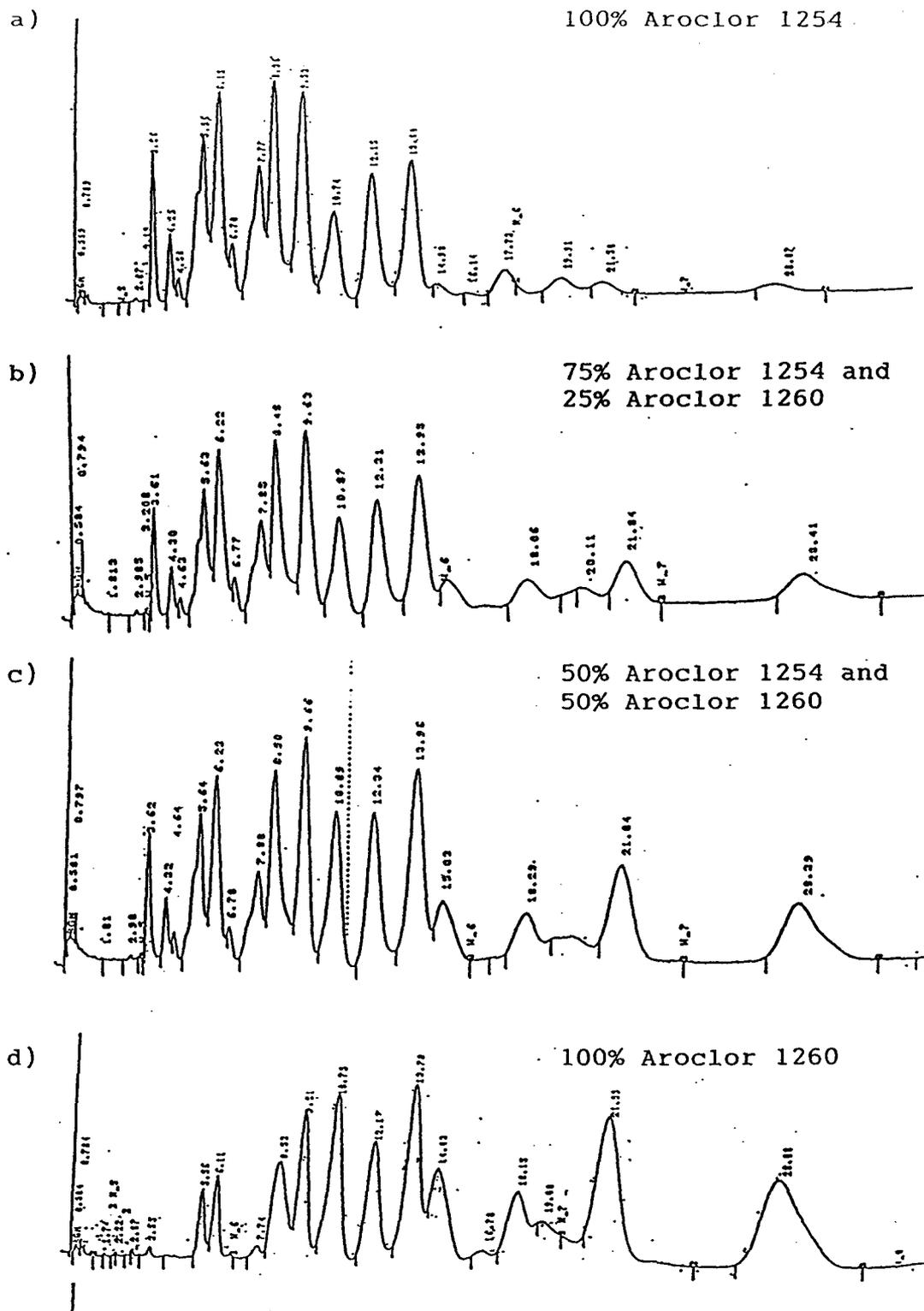


Figure 3-4. Comparison of Chromatograms for a) 100% Aroclor 1254, b) 75% Aroclor 1254 and 25% Aroclor 1260, c) 50% Aroclor 1254 and 50% Aroclor 1260, and d) 100% Aroclor 1260.

Although environmental weathering is well known and widespread in environmental samples, no chromatograms of NBH sediments were observed which exhibited this phenomenon exclusively; namely, low-end drop-off in combination with high-end enhancement of peaks. Preferential dissolution of the more soluble PCB congeners from the sediments undoubtedly occurred, but was less obvious than the anaerobic dechlorination exhibited by the sample chromatograms.

3.1.3 Evidence of Anaerobic PCB Biotransformations in New Bedford Harbor Sediments

The most significant Aroclor pattern alteration observed in NBH sediment samples was that due to anaerobic biotransformations. Specifically, the congener distribution patterns exhibited by the samples show evidence of anaerobic reductive dechlorination. The key reaction in this process, previously observed in Hudson River and Silver Lake samples, as well as in laboratory experiments, involves the replacement of the chlorine atoms(s) with hydrogen. In many cases, the compounds formed when a chlorine atom is removed are more biodegradable and less toxic.

Anaerobic reductive dechlorination pattern alterations produced unique chromatograms for the NBH samples. New peaks were present in the patterns, and significant reductions of the higher-chlorinated (penta- and hexa-) congeners were evident. Peak enhancements, reductions and disappearances were observed throughout the chromatograms. Samples exhibiting advanced Aroclor 1254 transformations showed wide distributional variations among the tri- and tetrachlorobiphenyl congeners. The peaks at RTs 2.87 and 3.80 (refer to Appendix IV, Task 7 chromatograms) are known to be the major transformation products formed during the anaerobic dechlorination of Aroclor 1254. Samples undergoing transformation of Aroclor 1016/1242 showed alterations in the lower

chlorinated (di- and tri-) peak distributions and, in some samples, the complete disappearance of a number of peaks. Many samples showed Aroclor 1016/1242 weathering; however, the pattern alterations seen in the Aroclor 1016/1242 region of the chromatograms were too extensive to be explained solely by weathering. A number of chromatograms for USACE samples (refer to Appendix II, Task 2), especially those taken at depths below 12 inches, appeared to demonstrate more advanced Aroclor 1254 degradation than was observed by YAI in any of the Task 7 samples (Appendix IV). The chromatograms for three of these samples are shown in Figure 3-5. The tri-, tetra-, and pentachlorobiphenyls are reduced significantly in these samples while the occurrence of very early eluting peaks suggests the presence of new mono- and dichlorobiphenyls and, possibly, biphenyl.

Congener analysis of the NBH sediment samples showed selective loss of non-ortho-substituted chlorine atoms. This observation provided additional evidence of dechlorination in these samples because the observed ratio of ortho-substituted chlorine to meta plus para-substituted chlorine was higher than the ratios for any theoretical combination of Aroclor 1016/1242 and Aroclor 1254.

3.1.4 Extent of PCB Biotransformations Occurring in New Bedford Harbor Sediments

The reductive dechlorination patterns observed by YAI in NBH sediments fall into three basic categories:

- o a pattern essentially corresponding to Pattern H as defined by Brown (1986);
- o a pattern resembling Pattern H but showing less transformation; and
- o a pattern showing new peaks and additional transformations not seen in Pattern H.

There is evidence from Task 7 data (Appendix IV) to indicate that transformation of both Aroclor 1016/1242 and Aroclor 1254 is proceeding simultaneously by a step-wise dechlorination process. When compositional ratio changes are discounted, a multiphased sequence of transformation changes reflecting different stages of the anaerobic dechlorination process is apparent. Based on data evaluations performed to date, it appears that only one anaerobic transformation process is occurring in New Bedford Harbor and that the pattern differences exhibited by the samples are related to different stages in the process rather than separate, distinct dechlorination mechanisms.

Because of the cascading effect of the dechlorination transformations and the uniqueness of the Aroclor patterns exhibited by the various pattern altering factors, a qualitative classification of the degree of Aroclor transformations occurring in NBH samples is possible. (See Appendix VI for classification definitions, representative chromatograms, and USACE FIT sampling program results.)

All of the packed column chromatograms evaluated for the YAI Tasks were produced using the primary analysis column prescribed by EPA for PCB determinations (1.5% SP-2250/1.95% SP-2401 mixed phase on Supelcoport). This coating affords the best resolution available for the major Aroclor components. As can be seen from Figure 3-6, the PCB congener elution sequence for this column (Figure 3-6b) closely paralleled that of the DB-5 capillary column (Figure 3-6a) used in the Task 7 investigations. In fact, the separation of the hexachlorobiphenyl congener (245-245) at RT 11.20 from the peak at RT 12.67 composed of the hexachlorobiphenyl (234-236) and pentachlorobiphenyl (234-34) congeners was better than that of the DB-5 capillary column. Consequently, transformations associated with the reductive dechlorination of the major PCB components present in the original Aroclor(s) could be tracked relatively easily using packed column chromatograms. Certain subtleties could not be seen, but the overall transformation process was quite apparent.

DATA: AR540714 #1 SCANS 800 TO 1650
CALI: CAL0329 #3

1/30M/1UM 40-325010C/M 1UL INJ
QUAN: A 0, 1.0 J 0 BASE: U 20, 3

6168.

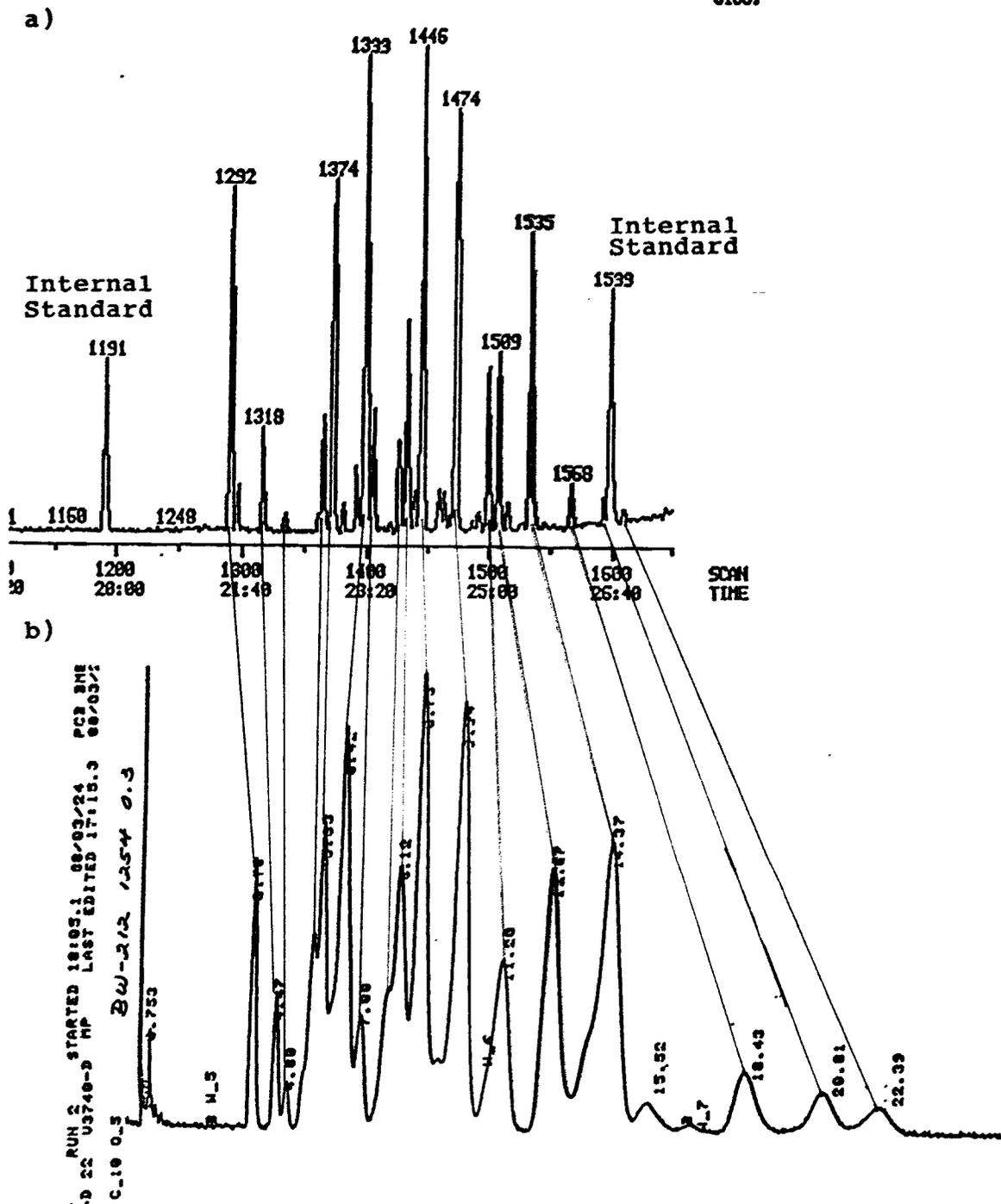


Figure 3-6. Comparison of GC/MS Capillary Column RIC (a) and GC/EC Mixed Phase Packed Column Chromatogram (b) for Aroclor 1254

3.1.4.1 Transformations Observed in Acushnet River Upper Estuary

The chromatograms evaluated showed strong evidence of PCB biotransformations associated primarily with anaerobic dechlorination at approximately 97% of the sampling sites located in the Acushnet River Upper Estuary.

Distribution of Aroclor Transformations

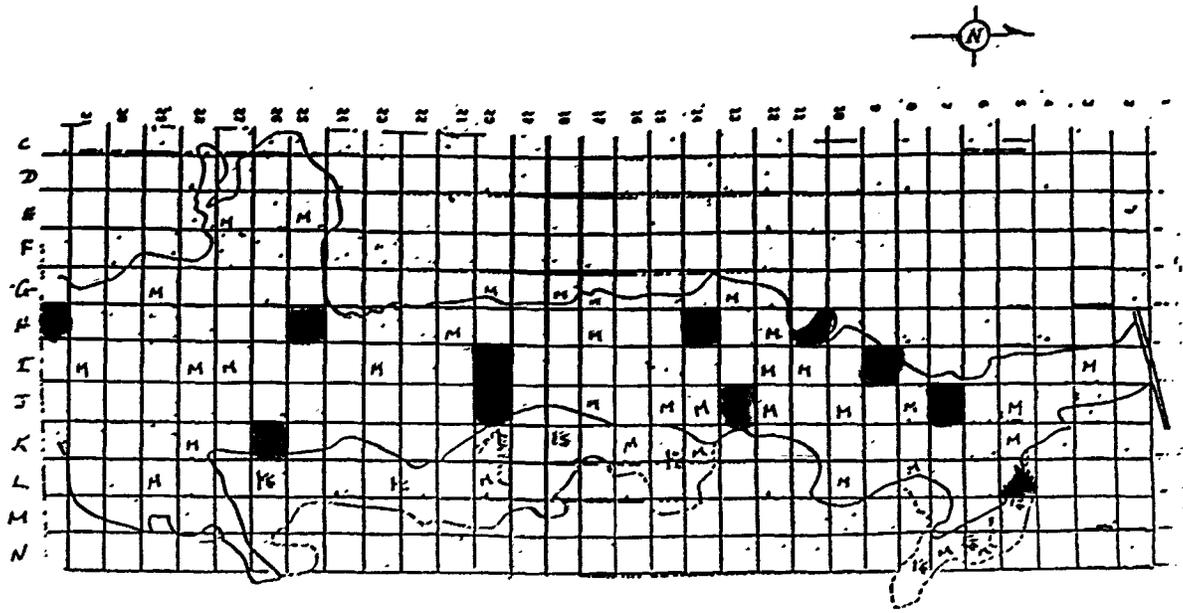
Plots showing the spatial distribution and degree of transformation for both Aroclor 1016/1242 and Aroclor 1254 for the samples evaluated in YAI Tasks 2, 3, 7, and 8, have been developed. Figure 3-7 represents samples from the 0-12" depth stratum. A similar plot for sediment PCB transformations observed in samples collected from depths greater than 12 inches is shown in Figure 3-8. Definitions for these transformations are contained in Appendix VI (Task 10). A color-code was used to represent the transformation classifications as follows:

- Green = Advanced
- Blue = Moderate to Advanced
- Yellow = Moderate
- Orange = Slight to Moderate
- Pink = Slight
- Red = None

Based on the data presented in Figure 3-7, the following observations were made for 0-12 inch sediment depth stratum:

1. The moderate transformation classification for Aroclor 1016/1242 predominated, and was observed at 73% of the sites. Its distribution was widespread throughout the entire Upper Estuary.

a) Aroclor 1016/1242, Depth 0-12"



b) Aroclor 1254, Depth 0-12"

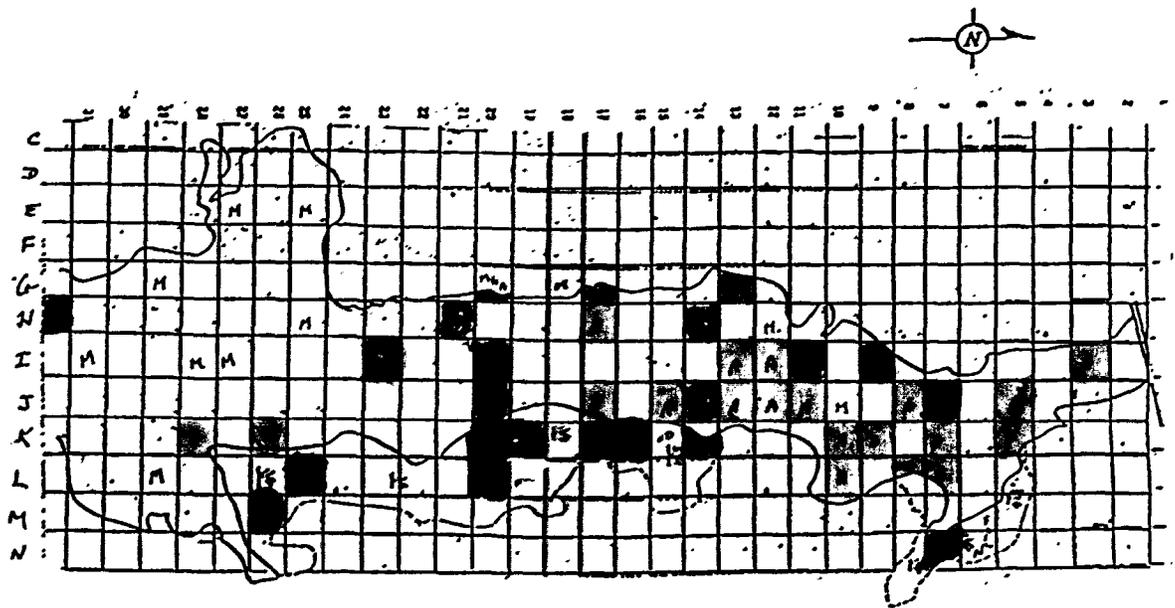


Figure 3-7. Aroclor Transformations in Upper Estuary Samples (Depth 0-12")

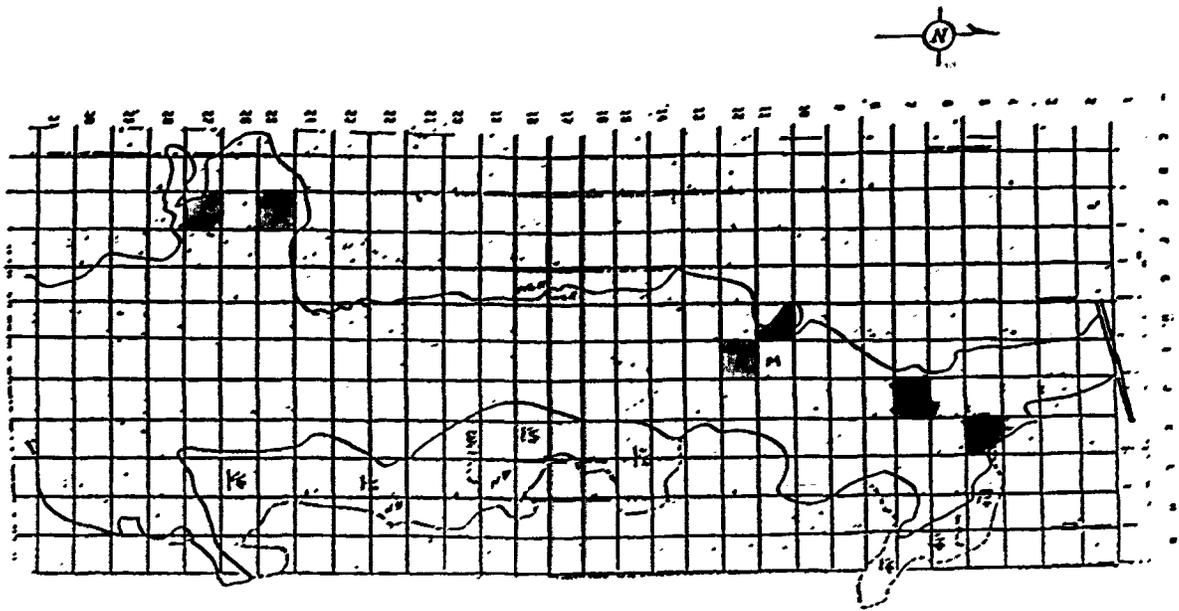
2. For Aroclor 1254, 45% of the sediment sites showed advanced transformations; all but two of these sites were located in the northern half of the Upper Estuary where higher PCB concentrations have been reported present. Advanced Aroclor 1254 transformations were seen in two-thirds of the samples from the northern half of the Upper Estuary.
3. Moderate, moderate to advanced and advanced transformations of Aroclor 1254 were present in all but three of the sites in the southern half of the estuary (14 of 17 locations or 82%).
4. In the wetland soils, "moderate" transformations of Aroclor 1016/1242 were observed. No transformations were observed for Aroclor 1254.

In sediment depths greater than 12 inches, the following conditions are notable from review of Figure 3-8.

1. Moderate to advanced and advanced transformations of Aroclor 1016/1242 were present at 6 of the 9 sites (67%) where PCBs were detected in sufficient quantity to be classified.
2. Advanced transformation of Aroclor 1254 was observed at 12 of the 14 sites (86%) where the presence of PCBs could be confirmed.

In summary, Aroclor transformations were observed at 97% of the sediment sampling sites. Only two sites, one each from Task 2 and Task 7, showed no apparent Aroclor pattern alterations.

a) Aroclor 1016/1242, Depth >12"



b) Aroclor 1254, Depth >12"

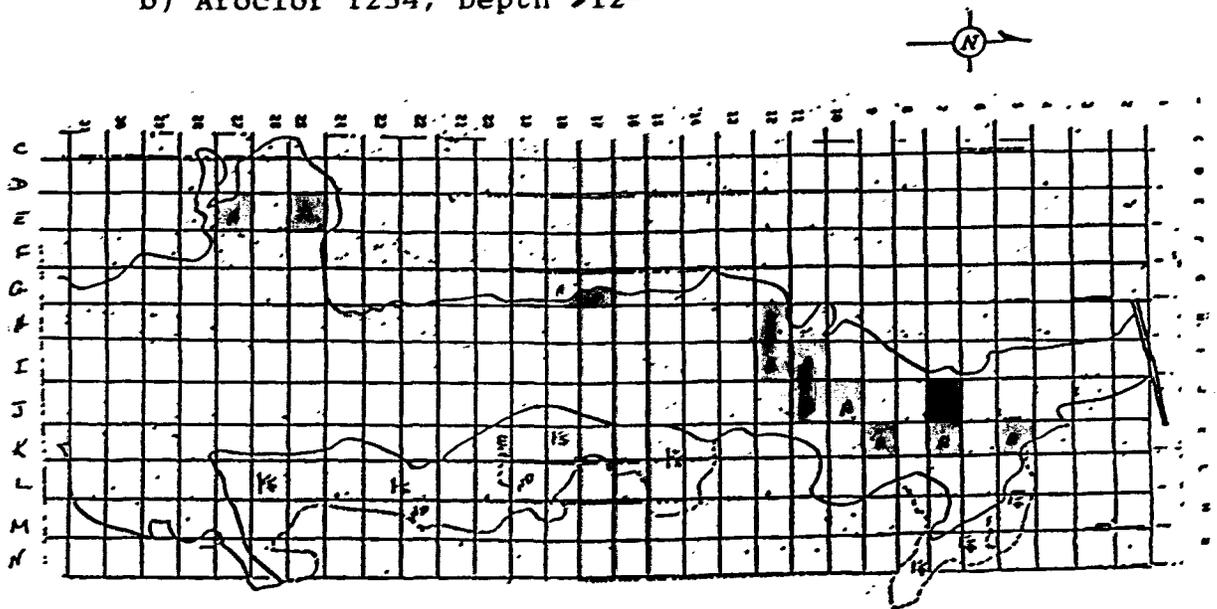


Figure 3-8. Aroclor Transformations
in Upper Estuary Samples
(Depth >12")

Evaluation of Sediment PCB Concentrations and Aroclor Transformations

Total PCB concentrations (ppm) for the 0-12" and >12" sediment depths have been plotted in Figure 3-9. Concentration ranges have been color-coded as follows:

PCB Concentration (ppm)		Color
<1	=	Green
1-9.9	=	Blue
10-99	=	Yellow
100-99	=	Orange
1000-9999	=	Pink
>10,000	=	Red

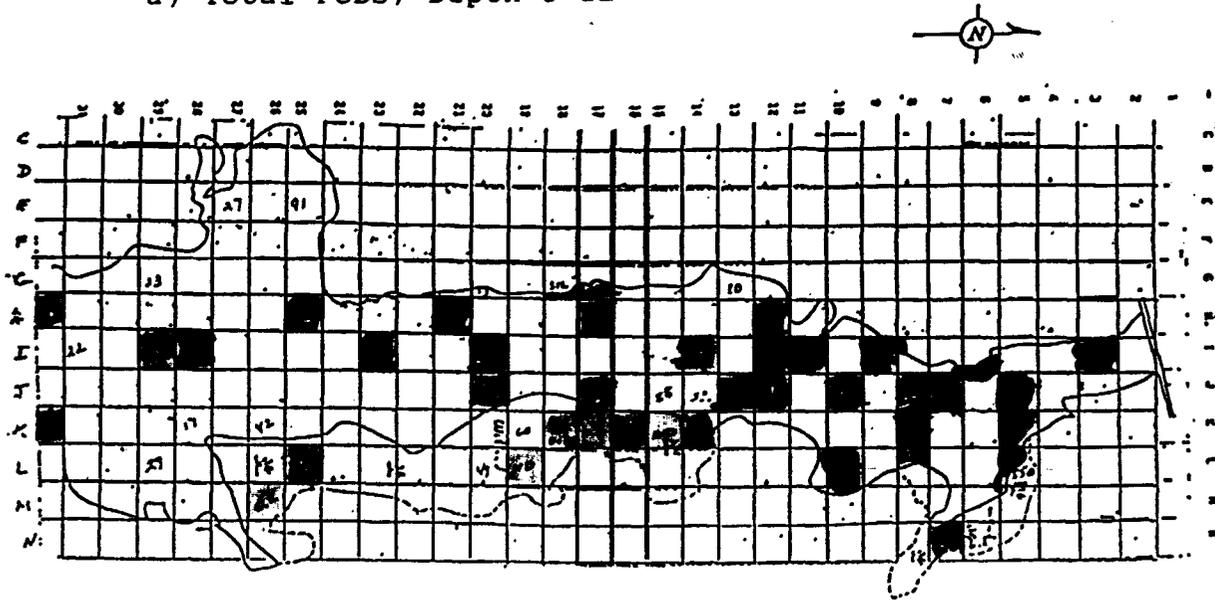
A comparison of Figures 3-7 and 3-9 showed that there did not appear to be a correlation between the moderate Aroclor 1016/1254 transformation and total PCB concentrations in the Upper Estuary. However, in the northern half of the Upper Estuary, there is a direct correlation between high total PCB concentrations (up to 36,000 ppm) and the advanced transformation of Aroclor 1254.

By comparing Figures 3-8 and 3-9, it is seen that for areas with high PCB concentrations at depths greater than 12 inches, advanced transformations of both Aroclor 1016/1242 and Aroclor 1254 are occurring.

3.1.4.2 Transformations Observed at Selected NUS/GZA Drilling Stations in the Middle, Lower and Outer Areas of New Bedford Harbor

Pattern alterations resulting from environmental aging of Aroclor 1016/1242 were observed in all but one of the samples where PCBs were detected. Evidence of Aroclor 1254 biotransformation was seen in six of the nine sampling sites evaluated, including two of three Middle Harbor sites, one of three Lower

a) Total PCBs, Depth 0-12"



b) Total PCBs, Depth >12"

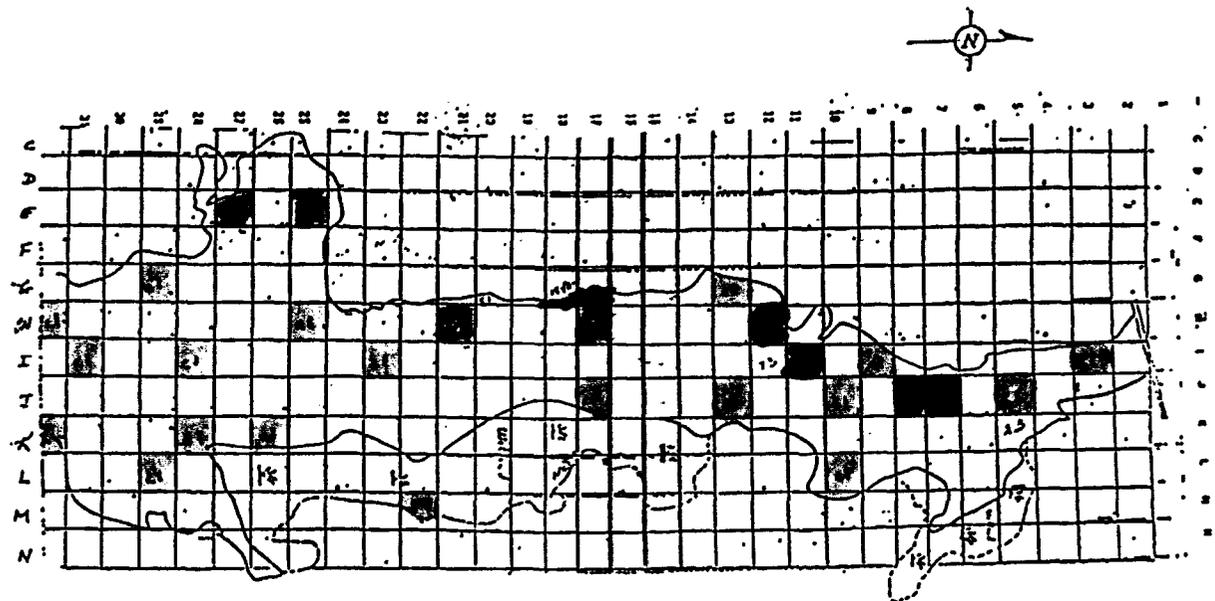
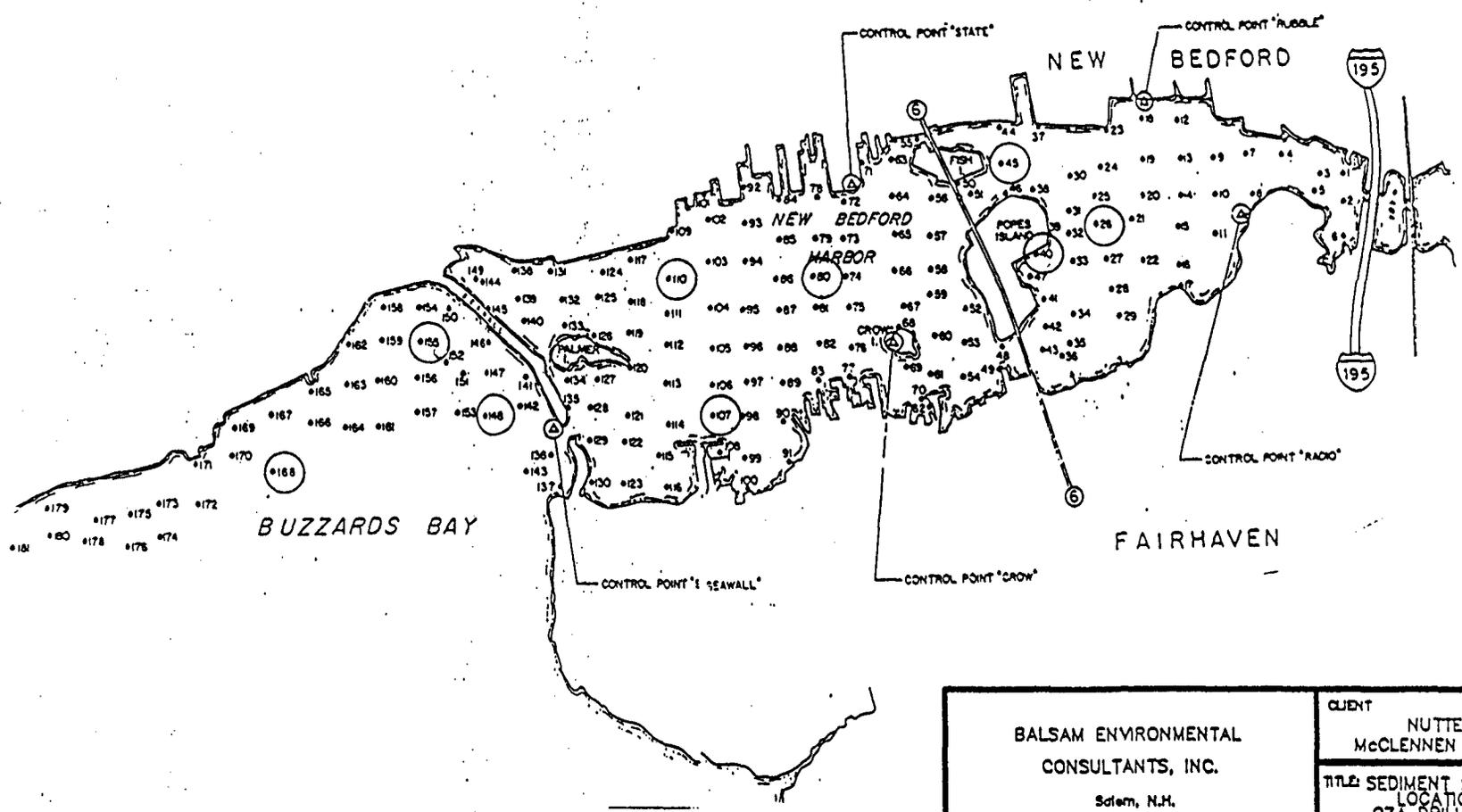
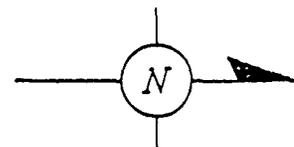


Figure 3-9. Total PCB Concentration (ppm) Profiles of Upper Estuary

Harbor sites, and three of three Outer Harbor area sites. (These sampling locations are shown in Figure 3-10.) One sample, from Site #155, showed pattern alterations which suggested biotransformation in the characteristic Aroclor 1016/1242 region of the chromatogram. The PCB transformations observed at NUS/GZA Drilling sampling sites were less extensive than those observed in Upper Estuary samples. (See Appendix VII for additional details.)

3.1.5 Current YAI Research Program

YAI presently is conducting a second phase of its investigation of PCB biotransformations in selected Task 7 samples. This work involves the use of full-scan, capillary column GC/MS analyses to develop a more complete understanding of the PCB biotransformation process(es) occurring in Upper Estuary sediments. Review of RICs from GC/MS analysis should permit identification of the congener-specific dechlorination regime and quantitation of PCB congener losses and enhancements resulting from biotransformations. With such information in hand, a more refined analysis of the role of biotransformations in the detoxification of NBH sediments will be possible.



SEDIMENT SAMPLING LOCATIONS
NEW BEDFORD SITE, NEW BEDFORD, MA

BALSAM ENVIRONMENTAL CONSULTANTS, INC. Salem, N.H.			CLIENT NUTTER McCLENNEN & FISH	
			TITLE: SEDIMENT SAMPLING LOCATIONS - GZA DRILLING / NUS SAMPLING PROGRAM	
DATE 3/17/88	DRAWN BY D.J.P.	CHECKED T.P.W.	PROJECT NEW BEDFORD HARBOR	
SCALE 1" = 2250'	DESIGNED T.P.W.	APPROVED L.C.S.	FIGURE NO. FIG. 1	PROJECT NO. 6002

Figure 3-10. Nine Sampling Locations Evaluated for PCB Biotransformation (Task 12, Appendix VII)

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