

## PCB DECHLORINATION AND DETOXICATION IN THE ACUSHNET ESTUARY

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**Abstract --** The PCB congener distributions in sediments and waters of the Acushnet Estuary (New Bedford, MA) were characterized by capillary gas chromatography and mass spectrometry in order to identify the PCB transformation processes underway. The PCBs in the upper Estuary sediments were found to be undergoing some extraction into the water, with consequent decline in the proportion of lower congeners. However, the dominant transformation process was a reductive dechlorination that removes *meta* and *para* chlorines selectively from many of the higher PCB congeners, including all those associated with toxic effects. The resulting congener distribution alteration pattern, designated H, was different from those of previously reported anaerobic microbial dechlorinations, but has since been observed at several other aquatic PCB spill sites. In the Acushnet, the dechlorination/detoxication process appears to have commenced near the upper end of the Estuary and gradually moved south, with movement into areas with lesser PCB levels probably driven by seeding from the upper Estuary.

## INTRODUCTION

The polychlorinated biphenyls (PCBs) are a group of relatively persistent environmental contaminants that possesses a unique combination of chemical characteristics [1]. These are first, that the commercial PCB products (e.g., Aroclors) that were originally released each consisted of a complex mixture of isomers and homologs (generically referred to as "congeners") that were produced in almost invariant relative proportions by the manufacturing process used. Second, these congeners all possess very similar physical properties (water-insolubility, lipophilicity, slight volatility, etc.), and hence tend to move together as a group when subject to simple physical forces such as winds or currents. Third, the individual PCB congeners differ somewhat in their responses to inter-phase transfer processes, and greatly in their relative susceptibilities to the metabolic enzymes present in the microbes and higher organisms of particular environmental compartments. Furthermore, the patterns of relative susceptibility to biodegradation differ enormously from one enzyme system, microbe, or environmental compartment to another. A consequence of this combination of characteristics is that the PCB residues isolated from an environmental sample will display, in their distribution of residual PCB congeners, a record of all of the congener-selective alteration processes to which that particular specimen of PCB had been subjected since its release.

In order to be able to actually read such records (which are conventionally displayed as gas chromatographic (GC) or gas chromatographic-mass spectrometric (GC-MS) tracings) it is helpful, though not essential, to know which of the commercial Aroclors were originally present. More essential is knowledge of how the various possible inter-phase transfer processes and biodegradative processes affect the congeneric distribution. This can be obtained through laboratory studies of Aroclor alteration by known physical, chemical, or

biological agents, and field studies aimed at finding out which alteration processes, whether previously known or unknown, are actually occurring in the environment.

In the recent past, laboratory studies have revealed distinctive patterns of PCB congener elimination for more than two dozen strains of aerobic, terrestrial, PCB-degrading bacteria [2] and for the two cytochrome P-450 isozymes commonly involved in PCB metabolism in higher animals [3,4]. Previous field studies have indicated the occurrence of at least seven distinguishable types of reductive dechlorination, presumably mediated by various strains of anaerobic bacteria in aquatic sediments [5-7]. One of these reductive dechlorination processes was recently reported to have been duplicated under anaerobic culturing conditions [8], and further experimental studies of this and other anaerobic dechlorination systems are now underway in several laboratories. None of the previous studies, however, have indicated what sorts of inter-compartment transfer or intra-compartment degradation processes might be occurring in marine environments.

In order to obtain such information, we undertook high-resolution GC and GC-MS studies of the PCB residues in the sediments and waters of the Acushnet Estuary (New Bedford, MA). This site appeared attractive because there already existed a considerable body of information on the levels of PCB in Acushnet sediments [9,10] and water [11], and on sediment stability [12]. Also available were a few high-resolution GCs of the PCBs recovered from the sediments and water of the outer harbor [13-15], and a large collection of unpublished low-resolution GCs of sediments from their entire region [16]. The latter suggested that some unusual PCB transformations might be occurring in the sediments of the uppermost part of the Estuary, which is also the section showing the highest levels of PCBs present.

Accordingly, our sediment sampling effort was focused on that area.

## MATERIALS AND METHODS

### *Sample collection*

Sediment samples were collected from the tidal flats near the low tide line by GHR Analytical, Inc. of Lakeville, MA in June 1986, from 17 sites along the west side of the Estuary and six along the east. At each site, the surface layers were removed and the two sets of samples taken: Set A at 5 to 7.5 cm depth and Set B at 15 to 17.5 cm. At least one sample of each set was retained by GHR for determination of total oil and grease content (reported below) and another was sent to us. In selecting samples of detailed PCB analysis, we first rejected two of the 17 west-side samples that appeared to consist mainly of coarse gravel or cultural artifacts. The six of the remaining 15 west-side sample pairs that permitted the most even spacing of sample sites, along with all six east-side sample pairs, were then taken for analysis.

Water samples were collected near high tide, also by GHR, at some of the sites [11] being used by an ongoing Battelle study in December 1986. At each site, separate collections were made of whole surface water, and of a water sample that was passed through a filter. Hexane extracts of the filtrates, filters, and whole-water samples were then sent to us for analysis. The locations of both sediment and water sampling sites are shown on Figure 1.

### *PCB alteration by evaporation*

In order to characterize the alteration in PCB congener distribution resulting from evaporative or elutriative processes, small flat dishes of Aroclor 1242 were held at 30° in a well-ventilated hood for periods of time ranging between two days and two months, then weighed to determine evaporative loss, and the residues analyzed.

### *Analytical procedure and nomenclature*

In this study, we followed previously described procedures [7] for PCB isolation, GC and GC-MS analysis, DB-1 capillary peak numbering, identification of PCB congeners contributing to each observed DB-1 capillary peak, and description of individual PCB congeners. Thus, we shall be continuing to refer to a congener such as 2,2',3,4',5,5',6-heptachlorobiphenyl (CB) as 2356-245 CB, or simply 2356-245, rather than as PCB 187.

### *Calculation of summary indices of composition*

The above analytical procedures provided, for every sample, a listing of the levels of all 118 PCB peaks resolvable by our DB-1 capillary, and for representative specimens, GC-MS data that permitted 22 of the peaks to be resolved into non-isomeric components. In order to compress and summarize such data, we calculated from it both the homolog distribution (i.e., proportions of the total PCBs present represented by mono-, di-, tri-, etc-chlorobiphenyls) and the overall levels of *ortho* and non-*ortho* (i.e., *meta* and/or *para*) chlorine atoms present per biphenyl nucleus. The latter parameters were determined by adding up the products of mole fraction times the number of *ortho* (i.e., 2-, or 6-) or non-*ortho* (i.e., 3-, 4-, or 5-)

chlorine atoms for all of the observed PCB peaks.

*Calculation of original Aroclor ratios and solubilization losses*

These calculations were carried out by an "indicator peak" procedure. This presumes that we can identify in the sample chromatograms at least two peaks, A and B, which, after correction if appropriate, can be considered to be unaffected by the chemical transformation(s) underway. We may then define the following parameters:

- $a$  fraction Peak A in sample
- $a_1$  fraction Peak A in Aroclor 1242 standard
- $a_2$  fraction Peak A in Aroclor 1254 standard
- $b$  fraction Peak B in sample
- $b_1$  fraction Peak B in Aroclor 1242 standard
- $b_2$  fraction Peak B in Aroclor 1254 standard
- $c_1$  relative effect of evaporative loss on A, i.e.,  $\Delta a/a\Delta y$
- $c_2$  relative effect of evaporative loss on B, i.e.,  $\Delta b/b\Delta y$
- $c$  relative effect of evaporative loss on A/B ratio
- $x$  original ratio of Aroclor 1242 to Aroclors 1242 + 1254
- $y$  weight fraction of original PCB lost by evaporation or other processes  
(i.e., true solution) having a similar effect on PCB congener distribution

Simple material balances indicate that:

$$a = [(1-c_1y)/(1-y)][a_1x+a_2(1-x)] \quad (1)$$

$$b = [(1-c_2y)/(1-y)][b_1x+b_2(1-x)] \quad (2)$$

$$\frac{a}{b} = \frac{(1-cy)[(a_1-a_2)x+a_2]}{[(b_1-b_2)x+b_2]} \quad (3)$$

Examination of the chromatograms (described below) indicated that congeners 26-34 and 236-34 were probably not being significantly formed or destroyed by the transformation processes at work in the sediments examined, and hence that Peak 39 (originally mainly 26-34 CB, with a little 236-4 and 234-2) and Peak 61 (originally mainly 236-34 CB, with a trace of 34-34) could be used as indicators for Aroclors 1242 and 1254, respectively. The only correction applied was that the 234-2 in Peak 39 was presumed to be originally present at the 10% level, but to then decline in proportion to any observed decline in Peak 50 (23-34 plus a little 234-4). For Peaks 39 as "A" and 61 as "B" we were able to evaluate the constants in equations 1 through 3 from Aroclor 1242 and 1254 standards, and from the evaporative weight loss data as follows:  $a_1$ , 0.03160;  $a_2$ , 0.00789;  $b_1$ , 0.00743;  $b_2$ , 0.0895;  $c_1$ , 0.43;  $c_2$ , 0.1;  $c$ , 0.382.

Using these values, equations 1 through 3 were solved for  $x$  and  $y$  by a process of successive approximations. Examination of the sensitivity of the solutions to variations in the observed parameters  $a$  and  $b$  indicated no particular magnification of errors in the case of the  $x$  values (mainly because the concentration ratios  $a_1/a_2$  and  $b_2/b_1$  are quite large for both peaks). For the  $y$  values, however, where  $1/(1-y)$  is roughly proportional to  $(a+b)$ , small

errors in  $a$  or  $b$  could be considerably magnified. As a check for badly deviant values, we roughly estimated  $y$  from the loss in the very strong pair of Aroclor 1242 peaks, Nos. 23 and 24, given by 25-4 and 24-4 CB, and made note of the cases where the calculation via equations 1 through 3 had given a questionable result.

#### *Calculation of indices of dechlorination*

As indicators of dechlorinative loss affecting Aroclors 1242 and 1254, we selected the dechlorination-sensitive DB-1 Peak 50 (23-34 plus a little 234-4 CB) and Peak 58 (234-25 plus traces of 2346-4 and 235-35 CB), respectively. Changes in these peaks were determined by reference to the same indicator peaks used above, and were expressed in terms of half-losses, thus:

$$\text{Half-loss (P50)} = -\log_2 \frac{(P50_{\text{sample}})/(P39_{\text{sample}})}{(P50_{\text{standard}})/(P39_{\text{standard}})} \quad (4)$$

$$\text{Half-loss (P58)} = -\log_2 \frac{(P58_{\text{sample}})/(P61_{\text{sample}})}{(P58_{\text{standard}})/(P61_{\text{standard}})} \quad (5)$$

## RESULTS

#### *Characteristics of the sampling site and sediments*

The upper Acushnet Estuary may be defined as the small (2.3 km long) highly protected [12] tidal cove located between the entrance of the Acushnet River (a small stream) at 41°40'37" N and the narrow passage under the Coggeshall Street bridge at 41°39'22" N (Figure 1). At low tide, it contains a shallow body of salt water (depth 0.2-1.0 m) surrounded

by tidal mudflats, which are surrounded in turn by spartina grass marshbeds except in some dock areas along the New Bedford side. The tideflat sediment samples taken at most sites consisted largely of the glacial outwash sands and gravels characteristic of the southern New England coast. Since there were no visible sources of influxes that could have provided such coarse-grained materials, it was concluded that sediment deposition rates in such areas must be either very low or negative. At two of the sites, however, where the samples taken consisted of soft, black, organic muds, a positive, but unknown, rate of sedimentation could be presumed.

#### *Results of sediment and water analyses*

Figure 2 shows GCs for Aroclor 1016, 1242, and 1254 standards, for an evaporated Aroclor 1242 specimen, and for two sediment samples that both showed progressive diminution of the peaks to the right of Peak 61 ("high-end drop-off") and extensive, though not quite identical, alterations of the relative intensities of the peaks between Peaks 21 and 58, inclusive, and of Peak 7. These two altered patterns were designated H and H'. One of these samples (19B) also showed a progressive diminution of the peaks to the left of Peak 21 ("low-end drop-off"). All of the other sediment and water samples examined gave patterns that could be regarded as combinations of those for Aroclors 1242 and 1254, modified to varying extents by whatever processes were responsible for the "high-end" and "low-end" drop-off patterns shown in Figure 2.

The "low-end drop-off" in GC pattern was obviously similar to that shown by the evaporated Aroclor 1242 specimen of Figure 2, or portrayed in more quantitative form in

Figure 3. Had this drop-off arisen from aerobic microbial biodegradation [2] we would have expected to see relative persistence for Peaks 10, 16, 17 and 39, which are given by PCB congeners (26-2, 26-3, 26-4, and 26-34 CB) that are relatively resistant to microbial 2,3-dioxygenase attack. Had it arisen from aerobic eucaryotic metabolism, we would have expected to see relative persistence for Peaks 24, 46, and possibly 34, which are given by PCB congeners (24-4, 245-4, and 24-24 CB) that are relatively resistant to cytochrome P-450 monooxygenase attack. Evidently, this low-end drop-off arose from a simple inter-phase transfer process, such as evaporation of volatiles or extraction of soluble components into the water column [17], both of which processes show very similar patterns of congener depletion.

The "high-end drop-off" pattern alterations of types H and H' involved complex sets of congener depletions and congener augmentations that are portrayed by the GC-MS pattern of Figure 4, and more fully described in a later section. Patterns H and H' (Figure 2) differed only in the degree of their effects on Peaks 37, 38, and possibly 27.

The results of the various upper Acushnet Estuary sediment analyses are summarized in Table 1. This shows that the samples analyzed consisted of sands, gravel, and biogenic muds in various proportions, as already indicated, but with no obvious connection between sediment texture and PCB level. Most samples contained high levels of total extractible "oil and grease", (average for all sites, 13,000 ppm) of which the PCBs constituted 7.8%, on the average. The PCBs present consisted mostly of tri-, tetra-, and pentachlorobiphenyls, with only 1% to 3% of hepta- and higher CBs (data not shown) and highly variable levels of dichlorobiphenyls (Table 1). The calculations of evaporative type loss for the various individual samples gave highly suspect values in several cases; however, the average for all sites (18%) was quite

consistent with the average observed retention of dichlorobiphenyls. (Predicted for 60% (Figure 3) retention of the 13.2% dichlorobiphenyls expected to be formed by 50% Pattern H conversion of a 61:39 1242:1254 mixture to dichlorobiphenyls, 7.9%; observed, 8.1%.) Pattern H or H' development, as indicated by the number of half-losses of Peaks 50 and 58, occurred to a somewhat variable extent (Table 1). The net effects of both evaporative/elutriative and dechlorinative losses upon the overall levels of *ortho* and non-*ortho* chlorines in the residual PCBs are shown in Figure 5.

A striking feature of the sediment analyses was that at almost every site the characteristics of the "A" level (5-7.5 cm) and "B" level (15-17.5 cm) samples were quite similar, whether described in terms of sample texture, total oil and grease, total PCB, percent dichlorobiphenyls, dechlorination indices, or appearances of minor, non-PCB peaks in the chromatograms. Conversely, there were often very large differences in both PCB content and composition between nearby sites, even some that were very close (e.g., Sites 18 and 19). The high variability in PCB level among Acushnet Estuary sites was also observed by previous investigators [10].

The analyses of the whole-water, filtered-water, and filtrate samples had to be delayed for some time after that of collection, and then showed that unacceptable levels of contamination had occurred in most of the filtered-water samples at some time during the process of collection, shipment, and analysis, so that they had to be discarded. Minor contamination of a few of the whole-water samples with Aroclor 1260 (absent from the filter samples and from all known Acushnet sediment samples) was noted and corrected for, giving the data reported in Table 2.

These data showed that at most of our December 1986 sites only about 20% of the PCBs present could be removed by filtration. In the unfiltered (whole) water samples the PCB levels and dechlorination status varied considerably from site-to-site, and sometimes even between two samples taken from opposite sides of the boat (at Site 4). Evidently, at the times of sampling the estuarine waters included some masses containing relatively higher levels of quite heavily altered (half-losses of P50, 58: 1.0 to 2.0) PCBs and some masses containing somewhat lower levels of almost unaltered (half-losses of P50, 58: 0.0 to 0.5) PCBs, with relatively little mixing between them.

#### *Characterization of original Aroclor release*

It is known from local history, 1958-1977 Monsanto sales records made available in connection with ongoing legal proceedings, and previous reports [9] that there were large annual purchases of PCBs by the two local capacitor manufacturers beginning in the 1930's or 1940's and continuing through 1977. The particular grade of PCB purchased was predominantly Aroclor 1254 until about 1960, when a gradual changeover was made to Aroclor 1242, which became the predominant PCB in use from 1965 to 1971, when it was replaced by Aroclor 1016. By the time of Aroclor 1016 introduction, however, there was already growing concern over PCB accumulations in the environment, and strenuous efforts were being made to control PCB releases. Accordingly, we felt it a reasonable presumption that the PCBs in the Acushnet sediments were originally largely or solely composed of Aroclors 1242 and 1254.

Unfortunately, however, previous examinations of the PCBs in Acushnet Estuary air, sediments, water, and biota by 23 different analytical laboratories have reported their findings in terms of Aroclors 1221, 1232, 1016, 1242, 1248, 1254, and 1260 [10]. This has happened because analysts have routinely reported their analyses of environmental PCB mixtures in terms of whichever Aroclor appeared most convenient as a standard for quantitation, the actual analysis being quantitative rather than qualitative. Nevertheless, the sheer volume of diverse "Aroclor" reports already on record made it imperative to verify our presumption that the original releases were largely or solely Aroclors 1242 and 1254 before proceeding with any detailed descriptions of the alteration processes.

Regarding the possible presence of Aroclor 1016, which was first produced in 1971, Figure 2 shows that in Aroclor 1242 there is a prominent Peak 50 (mainly 23-34 CB) that is much weaker in Aroclor 1254 and only 1.5% as strong in Aroclor 1016. Thus, in undechlorinated 1242 specimens (such as those of the outer harbor) loss of Peak 50 (relative to indicator Peak 39) can provide a sensitive measure of admixed Aroclor 1016. To extend this method to lightly dechlorinated samples, we found that in the deeper, and hence presumably older (pre-1016), sediments undergoing dechlorination by System H, the disappearance rates for the trichlorobiphenyl component of Peak 25 (mainly 34-2 CB) and for Peak 50 were about equal. Accordingly, we could subtract any percentage loss in Peak 25 trichlorobiphenyls from that in Peak 50, to get an approximate measure of the portion of the Peak 50 loss attributable to admixture with 1016. Application of this procedure to all of the more lightly dechlorinated upper Estuary specimens, i.e., samples 2A, 5A, 14A, 17A, 18A, and 18B, indicated an original Aroclor 1016 content of  $0 \pm 20\%$  in every case.

In the case of Aroclor 1248, which gives a chromatogram virtually identical to that of 1242 after *ca.* 50% evaporation, chromatographic proof of presence or absence in admixture with extractively devolatilized Aroclor 1242 would be very difficult. However, the site contamination history [9,10] indicates no known releases of Aroclor 1248, which was never used in electrical devices. Accordingly, we conclude that the "Aroclor 1248" reportings by previous analysts [10] all represent devolatilized Aroclor 1242 rather than actual 1248.

Regarding Aroclors 1260 and 1262, which is also reported to have been used in the area [9], careful inspection of the sediment chromatograms showed that the major octachlorobiphenyl peaks (Peaks 109, 110, 112, and 115) were always slightly stronger than in our Aroclor 1254 standard, i.e., with a total weight percent (of Aroclor 1254 content) about 0.3% rather than 0.15%. The excess octachlorobiphenyls were accompanied by only modest proportions of nonachlorobiphenyls (Peaks 113, 114, and 117) indicating the additional Aroclors, if any, to be Aroclor 1260 or 1262 rather than 1268. Since Aroclor 1262 contains 14% by weight of the measured octachlorobiphenyls, the observed increase in octachlorobiphenyls could have been produced by 1% contamination of the 1254 with 1262. We consider it more likely, however, that the average Aroclor 1254 produced during the period of discharge contained 0.15% more octachlorobiphenyl than did our analytical reference standard.

#### *Characterization of PCB alteration processes H and H'*

Figure 5 shows that despite a considerable amount of evaporative and/or elutriative losses, which would increase the content of *meta* and *para* chlorine atoms in the residue, a net loss of such chlorine atoms occurred at all sites, indicating the occurrence of a dechlorination

process that was *meta/para*-selective, like those of the upper Hudson [5-7] or Waukegan Harbor. In order to characterize this process, we carefully reviewed the Pattern H GC and GC-MS tracings shown in Figures 2 and 4, along with the accompanying peak quantitations, to determine which congeners were unaffected by the alteration, which were being depleted, which were being increased, and which of the latter two groups could be matched against each other. The results of this review are shown in Table 3. Definitive matchings between congeners lost and congeners formed could not be made in all cases, owing to complications arising from congener coelution and successive reactions; nevertheless, there were enough examples of consistent patterns of congener gains and losses to establish the conversion of 3,4- to 3-chlorobiphenyl groups (except when 2',6'-substituted), of 2,4,5- to 2,5-; of 2,3,4- to 2,4-; of 2,3,5- to 2,5- (probably); of 3,4,5- to 3,5-; of 2,3,4,5- to 2,3,5-; of 2,3,4,6- to 2,4,6; and, in trichlorobiphenyls only, of 2,3- to 2-. The relative rates of these conversions were estimated for a number of PCB congeners undergoing dechlorination by processes H or H', giving the results shown in Table 4. This shows that the relative reactivity of a PCB congener to this type of dechlorination is determined not only by the substitution pattern on the phenyl ring undergoing chlorine loss, but also, to a modest extent, by the substitution pattern on the opposite ring. The nature and magnitude of the latter effects are somewhat similar to those previously reported for upper Hudson dechlorination system B [7]. The dependency of reactivity upon substitution pattern on the reacting ring was, however, quite different from that of either the *o,m,p*-selective dechlorination system F [6,7] or the more typical *m,p*-selective dechlorination system B [6,7], as shown in Table 5. Basically, the Acushnet Estuary dechlorination systems H and H' effect a selective attack on the more heavily chlorinated PCB

congeners, and give as terminal dechlorination products mainly the mono-*ortho* trichlorobiphenyls 25-3 and 24-3 CB, the di-*ortho* tetrachlorobiphenyls 25-25, 24-25, and 24-24 CB, and a little 2,3'-dichlorobiphenyl. Gas chromatograms exhibiting Patterns H or H' may be recognized as such by the increased levels of the above congeners, increases also in the levels of the 2,3,4-chlorophenyl group-derived congeners 236-24 CB (Peak 49), 245-24 CB (Peak 54) and 2356-24 CB (Peak 67) and the particularly decreased levels of congeners carrying 3,4-, 2,3,4- or 2,3,4,5-chlorophenyl groups. System F, by contrast, gives about the same terminal dechlorination products but after an almost indiscriminate attack on the higher PCB congeners, while the B-like systems of the upper Hudson River, Waukegan Harbor, and the Sheboygan River (e.g., systems B, B', C, and W) give largely mono- and/or dichlorobiphenyls, along with 26-2 and 26-3 CB.

#### *Geographical range of pattern H/H' dechlorination*

Having delineated the recognition features of Pattern H/H' dechlorination, we undertook a review of available chromatograms from the New Bedford area and elsewhere to determine where it might be occurring.

For the New Bedford area, the most extensive record was presented by the 231 Versar SE-30 packed-column GC tracings [16]. These lacked the resolution to reveal the DB-1 capillary Peak 50, and all contained DDE (added as an internal standard), which obscured Peak 58. However, they were fully adequate for showing the "high-end drop-off" feature of the Pattern H/H' GCs. Accordingly, we scored the entire set for this feature and then obtained the key linking sample numbers to collection sites. This showed the scored feature

to be present in virtually all of the Versar sediment samples that had been collected north of the hurricane barrier (i.e., the upper or middle Estuary, including the inner harbor) but not in the samples from any of the other marine collection sites: e.g., those in the lower Estuary, south of the hurricane barrier, those in Clark's Cove, or in the surrounding areas of Buzzard's Bay. The only other sediment chromatograms exhibiting the "high-end drop-off" feature were those of a small group of otherwise 1254-like specimens that were collected in a short section of the East Rodney French Boulevard (ERFB) sewer line near David Street. The effluent from this line ultimately discharges into the outer harbor.

Brownawell and Farrington [15] have published SE-30 capillary GCs for two sections (3-5 and 35-45 cm) taken from a single outer harbor core collected in September, 1983. Reference to our Figure 2 standards indicated that the first of these resembled a simple mixture of Aroclor 1254 with evaporated 1242, while the second looked like nearly pure Aroclor 1254. The accompanying plots of peak height data for intermediate core sections showed a nearly smooth decline with depth for the Aroclor 1242:1254 ratio [15]. Our measurements on the published chromatograms indicated that for the upper sediment sample the peak corresponding to DB-1 Peak 50 had a height of  $103 \pm 5\%$  of that in the Aroclor 1242 standard, both measured relative to Peak 39, indicating that no detectable Aroclor 1242 dechlorination or admixture with Aroclor 1016 had occurred. However, the Peak 58 heights were depressed 37% and 8% relative to the Aroclor 1254 standard in the upper and lower sediment sections, respectively, indicating some deposition of dechlorinated 1254 (possibly from the ERFB sewer line) in the upper sample. The 3 to 5 cm sediment GC also showed small losses in congeners 105 and 138, corresponding to DB-1 Peaks 74 and 82 (234-34 and 234-245 CB),

and a small gain in Peak 54 (245-24 CB), consistent with, but not unambiguously demonstrative of, Pattern H. None of these small changes would have been large enough to produce an observable "high-end drop-off" in the packed-column GC.

The review of our collection of capillary GCs of samples from other areas turned up chromatograms showing well-developed (1-2 half-losses of P50 and P58) Pattern H or H' alterations in an Escambia Bay sediment sample taken from near the mouth of the Pensacola River (FL), in sediments from the Hudson Estuary taken near Troy, Albany, Kingston, or Poughkeepsie, NY; and among the many specimens of PCB that had been anaerobically dechlorinated in the laboratory following inoculation with sediments containing System B, B', C, E, and H mixed cultures from the upper Hudson River. (Results to be described elsewhere.) Less well-developed, but still unambiguous, Pattern H/H' alterations were seen in sediment specimens from Wood's Pond (near Lenox, MA), the Hudson Estuary near Catskill, NY, and in young striped bass from Newtown Creek (Brooklyn, NY), a tributary to New York Harbor. Alterations quite similar, but not identical, to Pattern H were seen in the sediments of Sheboygan Harbor (WI) and some of those from further upstream in the Sheboygan River.

GC abnormalities in the sediment PCBs taken from Hudson Estuary sites near Albany, Catskill, and Kingston, NY, were previously recognized by Bopp et al. [19,20], who attributed the observed decline in their packed-column Peak 9 (corresponding to our capillary Peaks 46-48) and Peak 10 (corresponding to our capillary Peaks 50-54) to admixture with Aroclor 1016. Review of the original chromatograms [20,19], however, showed that although the declines in their Peaks 9 and 10 could be explained equally well by Aroclor 1016

admixture or Pattern H/H' dechlorination, the remainder of the chromatograms, including the changes exhibited by Peaks 4, 5, 6, and 7, were compatible only with the latter interpretation. It thus appears that dechlorination processes yielding alteration patterns like H or H' have a fairly wide distribution in the environment, and may be reproduced in the laboratory.

#### *Effects of pattern H/H' dechlorination on toxic risk*

Human exposure to Aroclors 1242 and 1254, even at levels permitting uptakes of several grams per year [21] has not resulted in significant health effects [21-24]; however, toxic effects and induction of AHH (cytochrome P-450I) have been observed in more heavily dosed animals. The specific congeners associated with these effects (e.g., hepatomegaly [25], body weight loss [26] and thymic involution [25,26] in rats) have been identified as those carrying chlorine atoms in both of the *para* (4 and 4') positions, and in at least two of the four *meta* (3,3',5,5') positions, and in no more than one *ortho* (2,2',6,6') position, e.g., the congeners 34-34, 245-4, 245-34, 245-345, 2345-4, 234-34, 2345-34, and 234-345 CB [25,26], with 234-34 CB accounting for more than 95% of the toxic risk (i.e., toxicity-concentration product) for the PCB residues found in wildlife tissues [27]. Some of the minor toxic congeners were present in the Acushnet sediments at levels too low to permit direct assessment of their dechlorination status, but all were of the generic types that are highly responsive to System H/H' attack (Table 4). For the more easily detected species 34-34, 234-34, 2345-34, and 234-345 CB, however, the losses (Figure 4) were at least as great as those for the "indicator" congeners, 23-34 CB (Peak 50) and 234-25 CB (Peak 58). Accordingly, it would appear that the extent of dechlorination, as measured by the declines in Peaks 50 or 58, can also be

used as a measure of the detoxication that has occurred.

## DISCUSSION

### *PCB dechlorination/detoxication processes of the Acushnet Estuary*

The results of this investigation showed that a previously unreported type of PCB dechlorination and detoxication process is occurring in the sediments of the upper and middle sections of the Acushnet Estuary. In sediment specimens examined to date, removals of up to 91% (3.5 half-clearances) have been seen for the "indicator" congeners 23-24 CB (Peak 50) and 234-34 CB (Peak 58), and for the main toxic congener, 234-34 CB (Peak 74, PCB No. 105). The dechlorinative congener transformations were found to be occurring in two very similar patterns, designated H and H' (Figure 2). These patterns are clearly different from the previously reported Patterns B, B', C, and E of the upper Hudson River [5-7], the Pattern W of Waukegan Harbor [6,18], or the Patterns F and G of Silver Lake [7]. They were similar, however, to unpublished dechlorination patterns seen at two other marine sites, i.e., Escambia Bay (FL) and New York Harbor (NY) and at several freshwater sites, i.e., Wood's Pond, near Lenox, MA, Sheboygan Harbor (WI), and sections of the Hudson Estuary, near Troy, Albany, Catskill, Kingston, and Poughkeepsie, NY; as well as in laboratory cultures grown up from upper Hudson River inocula. Thus H-like PCB dechlorinations appear to be occurring in a variety of geographical settings. Whether or not they are all mediated by the same type of microbe is still unknown.

The distinction between Patterns H and H' is a subtle one, and may not be significant. Pattern H' appeared at only two (adjacent) sites in the upper Acushnet (Table 1), but was also seen in the Hudson Estuary. In the latter case, it almost certainly arose from the

contribution of a different dechlorination system, M, which could also be cultured from Hudson River sediments in the laboratory. However, it is not known whether the Pattern H' of Acushnet Sites 9 and 12 arose from the incipient appearance of a second, M-like dechlorination system, a mutation of the local System H population, or simply a particular stage in the development of dechlorination Pattern H.

At most PCB spill sites it is easy enough to determine the extent of dechlorination (e.g., number of half-clearances) but difficult to determine the rate of dechlorination (e.g., the mean half-time for clearance) because of uncertainties as to just when the local population of PCB-dechlorinating anaerobes became established. At the Acushnet study site, however, we have data on the differences between the extents of clearance of the largely 1242-derived Peak 50 and the largely 1254-derived Peak 58, as shown by the P58-50 values given in the last column of Table 1. These show more extensive dechlorination of the Aroclor 1254 in the upper half of the study site and the Aroclor 1242 in the lower. A plausible interpretation would be that dechlorination began in the northern end of the upper Estuary in the 1950's, when the release was largely Aroclor 1254, reached the southern part of our sediment study area sometime after the 1960-65 changeover to Aroclor 1242, and the southern part of the inner harbor by the time of the GCA/EPA/Versar sampling [16] in early 1982. Thus in the northern part of the study site, dechlorination of Aroclor 1254 is further advanced because of the longer dechlorination time; in the southern part, the concentrated fresh deposits of Aroclor 1242 responded more rapidly to the arrival of the dechlorination system than did the underlying Aroclor 1254 deposits; and in the outer harbor, dechlorination had still not commenced in 1982. This means that we may estimate the mean dechlorination initiation time

(and also the mean arrival time) of the Aroclor 1242 in the southern half of the study site as about 1966, 20 years before the time of sampling. Since the extent of Peak 50 dechlorination in all but the most lightly contaminated parts of that area was  $2.5 \pm 0.6$  half-losses (Table 1) we may estimate the mean half-time for Peak 50 (23-34 CB) removal as  $8 \pm 2$  years, and the half-clearance times for many other congeners from the relative rate factors listed in Table 4. Taking the clearance rate of the main toxic congener, 234-34 CB, as virtually the same as that for Peak 50 (Figure 4), we may also estimate  $8 \pm 2$  years as the half-time for upper Estuary sediment PCB detoxication.

Quensen's experiments indicate the rates of PCB dechlorination by mixed anaerobic microbial inocula (now known to contain the organisms responsible for dechlorination Patterns B, C, E, and H) to be a very steep function of the PCB dosage [8]. When the Aroclor 1242 level was 700 ppm, dechlorination was extensive; when 140 ppm, much slower; and when 14 ppm, unobservable [8]. An obvious explanation for this phenomenon is that the PCBs are being used by the PCB-dechlorinating anaerobes as terminal electron acceptors, an energetically highly feasible process [7], rather than as carbon sources. This means that the PCB-dechlorinating microbes must compete for metabolizable carbon sources and other nutrients with other anaerobes that use commoner terminal electron acceptors, such as sulfate or  $\text{CO}_2$ . If the PCB level is too low, no significant population of PCB-dechlorinating microbes can develop, and no dechlorination will occur. At least not under closed system conditions, as in a laboratory culture.

A river-bottom or estuarine sediment bank is not a closed microbiological system, however, and the dependency of environmental dechlorination upon the local PCB level is not as sharp as that seen in the laboratory. Field observations to date have indeed failed to turn up examples of PCB dechlorination at isolated low level (1-3 ppm) sites, in accord with the laboratory observations; however, we have often seen appreciable dechlorination in low level samples collected near sites of active dechlorination, as in the samples 14B, 24A, 24B, 26A, and 26B of Table 1 or the Versar samples (many in the 1-10 ppm range) of the middle Acushnet Estuary. Evidently, although the local PCB level in such sites is probably insufficient to allow development of a significant population of PCB-dechlorinating microbes, there can occur sufficient microbial recruitment from other nearby richer sites to permit a modest rate of dechlorination. This suggests that continued microbial seeding from the actively dechlorinating PCB "hot spots" of the upper Estuary may be required for PCB detoxication to progress in the middle Estuary and advance into the outer harbor.

Another intriguing finding emerging from Quensen's and other ongoing laboratory studies is that dechlorination rates may be sharply enhanced by the addition of organic or mineral nutrients to stimulate anaerobic cell growth. It will be important to determine whether such dechlorination rate accelerations can also be accomplished in the field.

#### ACKNOWLEDGMENT

The authors are indebted to Stephen O'Neil of GHR Analytical, Inc., for collecting the Acushnet sediment and water samples; to Dr. J.M. O'Connor of New York University for the Escambia Bay sediment and Brooklyn, NY striped bass samples; to Ms. Dawn Foster of

Blasland and Bouck Engineers and Dr. Tom Dillon of the USA COE Waterways Experiment Station for the Sheboygan Harbor sediments; to Dr. J.C. Carnahan of this laboratory for the Aroclor 1242 evaporation experiment and the Hudson Estuary sediments; to Dr. J.F. Quensen III of Michigan State University and Dr. D.A. Abramowicz and Mr. M.J. Brennan of this laboratory for the chromatograms of Aroclors dechlorinated by laboratory cultures; to Mr. R.J. May of this laboratory for the mass spectral determinations; and to Dr. D.L. Bedard of this laboratory for a Wood's Pond PCB chromatogram and many helpful discussions.

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**Table 1. Results of analyses of upper Acushnet Estuary tideflat sediments collected in June, 1986**

Site No.: depth <sup>a</sup>	Sample texture <sup>b</sup>	Total oils, ppm <sup>c</sup>	Total PCBs, ppm <sup>c</sup>	PCB % Cl <sub>2</sub> CB	Calc. comp. <sup>d</sup>		Dechlorination Indices			
					% sol. loss	1242: 1254	Pat-tern	half-losses <sup>e</sup>		
							P50	P58	58-50	
19A	sft mud	20,000	1,637	6.0	40	68:32	H	2.5	3.1	0.6
19B	sft mud	28,400	1,126	4.0	40 <sup>f</sup>	57:43	H	3.2	3.5	0.3
18A	snd	20,700	3,285	1.0	5	05:95	H?	-0.0	0.6	0.6
18B	snd	7,040	739	0.9	6	06:94	H?	-0.1	0.8	0.7
21A	gr, snd	11,100	3,775	6.9	4	47:53	H	1.9	2.2	0.3
21B	gr, snd	1,400	417	4.9	5	40:60	H	2.0	2.2	0.2
17A	sft mud	46,300	3,292	10.3	9	80:20	H	0.8	2.3	1.5
17B	sft mud	40,300	3,724	10.3	12	70:30	H	1.9	3.2	1.3
22A	snd	5,390	765	13.4	33 <sup>g</sup>	81:19	H	2.3	3.1	0.8
22B	snd	8,110	1,444	8.7	14	64:32	H	1.9	3.5	1.6
14A	snd, mud	3,840	40.4	5.7	34	74:26	H	0.9	1.6	0.7
14B	snd, mud	3,390	0.9	--	--	-76:24	H?	-0.7	-0.8	--
12A	gr, snd	8,730	505	15.2	11	84:16	H'	2.1	1.6	-0.5
12B	gr, snd	6,070	526	9.0	51 <sup>g</sup>	82:18	H'	3.1	2.3	-0.8
24A	gr, snd	<150	0.7	--	--	-70:30	H?	-0.6	-1.6	--
24B	gr, snd	<150	0.3	--	--	-65:35	H?	-0.9	-1.6	--
9A	gr, mud	26,700	490	17.7	8	94:06	H'	1.9	1.0	-0.9
9B	gr, mud	22,900	1,135	15.9	30	91:09	H'	2.7	1.8	-0.9
5A	gr, snd	12,800	304	8.5	44 <sup>g</sup>	82:18	H	1.2	1.1	-0.1
5B	gr, snd	34,500	785	13.9	22	86:14	H	2.3	1.4	-0.9
2A	gr, snd	1,570	150	7.1	29	71:29	H	0.9	0.7	-0.2
2B	gr, snd	2,050	171	10.2	22	67:33	H	2.3	1.6	-0.7
26A	fiber	<440	3.2	--	--	-54:46	H	-1.3	-1.9	--
26B	fiber	<370	0.6	--	--	-64:36	H?	-0.5	-1.3	--
Avg for all sites:		13,000	1,013	8.1	18	61:39	--	1.6	1.6	0.0

a. Locations of collection sites shown on Figure 1; listed here in order from north to south. Depth of "A" samples, 5-7.5 cm; of "B" samples, 15-17.5 cm.

b. Key: sft = soft biogenic black mud, H<sub>2</sub>S odor; snd = sand; gr = gravel; fiber = apparently spartina root mass (marshbed).

c. Parts per million of air-dried sediment weight.

d. For calculation procedure, see METHODS section of text.

e. -Log<sub>2</sub> fractional retention of Peak 50 (mainly 23-34 CB from Aroclor 1242) or of Peak 58 (mainly 234-25 CB from Aroclor 1254), or differences between these numbers of half-losses.

f. Judging from Peak 24, this calculated value probably an underestimate.

g. Judging from Peak 24, this calculated value probably an overestimate.

**Table 2. Results of analyses of Acushnet Estuary water samples collected in December, 1986**

Estuary Section <sup>a</sup>	Site No. <sup>a</sup>	PCB/Water ( $\mu\text{g/L}$ )		Half-losses <sup>b</sup> P50, P58
		Total	On Filter	
Sediment study area:	1A	0.5	0.18	1.0
	1	1.7	0.16	2.0
	1 (rep)	1.5	0.15	2.0
	1B	1.1	0.10	2.0
	1C	0.7	0.8	1.5
	2	0.4	0.23	1.0
	Between the bridges:	4	0.27	0.10
	4 (rep)	1.0	0.07	2.0
	5	0.36	0.07	0.5
	6	1.5	0.21	2.0
Inner harbor:	9	0.4	0.07	1.0
Outer harbor:	11	0.27	0.05	0.0
	12	0.4	0.06	2.0
	15	0.12	0.03	0.0

- a. Estuary sections and water-sampling sites as shown on Figure 1.
- b. Mean of  $-\text{Log}_2$  fractional retention of Peak 50 (23-34 CB), as referenced to Peak 39 (26-34 CB), and of Peak 58 (234-25 CB) referenced to Peak 61 (236-34 CB), rounded to nearest half-log unit.

**Table 3. Determination of selection pattern for PCB congener dechlorination by Acushnet Estuary sediment system H<sup>a</sup>**

1. No dechlorination of 2-, 3-, or 4-monochlorophenyl groups

No decr:	2-2	2-3	2-4	2-3	2-4
No incr:	2-	2-	2-	3-	4-

2. No dechlorination of 24-, 25-, 26-, or 35-dichlorophenyls

No decr:	24-2	24-3	24-4	24-25	24-24	24-26	
No decr:	25-2	25-3	25-4	25-25	25-24	25-26	
No decr:	26-2	26-3	26-4	26-25	26-24		26-23
No decr:		35-2					
No incr:	2-2	(2-3) <sup>c</sup>	(2-4) <sup>c</sup>	(25-2) <sup>c</sup>	(24-2) <sup>c</sup>	26-2	(24-2) <sup>c</sup>

3. No dechlorination of 236- or 246-trichlorophenyl groups

No decr:	236-2	(236-4) <sup>b</sup>	(236-23) <sup>b</sup>	236-24	236-25	(236-26) <sup>b</sup>
No decr:				246-24	246-25	
No incr:	26-2	26-4	26-23	26-24	26-25	26-26

4. No dechlorination of 2356-tetrachlorophenyl groups

No decr:	2356-25	(2356-34) <sup>b</sup>	2356-236
No incr:	(236-25) <sup>c</sup>	236-34	236-236

5. Extensive dechlorination of 34- to 3-chlorophenyl groups<sup>a</sup>

Decr:	2-34	(3-34) <sup>b</sup>	4-34	23-34	24-34	34-34
Incr:	2-3	3-3	4-3	(23-3) <sup>b</sup>	24-3	34-3
Decr:	235-34	245-34				
Incr:	235-3	245-3				

<sup>a</sup> Minor conversion of 34- to 4-CP may also occur, but cannot be proven because of high background level of 4-CP groups.

6. But 34-CP dechlorination blocked by 2',6'-di-substitution

No decr:	26-34	236-34	246-34	(2356-34) <sup>b</sup>
No incr:	26-3	(236-3) <sup>b</sup>	(246-3) <sup>b</sup>	(2356-3) <sup>b</sup>

7. Some dechlorination of 23- to 2-chlorophenyl groups

Decr:	23-2	(23-3) <sup>b</sup>	23-4	23-23	23-24	23-25
Incr:	2-2	(2-3) <sup>c</sup>	2-4	(23-2) <sup>e</sup>	24-2	25-2

8. But 23-CP dechlorination blocked by 2',6'-di-substitution

No decr:	23-26	(236-23) <sup>b</sup>	2356-23
No incr:	26-2	236-2	(2356-2) <sup>b</sup>

9. Extensive dechlorination of 234- to 24- and probably also 23-chlorophenyl groups

Decr:	234-23	234-24	234-25	234-245	234-234
Incr:	(24-23) <sup>e</sup>	24-24	24-25	24-245	(24-234) <sup>e</sup>
Incr:	(23-23) <sup>e</sup>	23-24 <sup>f</sup>	23-25 <sup>f</sup>	(23-245) <sup>e</sup>	(23-234) <sup>e</sup>

Note: 234-CP conversion occurs even with 2',6'-di-substitution.

Decr:	236-234	2356-234
Incr:	236-24	2356-24

10. Dechlorination of 245- to 25- and possibly also 24-chlorophenyl groups\*

Decr:	245-2	245-4	245-25	(245-24) <sup>d</sup>	245-245
Incr:	(25-2) <sup>c</sup>	(25-4) <sup>c</sup>	25-25	25-24	(245-25) <sup>e</sup>
?? Incr:	(24-2) <sup>c</sup>	(24-4) <sup>c</sup>	(24-25) <sup>c</sup>	(24-24) <sup>c</sup>	(245-24) <sup>c</sup>

\* 245-CP conversion possibly occurs even with 2',6'-di-substitution.

Probable decrease:	236-245
Probable increase:	236-25

11. Dechlorination of 235- to 25- and/or 23-chlorophenyls

Clear decrease: 235-4; probable decrease: 235-25

12. Dechlorination of 345- to 35- and possibly also 34-chlorophenyl groups

Decr:	(345-2) <sup>b</sup>	345-23	(345-24) <sup>b</sup>	345-25
Incr:	35-2	(35-23) <sup>b</sup>	35-24	(35-25) <sup>b</sup>
?? Incr:	(34-2) <sup>c</sup>	(34-23) <sup>c</sup>	(34-24) <sup>c</sup>	(34-25) <sup>c</sup>

13. Dechlorination of 2345- to 235- (and/or 245- and 234) CP

Decreased: 2345-4, 2345-23, 2345-24, 2345-25, 2345-34, 2345-236, 2345-245,  
2345-234

Possible increases, evidenced by retarded clearance: 235-23, 235-24, 235-235, 235-245

14. Dechlorination of 2346- to 246- and possibly 236-CP

Decr:	2346-25	(2346-24) <sup>b</sup>	2346-34	2346-236	2346-245
Incr:	246-35	246-24	246-34	(246-236) <sup>b</sup>	246-245
?? Incr:	(236-25) <sup>c</sup>	(236-24) <sup>c</sup>	(236-34) <sup>c</sup>	(236-236) <sup>c</sup>	(236-245) <sup>c</sup>

15. Dechlorination of 23456 to tetrachlorophenyl groups

Decreases seen in 23456-4, 23456-25 and 23456-34

- a. Key: decr = decrease; incr = increase in level of indicated PCB congener. Parentheses indicate observed change in peak containing indicated congener equivocal or contradictory for reason indicated by footnote.
- b. Indicated congener too small a component of observed peak to be certain of its level of change; or, observed peak itself too small for reliable measurement of change.
- c. Change or non-change due to conversion of indicated congener too small a part of total peak change to be certain of its contribution.
- d. Congener believed to be undergoing formation from other congeners faster than being consumed by the indicated process.
- e. Congener believed to be undergoing further dechlorination to other congeners faster than being produced by the indicated process.
- f. Actual increase seen at one site (21A, 21B); little or no net clearance at several others where 1254 levels high.

**Table 4. Approximate numbers of half-losses<sup>2</sup> shown by various PCB Congeners in sediments<sup>b</sup> showing well-developed dechlorination pattern H (or H')**

Subst. on presumably less active ring	Substitution pattern on presumably more active ring and observed dechlorination pattern												
	234 H	2345 H	34 H	345 H	2346 H	245 H	23456 H	23 H	23 (H')	235 H	235 (H')	236 H	236 (H')
3 or 4			>4			3	~1	2.5	(3)	1.5	(2.7)		
2			4			~2		>1	>1			0	(1)
24 or 25	3.5	3	3	2	2	1	~1	0.5	(2)			0	(0)
235 or 245	2	1	1	0.5	1	~0.7 <sup>c</sup>	~1					0	(0)
2345	1												
26	2		0					0	(0)			0	(0)
236	2	1.5	0			0?		0	(0)			0	(0)
2356	1		0	0				0	(0)				

- Log<sub>2</sub> fractional retention of indicated peak, measured relative to Peak 39 or 61.
- As represented by Acushnet Estuary sediment 19B for Pattern H, or 12B for Pattern H'. Values for "indicator peak" congeners, 23-34 and 234-34 CB, given in Table 1.
- Clearance of <0.5 half-loss for 245-245 suggested by the difficultly measured change in Peak 75; of >1 half-losses suggested by net gain in Peaks 31 plus 53 (25-25 plus 245-25).

**Table 5. Comparison of PCB dechlorination systems F, H, and B in terms of apparent relative reactivities to dechlorinating agent (R) and relative tendencies to appear in final dechlorination product (p) for the individual chlorophenyl groupings<sup>a</sup>**

Chlorination pattern	Response to dechlorination system:					
	F		H		B	
	React.	prod.	React.	prod.	React.	prod.
23456	RRR	-	R	-	?	-
2345	RRR	-	RRR	-	RR	-
345	RRR	-	RR	-	RR	-
235	RR	-	R	-	-	p
2346	RRR	-	RR	-	RR	-
2356	RRR	-	-	-	-	?
245	RR	-	R	-	RR	-
234	RR	-	RRR	-	RR	-
34	RR	-	RRR <sup>b</sup>	-	RRR	-
35	?	p	-	p	-	p
236	R?	p?	- <sup>c</sup>	-	R	?
25	-	ppp	-	ppp	RR	?
23	?	pp	R <sup>b</sup>	p	RRR	-
246	-	p	-	p	?	-
24	-	ppp	-	ppp	R <sup>c</sup>	-
4	-	p	-	?	- <sup>d</sup>	pp
2	-	?	-	p	-	ppp
26	-	p	-	-	-	pp
3	-	ppp	-	ppp	- <sup>d</sup>	pp

- For Systems H (Acushnet River) and B (upper Hudson River) relative reactivities based on disappearance rates of congeners having indicated substitution pattern on one ring and 24- and 25-distribution on the other. For both, reactivity is greater if opposite ring only mono-substituted, and lower if tri-substituted. Chlorophenyl groups are listed in order of increasing electrochemical reduction potential.
- Group apparently not dechlorinated when opposite ring carries chlorines in both 2 and 6 positions.
- Reactivity seen in the closely related System H', but not in H.
- Reactivity seen in the closely related System C, but questionable or negative in System B.
- Group probably not dechlorinated when opposite ring carries a chlorine atom in a 2 position.

**FIGURE CAPTIONS**

- Figure 1. Map of the greater New Bedford (MA) area, showing locations of collection sites for sediments (solid circles) and water samples (open circles).
- Figure 2. DB-1 capillary gas chromatograms of Aroclor reference standards and Acushnet sediment samples exhibiting alteration Patterns H and H'.
- Figure 3. Effect of evaporative weight loss on relative proportions of representative Aroclor 1242 peaks in residue.
- Figure 4. Gas chromatographic-mass spectrometric ion chromatograms, showing summed parent ion isotope peaks for di- through heptachlorobiphenyls in Aroclor standards and Acushnet sediment sample 19B. Peak numbering along horizontal axis corresponds to that of Figure 2. Vertical scale on each chromatogram adjusted to give full-scale response for highest peak present.
- Figure 5. Relationship between numbers of *ortho* and non-*ortho* chlorine atoms per biphenyl residue in upper Acushnet Estuary sediment PCB samples and Aroclor standards.

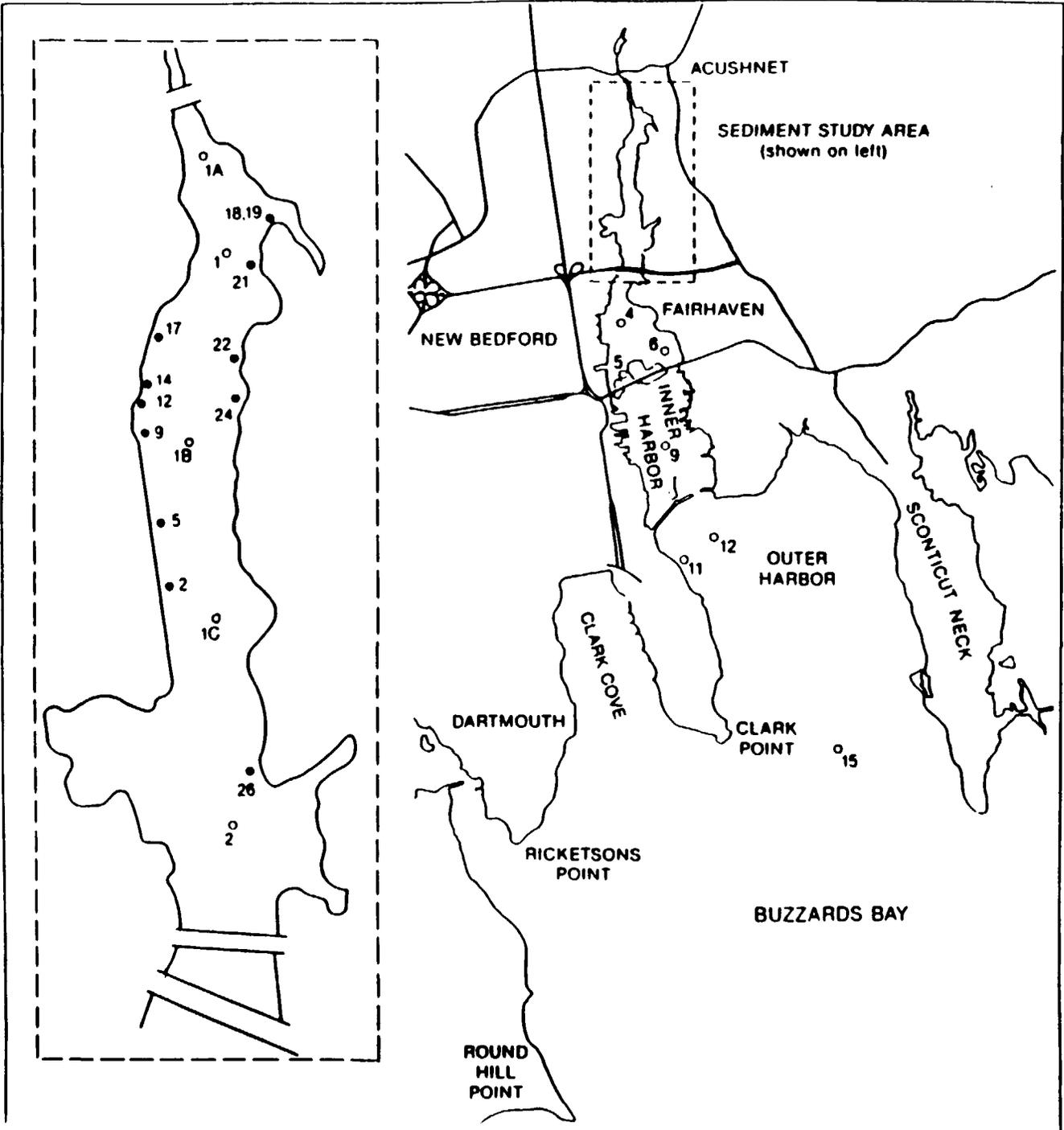


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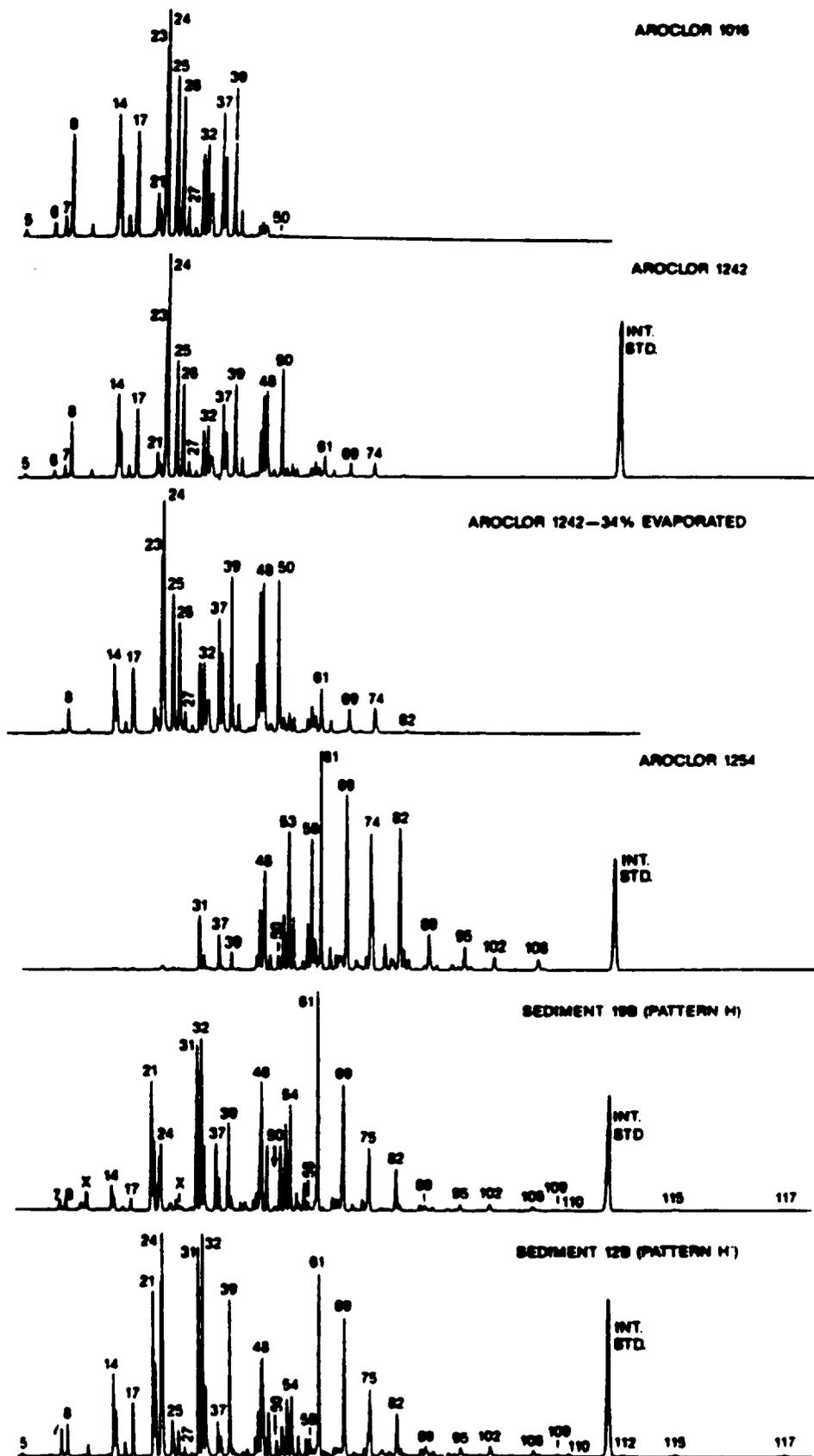


Figure 2. DB-1 capillary gas chromatograms of Aroclor reference standards and Acushnet sediment samples exhibiting alteration Patterns H and H'.

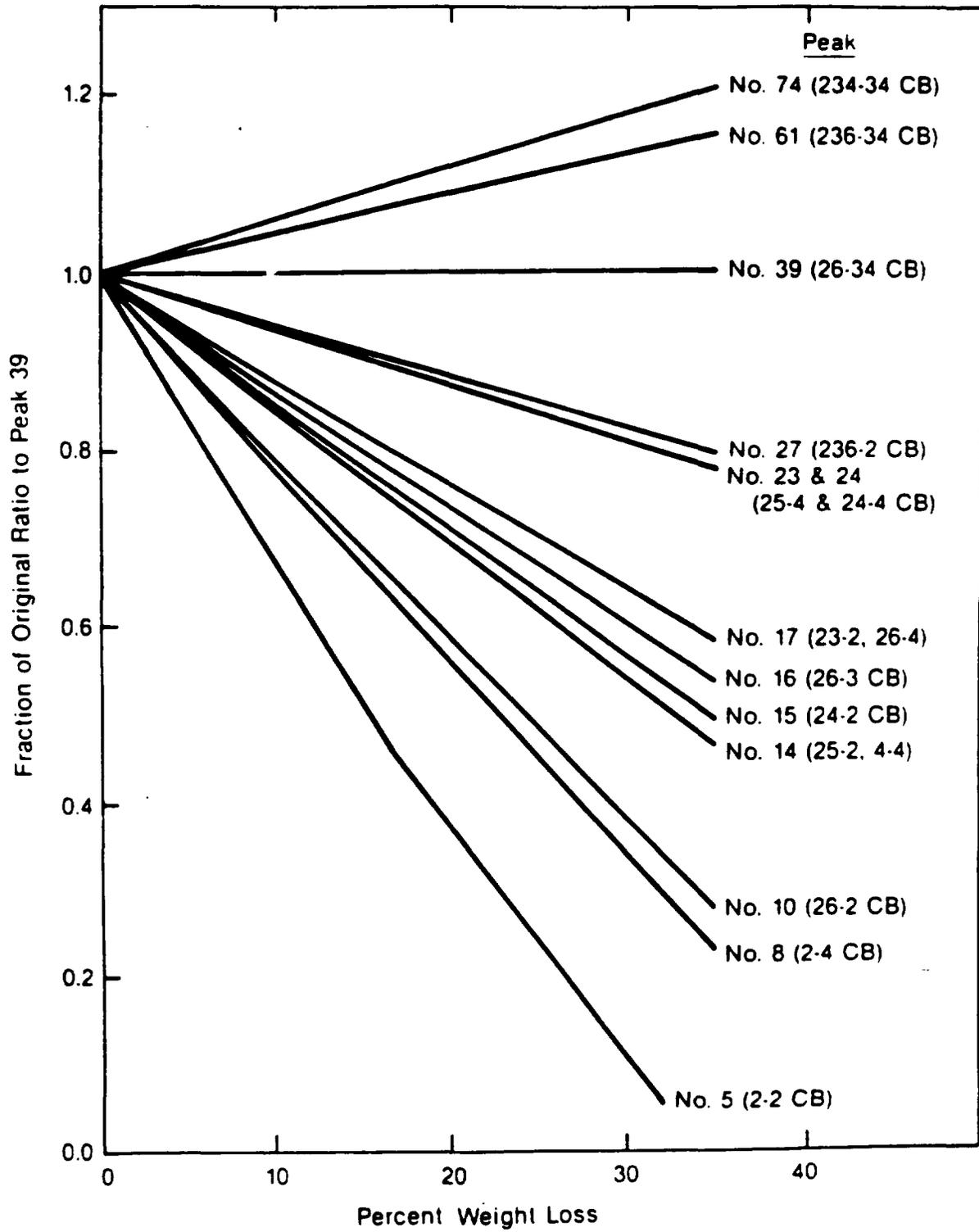


Figure 3. Effect of evaporative weight loss on relative proportions of representative Aroclor 1242 peaks in residue.

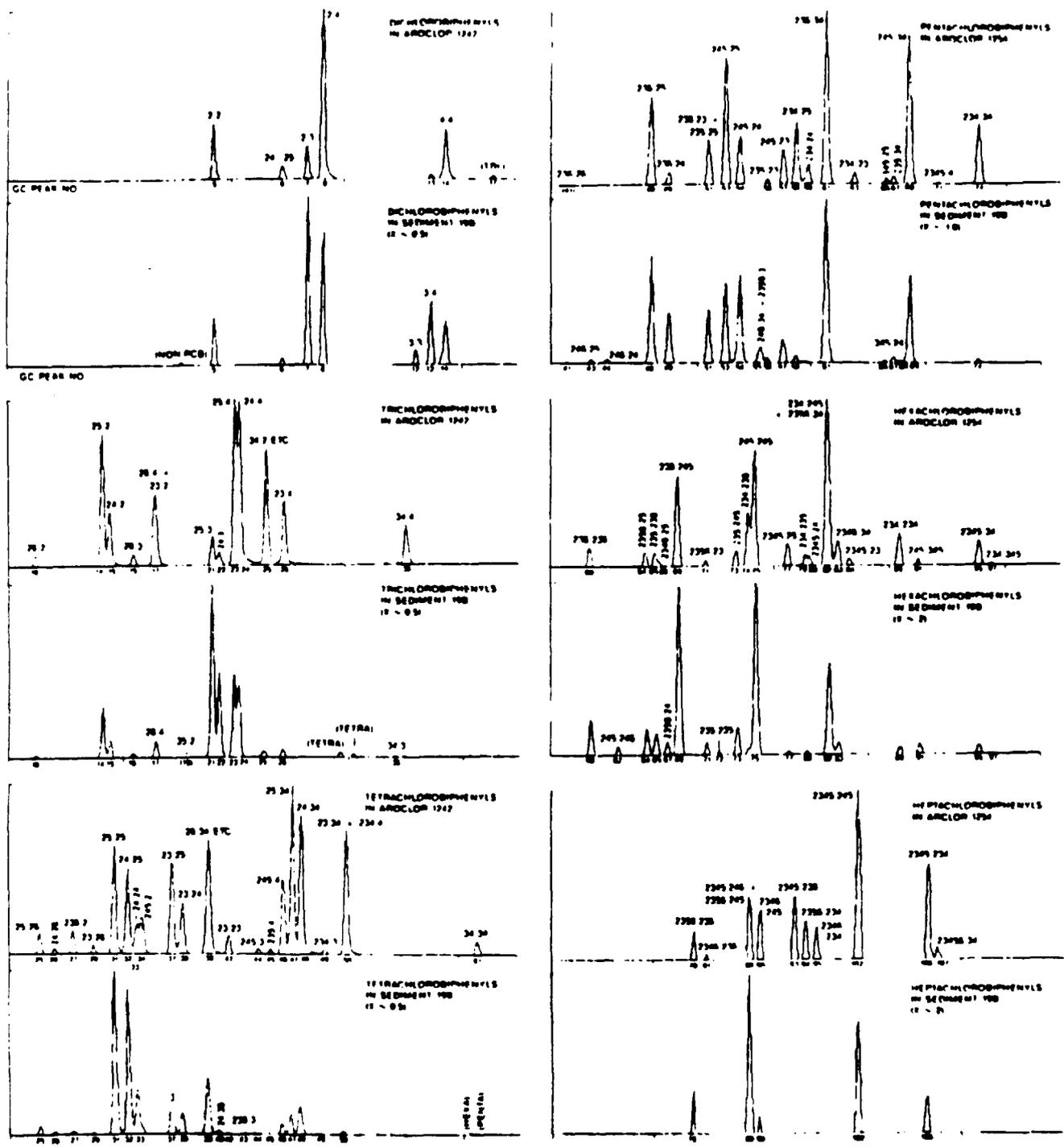


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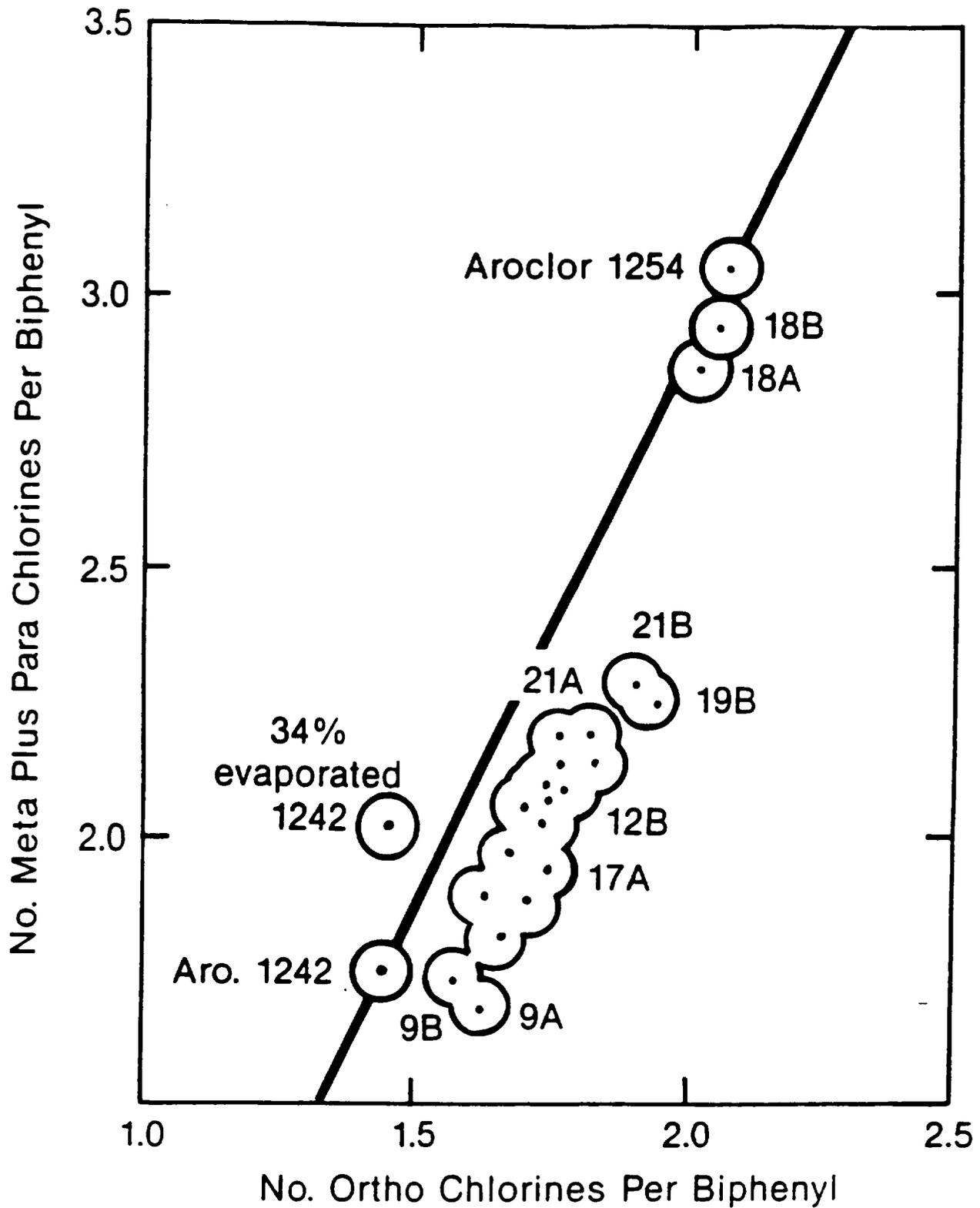


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