SATURATED HYDROCARBON MATERIAL IN SEDIMENTS

OF THE DELAWARE ESTUARY

AS DETERMINED BY GAS CHROMATOGRAPHIC ANALYSES


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Final Report

CMS-RANN-3-75




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This research project was part of a program designed
to delineate the effects on Delaware Bay of crude oil
transfer and upstream refineries.  Managed by the University
of Delaware's College of Marine Studies, the 15-month pro-
gram (1 March '74 - 31 May '75) was conducted under a $300,800
grant from the National Science Foundation's Research Applied
to National Needs (RANN) Program, incorporating socio-economic
assessments, engineering and oceanographic studies, as well as
biological/ecological research.  The research was conducted
by the College of Marine Studies, the Department of Civil
Engineering, Biology and Geology, and the College of Business
and Economics.  Further information is available from the
Program Manager, Dr. Robert Biggs, Assistant Dean, College
of Marine Studies, University of Delaware, Newark, Delaware,
19711, (302) 738-2842.

Already published under this program to date are:
CMS-RANN-1-75:  Sea Surface Drift Currents, by Jin Wu,
and CMS-RANN-2-75:  Sport Fishing in Western Delaware Bay:
Assessment of Critical Areas, by Ronal Smith.  Additional
reports are in press, including baseline biological data
on Delaware Bay.

ABSTRACT

This report presents a preliminary interpretation of the analyses of hydrocarbon material in sediments of the Delaware Estuary as determined by solvent extraction, column chromatography, and gas-liquid chromatography. The specific focus has been on the saturated group of compounds isolated by silica gel chromatography. Approximately 35 stations (out of a total of 100 sampled localities) from Philadelphia to the bay mouth have been analyzed, and several stations have been reoccupied and reanalyzed following the oil spill associated with the Corinthos tanker explosion on January 31, 1975. Many of these "post-Corinthos" samples are discussed in the appendix to this report.

Roughly three geochemical "provinces" are recognized in the estuary as delineated by the properties of the sedimentary hydrocarbons. Specific characteristics that have proven useful in outlining these provinces have been the amount of sedimentary saturated hydrocarbon material in relation to grain size and total organic carbon in the sediment, the odd carbon preference of the alkane mixture present, and the presence and abundance of unresolved complex mixtures of saturated hydrocarbons. The latter two properties are common parameters of measurement by other investigators but some specific aspects of their use are discussed in this report: the problem of reproducible quantification; the problem of measurement of alkane abundances in the presence of large unresolved mixtures; and the role and importance of adduction techniques in the clarification of the chromatographic mixture. These adduction techniques have been reported infrequently in the current literature of hydrocarbon mixtures in recent sediments.

Upstream of the Delaware Memorial Bridge, sedimentary hydrocarbons are characterized by large abundances, low (C.P.I. = 1.0) odd carbon preferences, and extremely large complex mixtures relative to the biological alkanes. Similar chromatographic patterns are observed in many of the sediments of the lower estuary, though the total amount of material found in lower bay sediments is two to three orders of magnitude less than in the upstream region. Between the Delaware Memorial

Bridge and Bombay Hook, Delaware, is perhaps the most interesting region, for here the sedimentary hydrocarbon mixtures are characterized by moderate to low total amounts (5-50 μg/gm), little or no complex unresolved material, and an alkane mixture with strong odd-carbon preference (C.P.I. = 4.0). To a large degree, these sediments appear much like unaltered marsh plant detritus and clearly reflect some physical/chemical process that preferentially deposits and preserves these mixtures in this region of the estuary. It is this region that is chromatographically most "sensitive" and that is why samples from this area have proven useful in documenting the probable influx of spilled oil from the Corinthos.

## INTRODUCTION

Since a large fraction (approximately 10%) of the United States petroleum refining capacity is located in the northern, urbanized segment of the Delaware Estuary, and since the lower estuary could become the locus of a large crude oil transport facility, the definition of "baseline" conditions in the estuary must include information on the abundance of selected organic compounds that may or may not be related to these particular industrial activities. This report will describe a preliminary investigation of hydrocarbon material in sediments and suspended particulate material from the Delaware River and Bay. The sediments of these areas provide some measure of the "impact" that a particular region might be recording, and by studying sediments from various environments within the estuary, some perspective on the relation between natural and "un-natural" processes can be gained.

The work has initially focused on the development of an analytical facility and the perfection of techniques. During the course of this phase of the program, a few sediment samples have been repeatedly analyzed, one as many as twelve times. Subsequent work has produced duplicate analyses on approximately thirty samples from a wide geographic range of the estuary, and approximately 25 more samples are awaiting analysis at the time of this report. These samples represent only a fraction of a large collection (approximately 150 samples) that has been obtained during the past year. They have been stored in a careful manner so as to be available for future studies by this investigator and others. Much of the sampling and analytical data described herein has focused on the region of southwestern Delaware Bay, where tanker-lightering operations are conducted on a routine basis (see Figure 1 and 1a). There is an obvious need to establish the magnitude of any "impact" that may exist in this area at present. The area has been used as a test of variability for closely-spaced samples and of variability of results for replicate analyses of single large samples. Such information is especially useful when placed in the context of a broad regional pattern of hydrocarbon abundances in sediments.

This report is preliminary in nature; it will describe the development of the analytical technique and discuss some of the pitfalls that have been encountered. A "library" of chromatograms of sample extracts will be presented and general features of each sample cited. It is important that these chromatograms be available for comparison with other work in related areas. General trends of chromatographic features will be summarized, and conclusions regarding the possible geochemical, biological, and "un-natural" processes involved in the generation of these chromatographic features will be suggested.

## PROCEDURES: SAMPLING AND ANALYTICAL

Figure 1, 1a, and Table I summarize information on the location of all samples discussed in this report. Samples have been spaced over almost the entire estuary from the bay mouth to just upstream of the Philadelphia International Airport. The samples have been taken at various times during the period from December, 1972 to April, 1975. The largest collection of samples (approximately 100 surface sediment grabs and seven cores) was taken during January, 1975 on a ten-day cruise on board the RV Ridgely Warfield. Several stations initially occupied during January, 1975 have been re-occupied for repetitive sampling and monitoring in early February, 1975 and again in early April, 1975 following the explosion and sinking of the tanker Corinthos at a dock in Marcus Hook, Pennsylvania, in late January, 1975. Existing data on a few of these "post-Corinthos" samples are included in Table II adjacent to results for "pre-Corinthos" samples. Many more "post-Corinthos" samples have been taken that are awaiting analysis, so this phase of the program has just begun. Such a study has obvious implications for the evaluation of the fate of spilled oil in the estuary, and the few results available at this time will be discussed in this light. These results also have implications for the analytical techniques involved, as will be discussed.

Prior to January, 1975, sampling had been concentrated in the
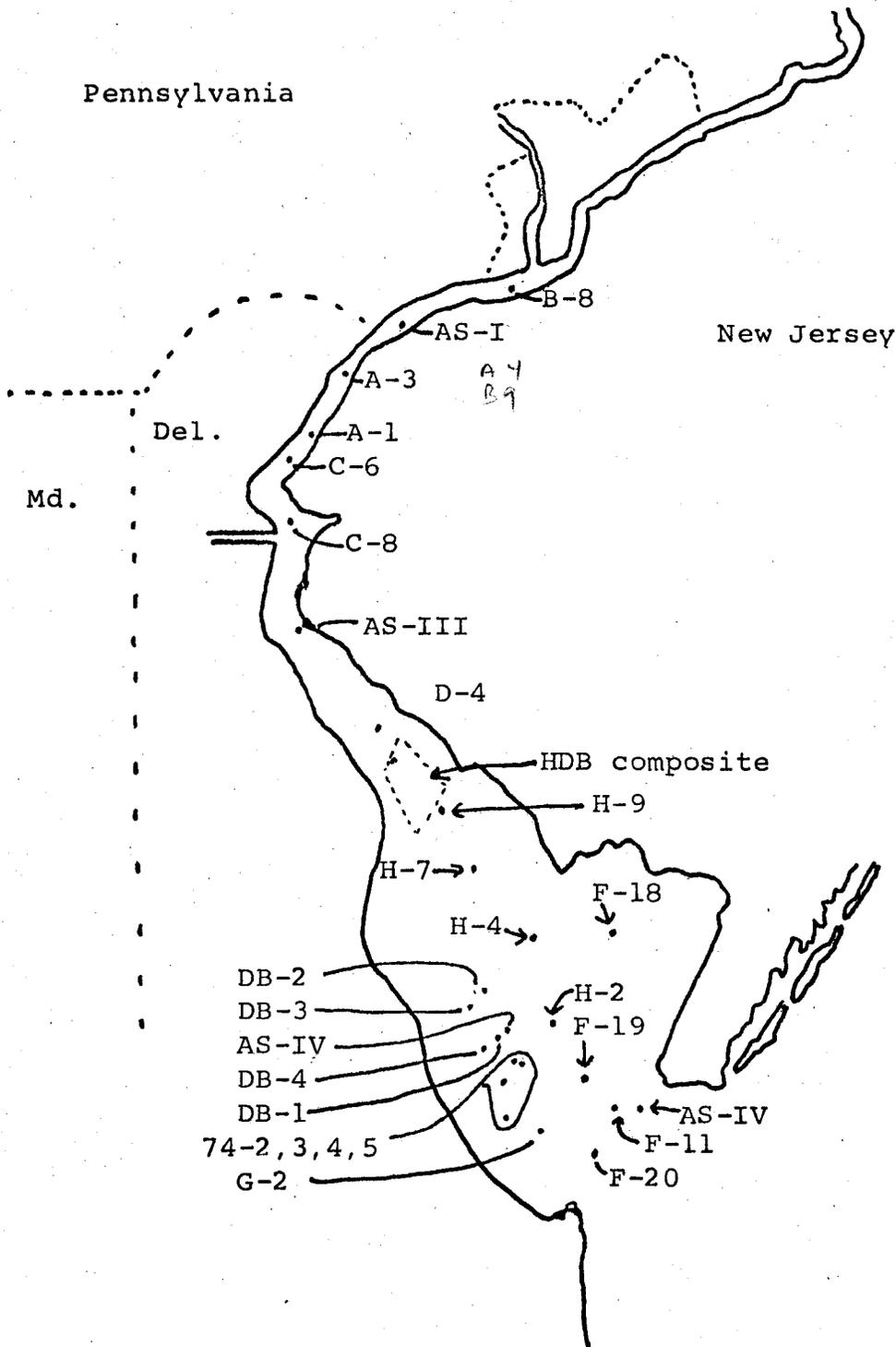
Figure 1:  Sample Locations

lightering area: four large samples (approximately 2 kg each) were taken in October, 1973 and have been used as reference samples in many phases of this work (these are samples DB-1, DB-2, DB-3, and DB-4). Four additional samples were taken in or near the lightering area in November, 1974 and these too have been extremely valuable in the development of the sampling and analytical program as it presently exists. One additional sample (HDB) represents a composite of eight small (100 gms each) samples taken in the upper bay area (see Figure 1) in December, 1972. Samples from the Great Marsh near Lewes, Delaware have provided a comparison standard for relating the samples from the bay and river. A four-meter core from the marsh is representative of the results obtained (Swetland, 1975) and selected analyses from this core will be included in this report.

All surface sediment grab samples were taken with a Shippeck grab sampler and immediately transferred to sample containers for storage in dry-ice chests on shipboard. In no case did more than ten minutes elapse between sample recovery and cold storage. Storage on shore has been at -40°C. All samples taken from November, 1974 to the present have been stored in pre-cleaned (10% $HNO_3$, hexane, methanol) aluminum sample cans with press-fit aluminum lids. These cans hold approximately 250 gms of wet sediment and have proven to be ideal containers for handling optimum-sized samples. Each Shippeck grab usually provides enough sediment to fill three of these sample cans, and wherever enough material was available, multiple sampling of each grab was performed. (Care was always taken to avoid sediment that was in actual contact with any of the metal surfaces of the grab sampler.) In this manner, sub-samples can be stored or analyzed independently; all samples discussed here have counterparts that are available for further work. Samples taken prior to November, 1974 have been stored in plastic containers of various types but otherwise have been handled as described above.

Each sediment sample has been freeze-dried prior to extraction. Frozen samples (still in their original container) have been placed in a Virtis chamber-type freeze-drying apparatus. Thus, no excessive handling (thawing, re-freezing, etc.) has been necessary in order to
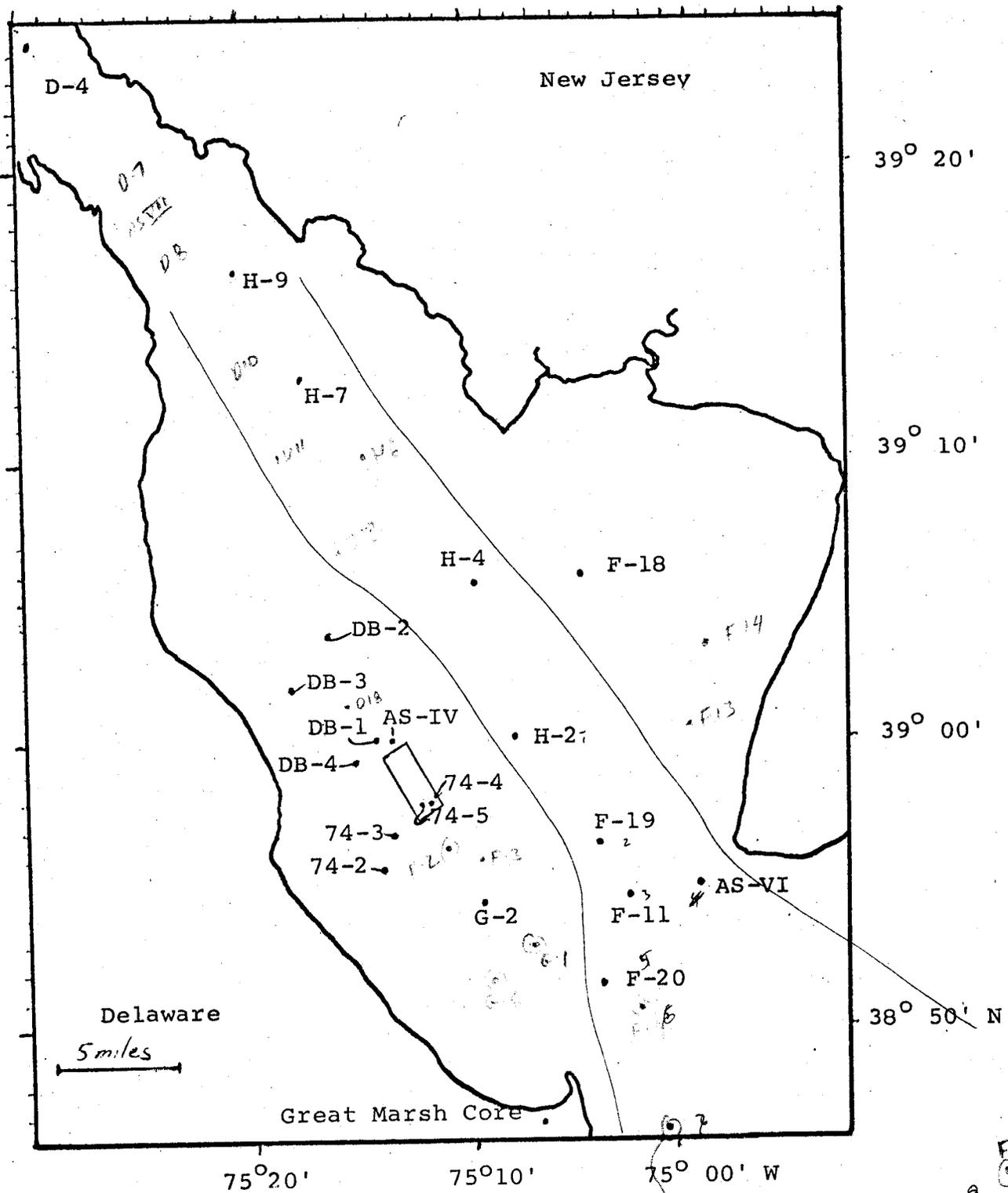
Figure 1a: Expanded Map of Delaware Bay Sample Locations

Table I

Delaware River and Bay Sample Locations

| Station | Latitude | Longitude | Water Depth (feet) | Naut. Miles from Del. Mem. Bridge |
|---------|----------|-----------|--------------------|-----------------------------------|
| B-8 | 39°51'18" | 75°14' 7" | 38 | - 17.9 |
| AS-I | 39°48'22" | 75°24'41" | 45 | - 8.9 |
| A-3 | 39°44'21" | 75°29'29" | 34 | - 3.6 |
| A-1 | 39°41'15" | 75°31'17" | 40 | + 0.1 |
| C-6 | 39°39'32" | 75°32'53" | 20 | + 2.2 |
| C-8 | 39°34'43" | 75°33'05" | 29 | + 7.8 |
| AS-III | 39°27'31" | 75°32'16" | 27 | + 15.2 |
| D-4 | 39°24'10" | 75°29'24" | 21 | + 19.4 |
| H-9 | 39°16.26' | 75°20.2' | 28 | + 30.0 |
| H-7 | 39°12.7' | 75°17.1' | 42 | + 34.3 |
| DB-2 | 39°3.50' | 75°16.20' | 39 | + 42.5 |
| H-4 | 39°5.36' | 75°10.0' | 19 | + 43.4 |
| F-18 | 39°5.72' | 75°5.21' | 20 | + 45.5 |
| DB-3 | 39°1.95' | 75°17.98' | 31 | + 43.4 |
| DB-4 | 39°51.18' | 75°15.1' | 25 | +47.2 |
| 74-5 | 38°57.72' | 75°12.15' | 65 | + 47.0 |
| 74-4 | 38°57.72' | 75°11.50 | 60 | + 47.0 |
| DB-1 | 38°59.85' | 75°11.20' | 38 | + 47.0 |
| AS-IV | 38°59.80' | 75°13.45' | 64 | + 47.1 |
| 74-3 | 38°56.83' | 75°13.20' | 16 | + 50.0 |
| 74-2 | 38°55.42' | 75°13.70' | 26 | + 51.3 |
| G-2 | 38°54.05' | 75°9.65' | 48 | + 54.3 |
| H-2 | 39°0.15' | 75°8.30' | 40 | + 48.1 |
| F-19 | 38°56.40' | 75°4.60' | 49 | + 54.1 |
| F-20 | 38°51.32' | 75°4.70' | 151 | + 58.5 |
| AS-VI | 38°54.48' | 75°0.75' | 34 | + 57.0 |
| F-11 | 38°54.40' | 75°3.30' | 45 | + 56.8 |

get an optimum amount of dried sediment material for extraction. All
samples have been carried through the procedure in duplicate: each
sample can normally contain enough dried material for two 100-gm
separates for analysis. Each of these separates is placed in a pre-
extracted (benzene:methanol soxhlet, 48 hours) paper thimble for
soxhlet extraction with a benzene:methanol azeotrope for forty-eight
hours. Preparative steps have generally followed the pattern of
Zafiriou et al. (1972) with modifications as described by Swetland
(1975). The total benzene:methanol extract is reduced to dryness by
rotary evaporation at room temperature and then is separated into two
fractions by hexane and then benzene elution (2 column volumes each)
from a column (1.8 x 30 cm) prepared with pre-extracted, activated
(120°C) silica gel (Davidson Grade 923) overlain by a 5-cm bed of
pre-extracted, activated (250°C) alumina (Alcoa F-20). Recovery of
fuel-oil hydrocarbons from such a column in the hexane eluate is com-
plete to within 1% (Zafiriou et al., 1972; Wehmiller, unpublished).
The hexane eluate will be the subject of this report, since it is in
this fraction that non-polar (saturated) hydrocarbons from natural and
both crude and refined petroleum products are found.

The hexane eluate is reduced to a small volume by rotary evapora-
tion and freed of sulfur by the activated copper column technique
described by Zafiriou et al. (1972). The hexane eluate from the
copper column is reduced to dryness by rotary evaporation in a tared
screw-cap (teflon-lined) test tube that serves as an extract storage
container (at -40°C). Weights of these residues from hexane elution
are converted to μg/gm of total dried sediment and are reported in
Table II. These weights usually are reproducible to within 25%, but
in several cases show discrepancies that should probably be inter-
preted as a consequence of incomplete drying. Quantitative inter-
pretation of the gas chromatograms (see below) generally confirms this
conclusion. Exhaustive evaporation of extracts is generally not
recommended since loss of lower boiling material might occur. An
additional cause of the variability in extract weights is the fact
that reagent blanks carried through the entire procedure do give finite

TABLE II

ANALYTICAL RESULTS

| Sample | Location | Sampling Date | %C[1] | Sat. HC, μg/gm VW | GC | CPI | Grain Size (%) ≥250 | ≤63 | Sat. HC Org. C[2] |
|---|---|---|---|---|---|---|---|---|---|
| 75-16AI AII | B-8 | 1/7/75 | 0.21 (0.14) | 64 67 | 53 62 | 1.06 | 88 | 0.7 | 0.0290 (0.0448) |
| 75-5AI AII | AS-I | 1/6/75 | (0.55) | 97 321 | 131 199 | 1.55 | 8.6 | 7.9 | (0.0300) |
| 75-110BI BII | AS-I | 2/6/75 | (3.55) | 965 904 | 468 492 | 1.40 | | | (0.0135) |
| 75-106BI BII | A-3 | 2/6/75 | 0.38 (0.44) | 85 98 | 61 25 | 0.90 | 20.4 | 1.0 | 0.0065 0.0057) |
| 75-133AI AII | A-3 | 4/2/75 | | 36 67 | 25 | | | | |
| 75-1BI BII | A-1 | 1/6/75 | 1.76 (2.19) | 17 25 | 24 13 | 3.55 | | 40[3] | 0.0014 (0.0011) |
| 75-104AI AII | A-1 | 2/6/75 | (0.92) | 92 539 | 43 41 | 3.50 | | | (0.0046) |
| 75-25BI BII | C-6 | 1/8/75 | | 163 387 | 59 36 | 4.48 | | 54 | |
| 75-27CI CII | C-8 | 1/8/75 | 2.05 | 338 197 | 209 138 | 3.85 | | 85 | 0.0084 |
| 75-102AI AII | C-8 | 2/6/75 | | 263 194 | 139 198 | 3.15 | | | 0.0082 |
| 75-36BI BII | D-4 | 1/9/75 | 2.7 | 64 97 | 28 17 | 2.9 | | 82 | 0.0008 |
| C-11 (Core) | AS-III | 1/8/75 | | | | | | | |
| -3I -3II | 4-6" | | (1.8) | 32 70 | 20.4 20.5 | 3.8 | 20 | 29 | (0.0011) |
| -8I -8II | 14-16" | | | 137 99 | 57.3 17.0 | 2.6 | 17 | 24 | |
| -13I -13II | 25-26" | | | | 42.0 71.0 | 4.9 | 54 | 19 | |
| -17I -17II | 32-34" | | (0.96) | | 25.4 40.4 | 3.6 | 34 | 27 | (0.0035) |
| HDB | Composite D-4 to H-9 | 12/72 | 1.50 | 67 | | 1.8 | | | 0.0044 |
| 75-97AI AII | H-9 | 1/13/75 | 0.57 | 61 | 81 89 | 2.20 | | | 0.0149 |
| 75-95BI BII | H-7 | 1/13/75 | | 36 28 | 10.0 8.2 | 2.45 | | 1[3] | |
| DB-2 | DB-2 | 10/73 | 0.33 | 7 16 17 | 11.0 14.0 | 0.95 | 87 | 0.6 | 0.0021 |
| 75-92AI AII | H-4 | 1/13/75 | | 18 33 | 10.0 11.3 | 2.2 | 4.4 | 2.7 | |
| 75-89AI AII | F-18 | 1/11/75 | 0.34 | 21 21 | 15.3 12.0 | 1.0 | 5.3 | 6 | 0.0040 |
| DB-3 | DB-3 | 10/73 | 0.47 | 33 30 36 | 16.0 51.0 | 2.4 | | | 0.0047 |
| DB-4 | DB-4 | 10/73 | 0.88 | 49 | | 2.3 | | | 0.0055 |

$\bar{x}$ 13.3    $\overline{12.5}$ (handwritten annotations in DB-2 row)

TABLE II (cont'd)

ANALYTICAL RESULTS

| Sample | Location | Sampling Date | %C[1] | Sat. HC, μg/gm | | CPI | Grain Size (%) | | Sat. HC / Org. C[2] |
|--------|----------|---------------|-------|------|------|-----|------|------|------|
| | | | | VW | GC | | >250 | ≤63 | |
| 74-5AI | 74-5 | 11/6/74 | 0.20 | 8 | 6.1 | 1.2 | 85 | 1.5 | 0.0021 |
| AII | | | (0.21) | 6 | 5.0 | | | | |
| BI | | | | 14 | 3.1 | | | | |
| BII | | | | 12 | 2.3 | | | | |
| 74-4AI | 74-4 | 11/6/74 | 0.24 | | 12.8 | 1.15 | 61 | 1.0 | 0.0048 |
| AII | | | | | 11.4 | | | | |
| BI | | | | 12 | 10.5 | | | | |
| BII | | | | 9 | 11.1 | | | | |
| DB-1 | DB-1 | 10/73 | 0.47 | 38 | | | 15 | 5 | 0.0064 |
| | | | (0.87) | 31 | 30.6 | 1.60 | | | (0.0035) |
| | | | | 38 | 34.7 | | | | |
| | | | x̄ 31.7 | 50 | x̄ 29.96 | | | | |
| | | | | 22 | | | | | |
| | | | | 11 | 24.6 | | | | |
| 74-3AI | 74-3 | 11/6/74 | 0.28 | 27 | | | 7 | 3 | 0.0063 |
| AII | | | (0.24) | 15 | 11.8 | 1.05 | | | |
| BI | | | | 23 | 21.8 | | | | |
| BII | | | | 27 | | | | | |
| CI | | | | 27 | 19.0 | | | | |
| CII | | | | 41 | | | | | |
| 74-2AI | 74-2 | 11/6/74 | 0.81* | 39 | 34.2 | 2.1* | 11* | 18* | 0.0044 |
| AII | | | (1.05)** | 43 | 37.1 | | | | (0.0034) |
| BI | | | | 55 | | | | | |
| BII | | | | 32 | 31.9 | | | | |
| CI | | | | 36 | 32.9 | | | | |
| CII | | | | 33 | 36.4 | | | | |
| DI | | | | 41 | 33.0 | | | | |
| DII | | | | 26 | 35.0 | | | | |
| EI | | | | 38 | 40.9 | | | | |
| EII | | | | 26 | 19.0 | | | | |
| FI | | | | 52 | 57.0 | | | | |
| FII | | | | 43 | | | | | |
| 75-61AI | G-2 | 1/12/75 | 0.53 | 24 | 21.5 | 1.9 | 16 | 9 | 0.0043 |
| AII | | | (0.56) | 22 | 24.4 | | | | |
| 75-90AI | H-2 | 1/13/75 | 0.10 | 17 | 6.8 | 1.0 | 88 | 0.2 | 0.0062 |
| AII | | | (0.11) | 19 | | | | | |
| 75-81AI | F-19 | 1/11/75 | 0.28 | 9 | 8.7 | 1.45 | 69 | 0.9 | 0.0027 |
| AII | | | | 19 | 6.2 | | | | |
| 75-75AI | F-20 | 1/11/75 | 0.13 | 39 | 15.1 | 1.03 | 86 | 0.3 | 0.0100 |
| AII | | | (0.14) | 22 | 10.9 | | | | |
| 75-78CI | F-11 | 1/11/75 | | 11 | 10.7 | 1.8 | | 30[3] | |
| CII | | | | 40 | 11.0 | | | | |

1) Values as determined by ignition loss; %C values as determined by CHN analyzer are given in parentheses.

2) Ratio determined by dividing average Sat. HC value (GC) by carbon abundance; values in parentheses are determined with CHN %C data.

3) Estimated grain size determination.

\* Average of four determinations

\*\* Average of two determinations

Blank spaces imply data not determined.
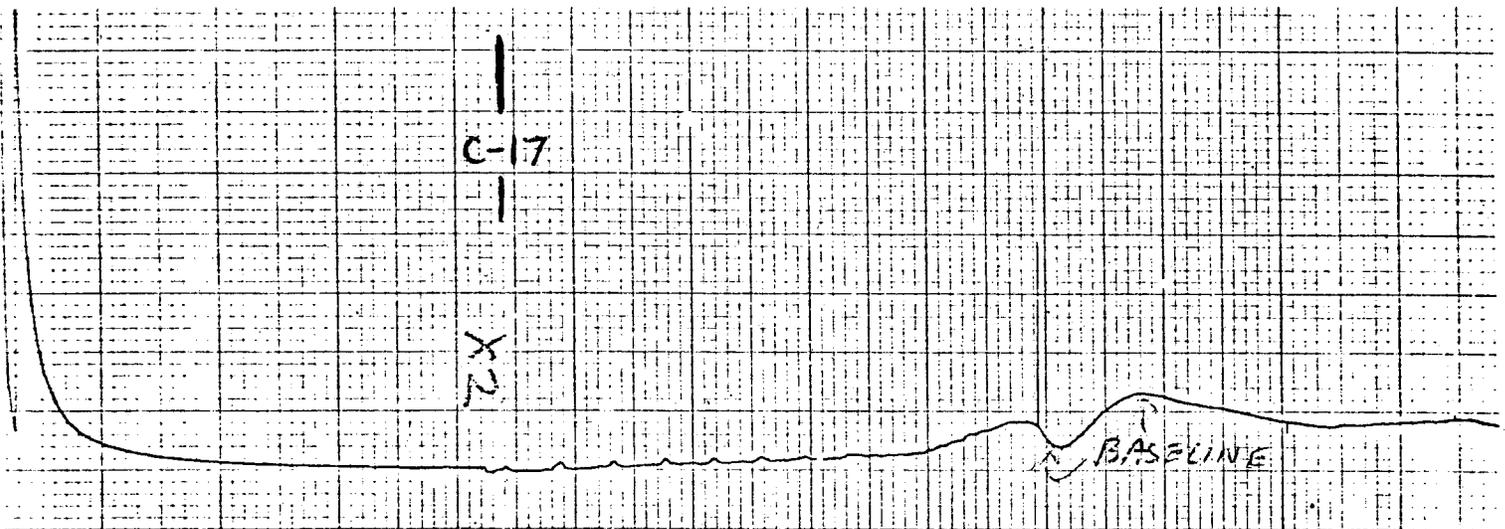
Figure 2: Analytical Blank Chromatogram. See subsequent
Figures for explanations and comparison.
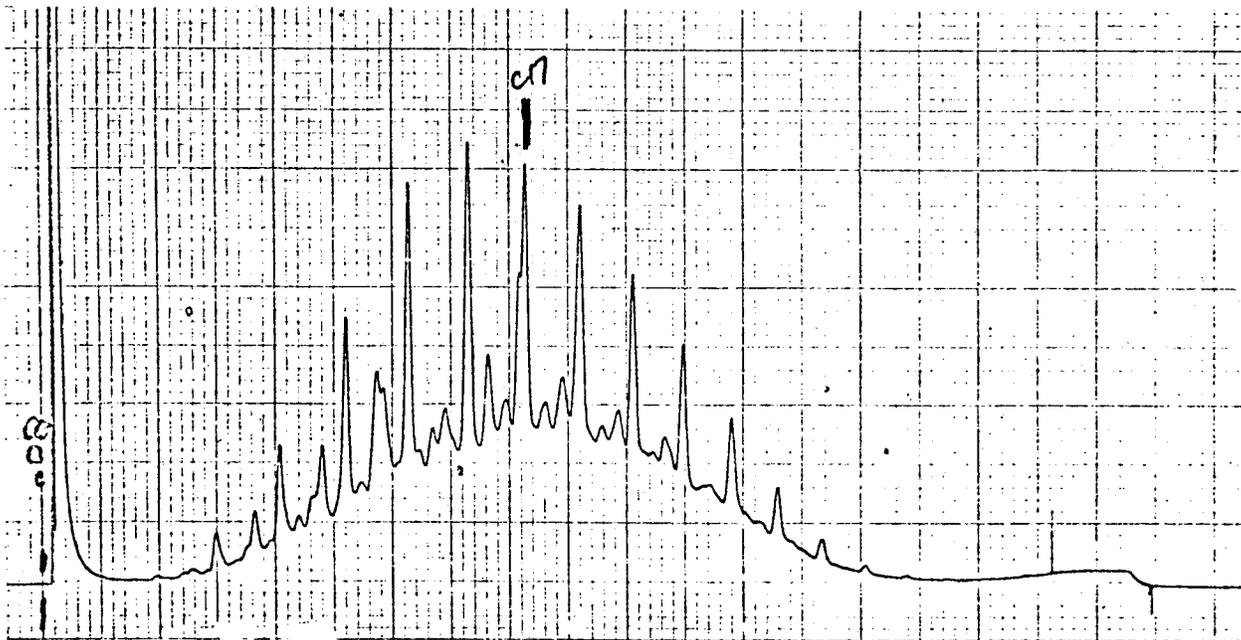


Figure 3: Chromatogram of # 2 Fuel Oil
(Source: M. Blumer, W.H.O.I.)

weights (though chromatographic peaks for these blanks are always less
than 1% of any peak encountered in a sediment analysis). These finite
weights again could be the result of incomplete evaporation rather than
actual blank contamination. No blank weight corrections are included
in the results shown in Table II.

Reagents used in this work have been Fisher Spectra-Analyzed
solvents. They have not been redistilled, and this investigator
recognizes that the omission of redistillation procedures can present
a serious problem. As mentioned previously, chromatograms of reagent
blanks do show small and finite amounts of the same material that is
under discussion in this report (see Figure 2). Though these amounts
are usually so small as to be "disregarded" in the quantitation of the
gas chromatograms, they should not be totally ignored in consideration
of the residue weights discussed above. For this reason, the gas-
chromatographic quantitative data (see below) are considered to be
more reliable.

Characterization and quantification of the hexane eluates has
been performed by packed-column gas chromatography. All chromatograms
have been obtained using a 6' x 1/8" stainless steel column packed
with 3% Apiezon L on 80/100 mesh Supelcoport solid phase (Supelco,
Inc., Bellafonte, Pennsylvania). The gas chromatograph used is a
Hewlett Packard model 5750 (purchased on this grant in December, 1974),
equipped with dual flame ionization detectors. Operating conditions
have been as follows: dual column mode, He carrier gas flow 50-60 ml/
min, programming rate 6°/min from 85° to 285°, isothermal at 285° for
at least 20 minutes. These operating conditions with the particular
column have produced satisfactory resolution of the major compounds
recognized in the hexane eluate (i.e., the n-alkanes) and partial
resolution of the pristane-n-C-17 pair. Phytane is recognized only as
a leading shoulder on n-C-18. Figure 3 is a chromatogram of a #2
Fuel Oil reference obtained from M. Blumer at Woods Hole Oceanographic
Institution. The resolution demonstrated in this chromatogram is
typical of the performance of the analytical column used for all
samples described in this report.

Examination of Figure 3 reveals a number of features that will
be identified and discussed in subsequent sections. The #2 Fuel
Oil consists of an homologous series of normal alkanes from C-12 to
C-24, as indicated in Figure 3. Also evident in the chromatogram
is a large envelope or "hump" that is commonly referred to as the
unresolved complex mixture (UCM). A chromatogram such as this, where
alkanes are superimposed upon an underlying envelope, presents some
problems in quantitative interpretation. Zafiriou et al. (1972)
suggest that the peak heights of the alkanes be read from the chromato-
graphic baseline, rather than from the top of the envelope. The
rationale for this approach is that the alkanes are probably part of
the UCM as well as being the dominant identifiable compounds in the
chromatogram. However, other workers have considered the envelope
and the superimposed peaks as being separate chromatographic features,
though none has attempted to quantify alkanes specifically. The
results for urea adduction experiments on one sample presented here
(75-27C) suggest that the complex mixture can in fact be considered
as an entity in itself and that alkane abundances can, in fact, be
determined by measurement from the top of the unresolved envelope.
It is recognized that such an approach may be valid for some samples
but not others, but is has been the method of calculation of alkane
abundances and odd/even alkane ratios for this report. Since the
carbon preference index (CPI) is a potentially useful tool in identi-
fying hydrocarbons of recent biological origin, the method of its
calculation and measurement with chromatograms such as these with an
unresolved complex mixture is critical and must be specifically
stated. The CPI as reported in this work is calculated from normal
alkane abundances as measured from the top of the UCM and is expressed
as follows:

$$CPI = \frac{2 \times \Sigma \; n\text{-}C\text{-}21 \; to \; n\text{-}C\text{-}31 \quad (odds)}{\Sigma \; n\text{-}C\text{-}20 \; to \; n\text{-}C\text{-}30 \; + \; \Sigma \; n\text{-}C\text{-}22 \; to \; n\text{-}C\text{-}32 \quad (evens)}$$

Quantification by gas chromatography has been performed by com-
parison of the total areas of each chromatogram with the areas of
n-C-20 and n-C-28 alkane standards, known amounts of which were injected

on each day of the chromatograph's operation. Continuous use of these
standards over a four-month period has indicated a random variation of
approximately 10% in the response of the chromatograph; this variation
can be due to inaccuracies in injection of microliter quantities and
to variation in detector operating conditions on any given day.

It should be pointed out that the analytical procedure outlined
above is appropriate for only a portion of the large group of compounds
that are referred to as hydrocarbons. The benzene:methanol extraction
is performed on non-saponified and non-acidified sediments, so the
extract consists of only the most "mobile" extractable material, though
no experiments have been performed here to document the completeness
of this extraction procedure. The hexane eluate contains only the
non-polar,or saturated, and few, if any aromatic compounds from the
extract. Due to the temperature range of operation of the gas
chromatograph, the range of the compounds detected have boiling points
between those of (approximate) n-C-10 and n-C-35. Thus the analyses
reported here represent only a fraction of the hydrocarbon material
present. Some indication of the size of this fraction is seen in
comparisons of the quantities determined by weighing with those
quantities determined by gas chromatography (further discussion follows
below). For all subsequent discussion of the quantitative results,
two abbreviations are used here that are more specific in their meaning
than "total hydrocarbons": SHC-VW and SHC-GC, referring to Saturated
Hydrocarbons as determined by vial weights (VW) and gas chromatography
(GC), respectively.


## RESULTS AND DISCUSSION


Data are presented in Table II for sample location, date of
collection, and SHC-VW and SHC-GC (as μg/gm). Also given in Table II
are results for total organic carbon and for grain-size distribution
as determined by standard sieving techniques. The latter two parameters
are very useful in the interpretation of data on organic compounds in

sediments and it is recommended that similar routine measurements be
included in all "baseline" studies of this type (Farrington and Quinn,
1973). Organic carbon has been determined by two different techniques:
loss on ignition at 375° for 16 hours (Ball, 1964) and by ignition in
a Hewlett-Packard CHN analyzer. Several of the samples have been ana-
lyzed by both techniques to obtain some control on the validity of both
methods. Results are given in Table II for both determinations, and in
general the results show good agreement, especially for sediments with
less than 0.5% carbon.

Specific sample chromatograms are discussed in following sections;
a few general comments on reproducibility and reliability of the
method are in order here.

The sample that has provided the best test of reproducibility is
sample 74-2, which has been carried through the entire analytical
procedure a total of twelve times. The quantitative results for this
sample are as follows: SHC-VW, mean 38.5 µg/gm, std. dev. = 8.6 µg/gm;
SHC-GC, mean 35.7 µg/gm, std. dev. 9.1 µg/gm. The difference between
the two means is not great but it is consistent with the prediction
that the dried residues may contain material that is not detected by
the gas chromatograph (Farrington et al., 1974, show similar results).
The standard deviation for these analyses is larger than desirable
but this is typical of the uncertainties that others have encountered
(Tripp, personal communication; Straughn, 1974). Just as the results
for sample 74-2 suggest that there may be more material in the total
hexane eluate than is detected by gas chromatography (GC), so do the
results for several other samples; specific examples are samples
75-110B, 75-106B, 75-25B, and 75-27C. The validity of these results
is presently under investigation, but the dramatic differences between
the SHC-VW and SHC-GC results for 75-110B can probably be explained by
the fact that this sample is a "post-Corinthos" sample taken approxi-
mately 300 yards from the site of the tanker explosion; one would
expect this location to be affected by high-boiling material. Note
should also be made of the consistency of the results in comparison to
the pre- and post-Corinthos data for this location. Both the SHC-VW

and SHC-GC values for this location (AS-I) increased by approximately a factor of two within five days of the accident.

The data given in Table II are results for duplicate analyses for both categories of results (SHC-VW and SHC-GC). There is a suggestion that, in general, the range of any pair of results is approximately 15% of the mean value, an observation much like that stated above for the replicate analyses of sample 74-2. There is also some suggestion that samples from the lower estuary show less of a difference between the SHC-VW and SHC-GC values, indicating that higher-boiling material (if that is indeed the cause of these divergences) is more significant in sediments from the upper estuary.

A useful approach to the understanding of the variations in saturated hydrocarbons (SHC) in estuarine sediments is to consider these results with respect to total organic carbon, a parameter which is complexly related to grain-size distribution in the sediments (as well as to other variables). Table II includes a ratio of the mean SHC-GC value divided by the organic carbon abundance in the sample. Figure 4 shows this ratio plotted as a function of distance upstream or downstream from the Delaware Memorial Bridge. It is important to consider that, on the basis of saturated hydrocarbon material alone, most of the sediment analyses reported here would fall in the category of "un-polluted." Blumer and co-workers, in studying the West Falmouth, Massachusetts oil spill of September, 1969, suggested that levels of 40 to 70 μg/gm are typical of uncontaminated sediments. However, many of their chromatograms of uncontaminated sediments are very different from any of those presented in this report. Grain-size properties of the sediments will have an effect on the transport and preservation of organic compounds and therefore absolute amounts of sedimentary hydrocarbons, considered without other information on the physical properties of the sediments, may be of limited value. As an example, sample 75-16 contains approximately 62 μg/gm saturated hydrocarbon material, yet it is one of the coarsest grained samples collected (87% > 250 μ). It is from the Delaware River near the Philadelphia International Airport and thus presumably one of the "dirtiest" samples
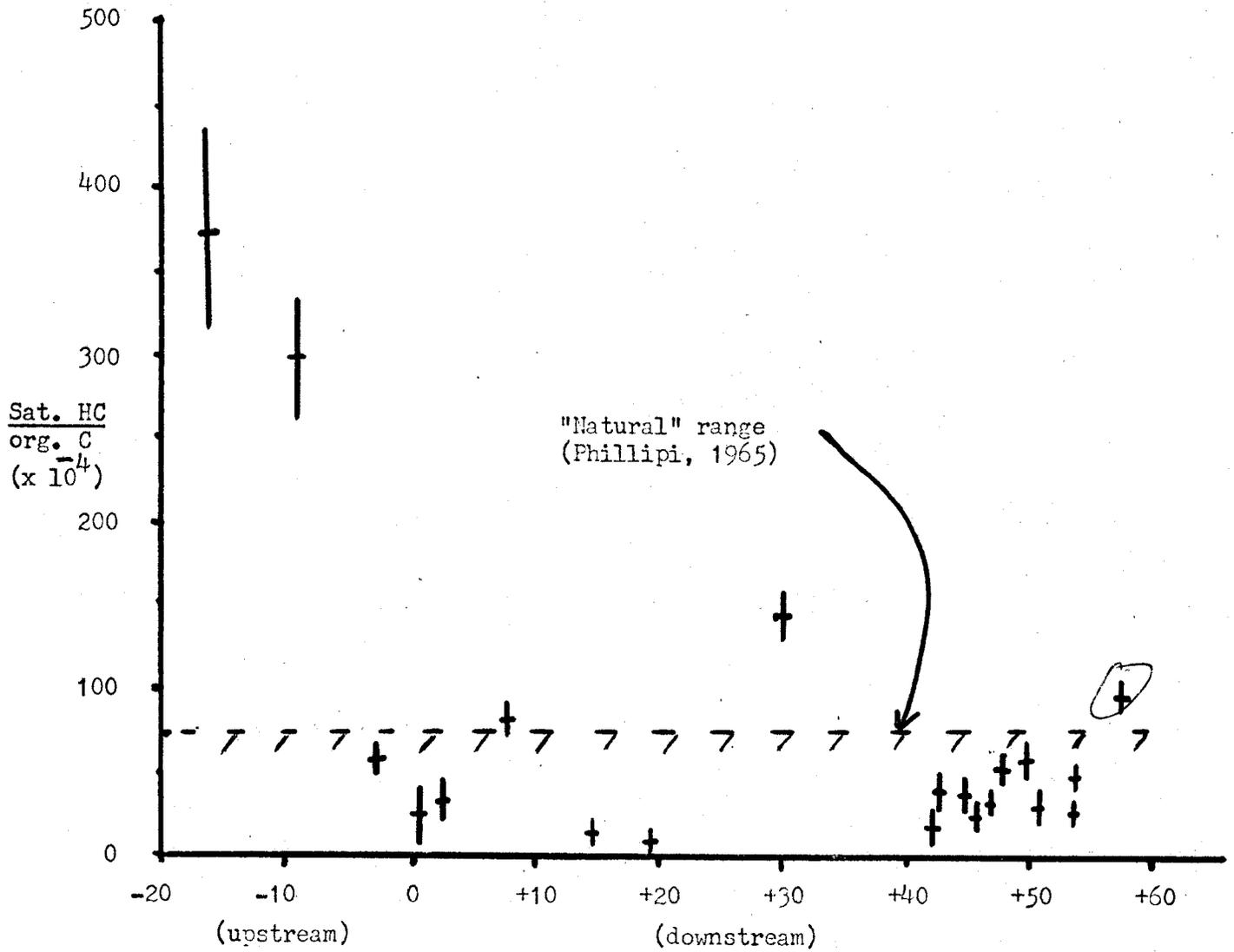
Figure 4:  Saturated Hydrocarbon/organic carbon ratio
vs. Nautical mile distance from Delaware
Memorial Bridge

studied. A sample from the lower estuary with similar grain size characteristics (74-5) contains only about 5 µg/gm saturated hydrocarbon material. Since grain size distributions and total organic carbon usually show some co-variation (Straughn, 1974), the ratio approach (SCH/org C) outlined in Table II and in Figure 4 suggests some areas of the estuary that may be receiving preferential "enrichment" of saturated hydrocarbons relative to the total organic carbon flux to the sediments. Eight samples in the lower bay have ratios that cluster in the range of 40 to $65 \times 10^{-4}$. It is suggested that this is a reference level to which other regions of the estuary should be compared. Three extremely coarse-grained samples from the lower bay area show ratios of $20 - 25 \times 10^{-4}$, suggesting that these coarser sediments are less effective at transporting or preserving hydrocarbon material than are the finer-grained materials mentioned previously. Nevertheless, all of these values are within the range of $9-67 \times 10^{-4}$ reported by Phillipi (1965) for presumably uncontaminated sediments.

Variations from this range identify samples that require further investigation. Station F-20 (sample 75-75) shows a ratio of $100 \times 10^{-4}$. This value is significantly greater than others in the lower bay, especially considering that the sample is coarse-grained. It is possible that the location of the sample in one of the deepest "holes" in the bay (150' water) leads to unusual accumulation and preservation phenomena.

High ratios ($>75 \times 10^{-4}$) are seen in samples from two other locations: in the Delaware River between Philadelphia and Marcus Hook, and at station H-9, near Bombay Hook, Delaware. Station C-8, at the eastern end of the Chesapeake and Delaware Canal, contains fine-grained sediments and abundant hydrocarbon material (approximately 150 µg/gm), but a ratio of SHC/org C only slightly above the range of $9-67 \times 10^{-4}$ quoted above. The area from station D-4 upstream to the Delaware Memorial Bridge (station A-1) is interesting in that all the samples are fine-grained and, with the exception of C-8, all samples within this region show low SHC/org C ratios, and all have a chromato-

graphic pattern that is rarely found in sediments either upstream or
downstream. This pattern will be discussed more fully below.


## SEDIMENT CHROMATOGRAMS:* DISCUSSION


This section will provide brief descriptions of the chromatograms
obtained on the hexane eluates as described above. A general discus-
sion of the interrelationships of selected chromatographic patterns
will follow this descriptive section. Figures 5-38 are chromatograms
of surface sediment grabs from the estuary; Figures 39-42 are chromato-
grams of extracts of core and soil samples in the Great Marsh area,
Lewes, Delaware; Figures 43-50 are of suspended particulate material
taken at several locations within the estuary. A few chromatograms of
dissolved and surface film-saturated hydrocarbon material are also
included for comparison (Fiest, personal communication). The method
of sampling is described in a following section.

Two major features of these various chromatograms will be considered
in the discussion below. The first is the carbon preference index
(CPI) defined earlier. The CPI quantitatively measures the odd-carbon
preference among the alkanes and therefore is a measure of modern
biological inputs and possible diagenetic alteration. CPI values in
sediments analyzed here range from low values of 1.0 ± .10 to high
values of almost 4.5. Low values can be interpreted as being the
product of extensive diagenesis or as being characteristic of
petroleum and some petroleum products, which are, of course, the
product of extensive natural diagenesis.

The second major feature that is immediately obvious in examination
of the chromatograms is the presence of a "hump" or unresolved complex
mixture (UCM). This unresolved complex mixture is not a common
characteristic of marine or terrestrial living biological material
(see Farrington and Quinn, 1973, for discussion) and its presence in
sediments has often been attributed to petroleum pollution. The
universal validity of this interpretation is very much open to question

*Figures 5-55 are on pages 43-79.

(Eglinton et al., 1974), and a case can be made for the UCM being a product of natural diagenetic alterations even on the comparatively short time scale represented by these surficial sediments. Blumer and co-workers have been able to use the presence or absence of the UCM to document the fate of a specific oil spill in an area where uncontaminated sediments were (and are) known to contain no complex mixture. Some of the samples presented here show little in the way of a UCM, especially in relation to the normal alkane abundances (see samples DB-1, 2, and 3; Figures 10, 11, 12). Nevertheless, most of the samples studied do show a significant UCM, and its abundance relative to the alkanes appears especially large in some of the upper estuary samples (see sample 75-16, location B-8, Figure 38). More significant, perhaps, is the boiling point distribution of the unresolved complex mixture. Some samples show no unresolved mixture; several show a mixture with a maximum boiling point in the n-C-17 to n-C-20 range; and many show a mixture that "peaks" in the n-C-28 to n-C-30 region. This latter type of unresolved mixture may be only a component of a mixture that has a boiling point maximum well above that of n-C-30. Since the instrumental temperature programming reaches its maximum at about the same temperature of elution of n-C-29, the peak in the high-boiling UCM could be merely the artifact of the temperature program. Programming of a few samples to lower temperatures (ca. 240°C) has shown that this is the case: the "peak" in the high-boiling UCM coincides with the maximum temperature of the program. Thus the samples fall into three general categories: those with little or no unresolved complex mixture, those with a low-boiling mixture, and those with a high-boiling mixture.

The estuary samples will be discussed in a sequence that begins with the lower bay samples and proceeds upstream. Figures 5-13 are of the nine samples from southwestern Delaware Bay around the lightering area. Two of these samples (74-4, 74-5) are from within the limits of the lightering area. All samples contain an unresolved complex mixture, though as stated above, it is relatively insignificant in samples DB-1, 2, and 3 in comparison to the large abundances of the

"light" alkanes n-C-15 to n-C-18 that are characteristic of marine algal contributions to the sediments. Sample DB-2 contains a large unidentified peak in the n-C-23 region; several other samples throughout the estuary also have this peak (plus a few smaller ones in the n-C-23 to n-C-25 region). Similar peaks have been seen in uncontaminated sediments from Buzzards Bay, Massachusetts (Blumer and Sass, 1972) and in sediments from Narragansett Bay (Farrington and Quinn, 1973). Philp (personal communication) has suggested that one or more of these peaks may be plasticizers, and at this time there is no way of deciding either the identity of the peak(s) or their origins. It is significant, however, that the uncontaminated Buzzards Bay sediments (Blumer and Sass, 1972) were dominated by a few peaks (simple mixture) that eluted in this alkane region (n-C-20 to n-C-25).

Samples DB-4, 75-61A, and 74-2C (Figures 13, 9, and 5) show the UCM and slight enrichment of the heavier alkanes n-C-27 and n-C-29 that are characteristic of terrestrial and marsh plant materials (see below). All of the above samples have moderate CPI values (1.6 to 2.4) and exhibit a peak in the UCM at about the n-C-29 position. The other three samples from this group of nine (74-3, 74-4, and 74-5, Figures 6, 7, 8) are characterized by a lower boiling point distribution for the UCM (peaking at n-C-21) and by lower CPI values (1.05 to 1.2). The last three samples are much coarser-grained than the other six samples and generally contain slightly smaller amounts of saturated hydrocarbon material than do the other six.

Four additional samples from the lower bay that follow this pattern are samples 75-90, 75-81, 75-89, and 75-92 (Figures 14-17). Sample 75-90 is coarse-grained, has a low CPI (1.03) and a peak in the UCM at n-C-22. There is a marked absence of plant detritus alkanes (n-C-27, 29, 31). Samples 75-81, 75-89, and 75-92 all show a maximum in the UCM at n-C-29, though there is a suggestion of a secondary maximum in the n-C-17 to n-C-20 region in all three samples and especially in 75-92. Sample 75-89 again shows the unidentified peaks in the n-C-23 region.

Samples 75-75 and 75-78 (Figures 18 and 19), also from the lower

bay, continue to show one or more of these features. Sample 75-75 is coarse-grained, has a low CPI value (1.03) and shows the maximum in the UCM in the n-C-23 region. It too shows the large unidentified peak in this same region. Sample 75-78 shows the same unidentified peak and exhibits the general chromatographic pattern that is encountered most frequently in the river samples farther upstream. This is a pattern in which the UCM is obviously lower-boiling (peak at n-C-17 to n-C-20) and in which there are large amounts of lower-boiling alkanes (n-C-12 to n-C-14). The significance of this pattern will be discussed more fully below.

Sample 75-95 (Figure 20) from station H-7, farther upstream, combines many of the features already discussed: peak alkane abundance at n-C-29, secondary alkane abundance at n-C-17, significant amounts of n-C-13 alkane, and an unresolved complex mixture that is a mixture of lower-boiling (n-C-17 to n-C-20) and higher-boiling (n-C-29) material.

Upstream from station H-7, the patterns outlined above continue to be observed and can be geographically grouped a bit more specifically than is possible for the samples from the lower bay. Sample HDB (Figure 21) is a composite of eight samples from an area just north of station H-9, from which sample 75-97 (Figure 22) was taken. The chromatograms of these two samples are very similar and are dominated by the unresolved mixture. The deficiency of n-alkane peaks is more dramatic for these samples than for any of those previously discussed.

From station D-4 upstream to the Delaware Memorial Bridge (station A-1), all but one sample (75-27, station C-8) are characterized by the pattern of high CPI values, large amounts of n-C-13, and relatively small unresolved complex mixtures, all of which peak in the lower boiling range (n-C-17 to n-C-20). Each of these samples shows these features in varying degrees, but it should be pointed out that all of the samples that do show this pattern of abundant n-C-13 and a low-boiling UCM are fine-grained sediments. The opposite is not true: a few fine-grained samples, notably 75-27, do not show this pattern. For those that do, some important generalizations can be

made.  A core taken at station AS-III provides a useful reference for
the discussion of these patterns.  The surface grab sample, taken at
this location in April, 1975 (sample 75-126, Figure 23), shows a high
CPI value and the dominance of the higher-boiling n-alkanes (C-27, 29,
31).  Station D-4, sample 75-36 (Figure 24) shows a similar pattern,
slightly "enriched" in the lower-boiling UCM and the n-C-12 and
n-C-13 alkanes.  Successively deeper levels in the AS-III core suggest
that these chromatographic features may be the product of diagenetic
reactions.  Figures 25-27 (three depths in core AS-III) show that there
is a steady increase in the relative size of the low-boiling UCM
and in the relative abundance of the n-C-13 alkane.  Hence it is
tentatively suggested that these lower-boiling components (both
unresolved and resolved) that are always found associated with each
other are at least partially derived from relatively rapid diagenetic
processes.  These processes (or at least the chromatographic pattern)
seem to be unique to fine-grained sediments and are not specifically
correlated to geographic regions of the estuary.  The rates of these
alteration reactions at AS-III can be estimated only approximately
from information on sedimentation rates in marshes of the Delaware
Estuary of about 6"/100 years and for lagoonal deposits of about
1-2"/100 years (Belknap, 1975).  Hence the lowest level of the AS-III
core is no younger than about 600 years and no older than about 3000
years, assuming constant sedimentation rates and no disturbances
such as dredging.  Diagenetic production of a similar saturated
hydrocarbon pattern has been seen by other workers (Palacas, personal
communication; Johnson and Calder, 1973) and is seen also in sandy
sediments that underlie the marsh sediments of the Great Marsh (see
Figure 42).

Sample 75-25 (station C-6, Figure 28) conforms to the patterns
described at the core at AS-III, and it too is an extremely fine-
grained sample.  Two samples at station A-1 generally fit this pattern,
though there are some differences that may be related to the Corinthos
tanker explosion.  Sample 75-1 (Figure 29) is from station A-1 in
January, 1975.  It shows a pattern characteristic of most of the other

fine-grained sediments in the area: high CPI, abundance of the
"terrestrial" odd carbon n-alkanes (C-25, 27, 29, 31) and little
unresolved complex mixture. This sample again has the unidentified
peak in the n-C-23 region. Sample 75-104 (Figure 30) was taken at
this same station (A-1) in early February, 1975). The post-Corinthos
sample contains only slightly more saturated hydrocarbon material, but
the SHC/org C does show a significant increase in comparison of the
pre- and post-Corinthos samples. (Neither value, however, is outside
of the "natural" range given by Phillipi, 1965.) The chromatographic
differences between these two samples is primarily in the "appearance"
of a significant low-boiling unresolved complex mixture in the post-
Corinthos sample. Thus it appears that, in spite of the fact that
the absolute amount of hydrocarbon material did not increase dramatically
at this location, the other data imply that some small "impact" was
recorded at station A-1 between early January and early February, 1975.

The samples at station C-8 (samples 75-27, 75-102, Figures 31-34)
are somewhat different from the others in this region of the estuary,
and the fact that this "anomaly" has been found in samples taken at
two different times supports its validity. The unresolved complex
mixture is a much more significant fraction of the total chromatogram
and the amount of saturated hydrocarbon material in the samples is
significantly greater than in samples from the surrounding area.
Sample 75-27C (Figure 31) represents the pre-Corinthos analysis,
75-102A (Figure 32) the post-Corinthos sample. There is no difference
between these two chromatograms except in the abundance of the lower-
boiling (C-12 and C-13) normal alkanes; this difference could be real
or could be an artifact of different evaporation conditions during the
samples' preparation.

Sample 75-27 has provided a test of urea adduction methods for
the separation of normal alkanes from the complex mixture (branched,
cyclic, and other compounds). As mentioned in the discussion of
analytical techniques, the calculation of the carbon preference index
(CPI) will depend on the choice of baselines from which peak heights
are measured and the adduction experiments performed on this one sample

offer some information for these calculations. Figures 33 and 34 are the adducted and non-adducted fractions of sample 75-27CI, whose total extract chromatogram is shown as Figure 31. The CPI values calculated from Figure 31 and from Figure 33 are 3.9 and 4.2 respectively, implying that there is some advantage in measuring CPI values on adducted material but that alkane peak heights calculated from the flat chromatographic baseline would not be correct, since the CPI value calculated from data obtained in this manner is only about 1.35 (from Figure 31). Figure 34 shows that significant amounts of the short-chain alkanes are not adducted well but that there is almost complete adduction of the alkanes longer than C-20. The effectiveness of the adduction is perhaps best seen in Figure 33, where there has been significant reduction in the unresolved complex mixture and the removal of pristane (19-carbon isoprenoid). These chromatograms represent a preliminary investigation of the adduction technique and further studies are anticipated; if alkanes in recent sediments are to be useful in defining geochemical and pollutant processes, then the adduction procedure should become more widely used.

Three stations upstream from the Delaware Memorial Bridge show chromatograms that are dominated by the unresolved complex mixture, unlike many of the samples just downstream from the bridge. If this mixture is in fact an artifact of pollution, then its abundance in this area of the river is not at all surprising. Sample 75-106 (Figure 35) is a post-<u>Corinthos</u> sample from station A-3; no pre-<u>Corinthos</u> analysis from this station is available as of this writing. Sample 75-106 has many of the features of the lower bay samples: coarse-grained, low CPI value (.90), and an SHC/org C ratio in the range of those observed in many of the lower bay samples. Samples 75-5 and 75-110 (Figures 36 and 37) represent the pre- and post-<u>Corinthos</u> samples taken at station AS-I within one-half mile of the site of the tanker explosion in Marcus Hook, Pennsylvania.

Differences in the samples are primarily in terms of quantities: the amount of saturated hydrocarbon material in the post-spill sample is approximately twice as great as in the pre-spill sample. However,

the SHC/org C ratio actually shows a <u>decrease</u> in the post-spill sample, so no clear statement can be made about the specific impact of the <u>Corinthos</u> spill on the sediments at AS-I. Such a decrease in the SHC/org C ratio might be explained by an influx of higher-boiling material that is not detected by gas chromatography. The post-spill chromatogram does not reveal any increase in the lower boiling complex mixture as was seen at station A-1, but the lower-boiling alkanes (n-C-11, N-C-12, and n-C-13) are much more abundant in the post-spill sample than in the pre-spill sample. The n-C-17/pristane ratio, which, upon increasing, has been used as a measure of the recent influx of petroleum into sediments from a specific spill event (Blumer and Sass, 1972), is approximately three times greater in the post-spill sample than in the pre-spill sample. This observation suggests that the ratio can be a useful tool in "mapping" the fate of spills in sediments of the Delaware Estuary, but proof of the above statement will require additional analyses at stations that were probably affected by the <u>Corinthos</u> event. The abundant n-alkanes seen in the chromatogram of suspended matter in the river near the spill (February 6, 1975, Figure 47) indicate the type of material that was probably being incorporated into sediments after the spill. The high ratio of n-C-17 to pristane in this suspended sediment sample (75-101Y) is again consistent with the Blumer and Sass (1972) observations and with the comparison of 75-5 and 75-110 as discussed above.

Sample 75-16 (Figure 38), from station B-8, is the sample that is probably the most dominated by the unresolved complex mixture. As mentioned earlier, it is a coarse-grained sample and on the basis of total saturated hydrocarbon material it would not be considered "polluted". Nevertheless, its SHC/org C ratio is very high, implying that is is "enriched" in saturates. The correlation of the unresolved mixture with this enrichment is important. Its low CPI value (1.06) again can be interpreted as being related to pollution or to active diagenetic processes that occur in coarser-grained sediments.

Figures 39-42 are chromatograms of saturated extracts of marsh and soil samples and are presented for comparison with the bay and river samples discussed above. Figures 39, 41, and 42 represent three levels (surface, 180-200 cm, and 320-340 cm respectively) in a

core taken in the Great Marsh near Lewes, Delaware (Swetland, 1975).
The surface sample is similar to some of the finer-grained sediments
of the lower bay (e.g., 75-61, Figure 9) in that it has an unresolved
mixture peaking at approximately n-C-29, and the "heavy" alkanes
(n-C-27, 29, 31) are abundant. However, the relative importance of
the alkanes in the chromatogram is much greater than in the bay
samples, indicating the nearness of the source of these compounds.
The presence of the unresolved complex mixture in marsh sediments
presents a question that requires further investigation: either the
marsh is contaminated or the UCM is a feature of "pristine" environ-
ments. Figure 40, a soil sample from Sussex County, Delaware, shows
little UCM and the "terrestrial" alkane mixture (abundant n-C-27, 29,
31). The absence of the UCM in the soil sample implies that the UCM
is either related to marine and estuarine sediments or to pollutants.

It has been suggested that some of the chromatographic patterns
observed in the river and bay sediments can be the products of
natural diagenetic reactions (see discussion of Core AS-III, above).
Two levels from the core in the Great Marsh add support to this
suggestion. The 180-200 cm level (Figure 41), in spite of the fact
that it shows only a small unresolved complex mixture (compare to
surface marsh saturates, Figure 39), seems to have a greater relative
amount of low-boiling material than does the surface marsh sample.
This is especially true of the suggested "hump" in the n-C-16 to
n-C-20 region. This pattern is much more dramatic in the lower level
of the core (320-340 cm, Figure 42). Here a dominant UCM in the
C-17 to C-20 region is present, and similar features have been
interpreted as being the result of immature diagenesis of natural
organic matter in the marine environment (Swetland, personal communication).
(Figure 42 was obtained on a capillary column gas chromatograph at the
U. S. Geological Survey in Denver, Colorado, and no baseline information
is available.) The sample represented by Figure 42 is a coarse-grained
(medium sand) sediment with a probable age of 3,000 to 5,000 years
(Swetland and Wehmiller, 1975). Other observers (Johnson and Calder,
1973) have documented similar rapid diagenetic alteration in coarse-

grained marsh sediments. Thus a general pattern of reactions seems to be associated with coarse-grained sediments in marsh environments and fine-grained sediments in estuarine environments (Core AS-III). The exact association between these two sets of reactions at this time can only be the subject of speculation.

## WATER COLUMN STUDIES

### Particulate and Dissolved Hydrocarbon Analyses

As an adjunct to the bottom sediment analysis program described above, a program of suspended and dissolved hydrocarbon analysis has been initiated. Proper sampling for these categories of material is much more difficult and intricate than for sediments, and the techniques for these operations are still under investigation.

The suspended material has been sampled with a device (here referred to as the Diatom Filter) that is commonly used for filtration and purification of swimming pools and large aquaria. It consists of a bed of diatomaceous earth packed against a cloth bag, through which pumped water circulates. The entire filtration bed is enclosed in a 2-quart glass jar with a small pump mounted on the lid of the jar. This device has been used in conjunction with the pumping systems of whichever vessel has been used for sampling (January, 1975: Ridgely Warfield; February, April, 1975: Wolverine). Both vessels pump "clean" water from depths of about four to six feet below waterline. The problem of procedural blank contamination by this method is serious and has not been completely evaluated, since the only true way to evaluate such a problem would be to pump approximately 100 liters of distilled water through the entire system, and this has not been feasible during any of the sampling periods.

Due to unanticipated problems in preparation, the diatomaceous earth used for all of the samples discussed here was not subjected to exhaustive extraction prior to its use in the filtering device. Thus, the blank correction for this material is rather large. The diatomaceous

Table III     Suspended Hydrocarbon Material as Determined
              By    "Diatom Filter" Device

| Sample | Location | Date | Sat. HC (µg/gm) | |
| | | | Vial Wt. | GC |
|---|---|---|---|---|
| AS-I | AS-I | 1/75 | 640 | 313 |
| 75-113 | A-1 to AS-I | 2/5/75 | 463 | 361 |
| 75-101Y | B-2 to C-9 | 2/6/75 | 15,292 | 4525 |
| 75-128 | C-8 to A-1 | 4/2/75 | 495 | 279 |
| 75-135 | A-3 to B-2 | 4/2/75 | 973 | 840 |
| AS-III | AS-III | 1/75 | 1473 | 230 |
| AS-IV | AS-IV | 1/75 | 573 | 21.1 |
| AS-VI | AS-VI | 1/75 | 250 | 250 |
| D-BL | Blank on diatomaceous earth | | 343 | 40.7 |

earth was extracted for about three hours at room temperature with chloroform (six separate washes) prior to use. The actual filtration operation consisted of loading approximately fifty grams of diatomaceous earth into the filtration jar; once circulation of water into the jar has begun, the diatomaceous earth becomes suspended and "hangs up" on the cloth bag support through which water is being pumped (from outside in). It is estimated that at least half of the diatomaceous earth is lost during this "seating" process, but that after a few minutes of operation, a solid bed of 20-30 grams of diatomaceous earth is developed and filtration commences. The pump was operated only while at anchor during the January, 1975 cruise. All subsequent samples have been taken during continuous cruising; the pump was routinely operated for between three and four hours, and its nominal flow rate was approximately 100 liters/hr. This flow probably varied by as much as one order of magnitude during the loading of the filter, so no estimates of actual water volume are included in this report.

When the filtration device is stopped, the bed of diatomaceous earth containing the entrapped material (manufacturer claims 99% retention of particles greater than 1 μ) becomes disengaged from the cloth bag support and can be decanted to a sample container. Subsequent processing is much as before: the sample is freeze-dried and subjected to the same soxhlet extraction and chromatographic procedures as were used for the sediments. The only step not performed is the activated copper column procedure for sulfur removal.

Table III presents quantitative results, and Figures 43-50 the chromatographic results, for these Diatom Filter samples. The quantities are reported as μg/gm of material extracted: usually approximately 8-10 gms of material was extracted, and it is estimated that about half of this was actual sample and the other half was diatomaceous earth. A blank on this diatomaceous earth yielded a value of 40.7 μg/gm of saturated hydrocarbons (by GC) and a chromatogram dominated by the C-23 to C-30 normal alkanes; there was little unresolved complex mixture in this blank. Since it is difficult to evaluate the significance of the blank in relation to the numerical values presented

in Table III, no blank corrections are actually made in any of the results, but caution is urged in their interpretation.

Figures 43-47 are chromatograms of the saturated extracts from the January, 1975 series of Diatom Filters. They correspond to stations AS-I, AS-III, AS-IV, and AS-VI, respectively, and represent a downstream transect from Marcus Hook to Cape May (see Figure 1). Amounts of material recognized in these extracts imply, as previously, that the gas chromatograph detects only a fraction of the total extract, and that as the amount of the total extract increases, the discrepancy between the two determinations also becomes larger. There is no obvious regional trend in "absolute amounts" ($\mu g/gm$): the GC values for the January, 1975 samples are 313, 230, 21, and 260 $\mu g/gm$, listed in the downstream order given above. The low value for station AS-IV might be interpreted as being representative of the lower bay if it were not for the high value detected for the station (AS-VI) near Cape May, New Jersey, on an incoming tide.

All the chromatograms are characterized by moderately low CPI values (less than 1.5); the "terrestrial" alkanes (n-C-27, 29, 31) are present in three of the four samples but do not dominate the mixture of alkanes significantly in any of these samples. All the samples contain an unresolved complex mixture that reaches a maximum near C-29, and the general impression that one has of the alkanes in these samples is that they constitute a rather evenly distributed homologous series that ranges from C-12 to C-35. A similar pattern of alkanes is observed in some of the dissolved hydrocarbon samples discussed below; this observation suggests that the active surfaces of the diatomaceous earth may actually sample dissolved material as well as the particulate matter.

Post-Corinthos Diatom Filter samples are shown in Figures 47-50. These represent samples taken in February and April, 1975, approximately between Wilmington, Delaware, and Philadelphia. Three of these samples appear very similar to the January, 1975 samples from either station AS-I or AS-III, both in absolute amounts and in their chromatographic appearance. Only sample 75-101Y (Figure 47), taken

on February 6, 1975 while in transit from Essington, Pennsylvania
to station C-8, appears different. This was a time of extensive
visible pollution as evidenced by suspended tar balls and an almost
continuous surface film from Philadelphia to the Delaware Memorial
Bridge. The chromatogram of 75-101Y indicates an abundance of lower-
boiling alkanes and an evenly distributed homologous series of normal
alkanes. As mentioned previously, the n-C-17/pristine ratio is much
greater than in the previous sample from this area (Figure 43),
consistent with the results for the sediments from station AS-I and
with the results of Blumer and Sass (1972).

Figures 51-54 are of dissolved hydrocarbon material extracted
from a series of four closely-spaced samples taken near a salinity-
front convergence in the lower bay near the lightering area in
January, 1975. The techniques for sample collection and extraction
will be the subject of a subsequent report (Fiest, in preparation).
Figure 55 outlines the spatial relationship of these four samples
to each other and to the visible surface slick that was associated
with the convergence.

There are significant differences in these chromatograms in spite
of the proximity of the samples. Each of the chromatograms contains
features discussed previously. All of the samples are characterized
by an homologous series of n-alkanes with a boiling point range
somewhat greater than observed in the sediments. CPI values are
generally low (less than 1.4). The shapes of the unresolved mixtures
and their maxima all vary from sample to sample. The surface slick
(Figure 51) is characterized by an unresolved complex mixture much
like that seen in the sandy sediments of the lower bay:  maximum at
n-C-29. Three different complex mixtures are seen in the dissolved
samples taken at one-meter depths at three points under the convergence;
perhaps the only association that can be pointed out at this time is
that the low-boiling UCM (Figure 52) has abundant low-boiling alkanes
associated with it, just as was the case in the sediments.

The variability among these four samples and their relation to
oceanographic parameters is under continuing investigation. Such

analyses clearly demonstrate that a diverse mixture of hydrocarbons
can be found as dissolved material in Delaware Bay and that, at
present, correlation with specific sources is difficult if not impossible.
The four chromatograms presented here are useful for comparison with
the sediments, and these preliminary results help to identify some of
the questions regarding transport of dissolved organics in the estuary.


## SUMMARY DISCUSSION

The information presented here represents a preliminary regional
overview of the geographic variability of saturated hydrocarbons in
sediments of the Delaware Estuary. A large collection of chromatograms
has been presented in order that these variations can be adequately
described and so that other investigators will be able to recognize
these features quickly for comparison with their own work.

The particular chemistry of a sediment sample is the product of
the combined processes of biological production, transport and sedi-
mentation, biological and non-biological transformation during early
diagenesis, and contamination. None of the samples presented here
specifically identifies any one of these processes. The regional
survey approach presented here probably recognizes a few contaminated
sediments, but more important, it also suggests a number of geochemical
relations that must be understood before "contamination" can be more
quantitatively evaluated.

The regional approach allows for several geochemical "provinces"
of the estuary to be defined, and two different approaches to this
definition yield roughly concordant results. The ratio approach
(SHC/org C) defines an "enriched" area upstream of the Delaware Memorial
Bridge, and a "natural" area in the lower bay. A few potentially
significant variations are seen in this lower bay province. Between
these two areas is the region of extreme variability in the SHC/org C
ratios (approximately two orders of magnitude): this is the area of
fine-grained sediments and of samples with chromatographic patterns that

are infrequently observed in either the upstream or downstream area. This is also the region of the estuary that is subjected to large variations in salinity under the influence of tidal mixing of waters from both the Delaware River and the Chesapeake and Delaware Canal.

The SHC/org C ratio probably recognizes the contaminated nature of the upstream sediments in comparison to those from the lower bay; variations in this ratio in both the lower bay and central "provinces" cannot be unequivocally explained as contamination. The fact that a particular chromatographic pattern is associated with many of the fine-grained sediments that show a low SHC/org C ratio suggests a selective sedimentological process that somehow removes to the sediments only a small fraction of the available hydrocarbon material. This process, and the specific sedimentological component that might be responsible for it, remain unidentified.

The geochemical provinces defined by chromatographic patterns generally correspond to those defined above. The major distinction to be made is between the samples that have a high-boiling (maximum at n-C-29 or greater) unresolved complex mixture and those that have a low-boiling (maximum at n-C-17) complex mixture. Very few of the samples can be characterized as having no complex mixture, and though the identity of the material in these mixtures is unknown, its presence and variability is given a great deal of significance in this work and in much previous work on similar samples. All the samples show an homologous series of n-alkanes, and some of these alkane mixtures show a biological "fingerprint." A majority of the samples, however, have CPI values low enough to be interpreted as the product of significant diagenetic alteration, either in situ or prior to sedimentation of the alkane mixture.

The fine-grained sediments (particularly those with more than 70% less than 63 μ) are characterized by a chromatographic pattern that may indicate selective sedimentation and a diagenetic origin for some of the unresolved material in the samples. The core at station AS-III (fine-grained with abundant organic carbon) shows a steady increase in the relative size of the low-boiling UCM, implying diagenetic

production. The marsh core would be interpreted identically. The increase in this UCM is not recognized by a decrease in the alkanes of the sample, but the abundant organic material in the core samples would provide an ample reservoir for production of the compounds that elute in this low-boiling UCM. The presence of this low-boiling UCM in surficial sediments at other localities could be due to the finite ages of these sediments and to transport of the mixture from other locations. Thus it is suggested that a low-boiling unresolved complex mixture, while in some cases an obvious indicator of pollution, can be produced by natural geochemical processes.

The fine-grained sediments, in almost every case, contain alkane mixtures with higher CPI values than found in most of the other samples studied, and in only one case (75-27) did a fine-grained sediment reveal a high-boiling unresolved complex mixture. The higher-boiling complex mixture is frequently observed in coarse-grained sediments. Thus there is an indication that finer-grained particles may preferentially retain only an ordered series of hydrocarbon molecules, i.e., the normal alkanes, and that the coarser sediments retain a less organized series of compounds. This again would be a natural geochemical process that may or may not occur without regard to pollution sources; it may be a process that can be recognized only where the loading of hydrocarbons to the water column is significant enough for the various mineral-organic equilibria to be recognized. Obviously it is a question that warrants further investigation, by analysis of different size fractions of estuary sediments and by laboratory experimentation. It is clearly important to establish the validity of such processes if a meaningful baseline is to be established.

The origin of the high-boiling complex mixture is even less understood than that of the low-boiling mixture. The higher-boiling mixture is abundant in sediments that one would expect to be contaminated by industrial activity, but it is also present in about the same relative amount (though lower in absolute quantity) in many of the sediments from the lower estuary, where contamination would not be expected to be so significant. It is a common feature of sediment

samples from Narragansett Bay (Farrington and Quinn, 1973) and is seen
in some (but not all) samples from "uncontaminated" coastal and
lacustrine samples (Eglinton et al., 1973). Such a complex mixture is
usually not associated with modern biological hydrocarbons. The lower
bay samples are perhaps most interesting in that they generally contain
small amounts of hydrocarbon material relative to those from Narragansett
Bay, though the SHC/org C ratios for the two estuaries are quite com-
parable. Thus is appears that the lower bay sediments are generally
low in hydrocarbon abundance, but much of what is present would be
characterized as being extensively altered since it was last part of
any living biological system. This alteration is reflected by the
low CPI values and the UCM. If modern biological hydrocarbon material
is being synthesized in Delaware Bay, it does not appear to be accumulat-
ing at significant rates over much of the lower estuary. Swain (1972)
has suggested that accumulation zones for organic material in the
estuary actually lie just outside the bay mouth on the continental
shelf. A few of the deep "holes" in the vicinity of the bay mouth
(including sample 75-25, Station F-20) may be these accumulation zones.

A sub-project that has obvious relation to the "baseline" geo-
chemical studies outlined above has been the investigation of the
consequences of the _Corinthos_ tanker accident. At the time of this
writing, only a few pairs of samples (before-after) have been processed,
and monitoring stations have been visited at one-week, two-, and three-
month intervals subsequent to the accident. Based upon other observations
of the movement of spilled oil in coastal waters (Blumer and Sass, 1972),
it is anticipated that sediments contaminated by the _Corinthos_ spill
will be recognizable over distances of tens of miles during the course
of the next two years. An investigation of such a phenomenon would be
of obvious value for all those interested in establishing the meaning
of any "baseline" information, and some effort will be made to continue
this investigation. It is hoped that the cooperation of other labora-
tories can be enlisted in this effort so that a meaningful number of
samples can be processed.

The results for the post-_Corinthos_ samples suggest that bottom

sediments as far as nine miles downstream may have recorded the impact of the spill within a week of the accident; the surface and shores of the river itself were visibly contaminated over much greater distances within this one week time. Suspended material within the river also reflected the spill's impact over a distance of at least several miles. Contamination over a longer period of time, or over a greater distance, has not been recognized in any of the samples analyzed, though samples collected in late April, 1975 at station AS-III were visibly contaminated with petroleum-like material that had not been observed in all previous sampling at that location.

The conclusions presented herein are meant as preliminary statements only. They do not reflect a complete interpretation of the available data, and additional analyses are required before the validity of some observations can be proven. Nevertheless, to the authors' knowledge, this work represents the most extensive sampling and analytical effort in the study of hydrocarbon material in sediments of the Delaware Estuary. It is hoped that the information presented in this report will serve as a guide for future research and as a stimulant for discussion with other scientists and user-agencies interested in the problems of establishing baselines in this and other estuarine and coastal environments.

## ACKNOWLEDGEMENTS

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Notes for sample chromatograms, Figures 5 through 55:

For all chromatograms except Figure 39, programming
was from 85° to 285° C. at 6°/min., with temperature
(time) increasing from left to right.  Figure 39 is
reversed, and programming was at 4°/min.  The vertical
axis is detector response, and all attenuation
(sensitivity) changes are marked.  The position of
n-C-17 is marked by a vertical dark line.  All
chromatographic baselines were horizontal through
the entire temperature program unless otherwise
marked.

Figure 5: 74-2CI
Site 74-2, 11/74
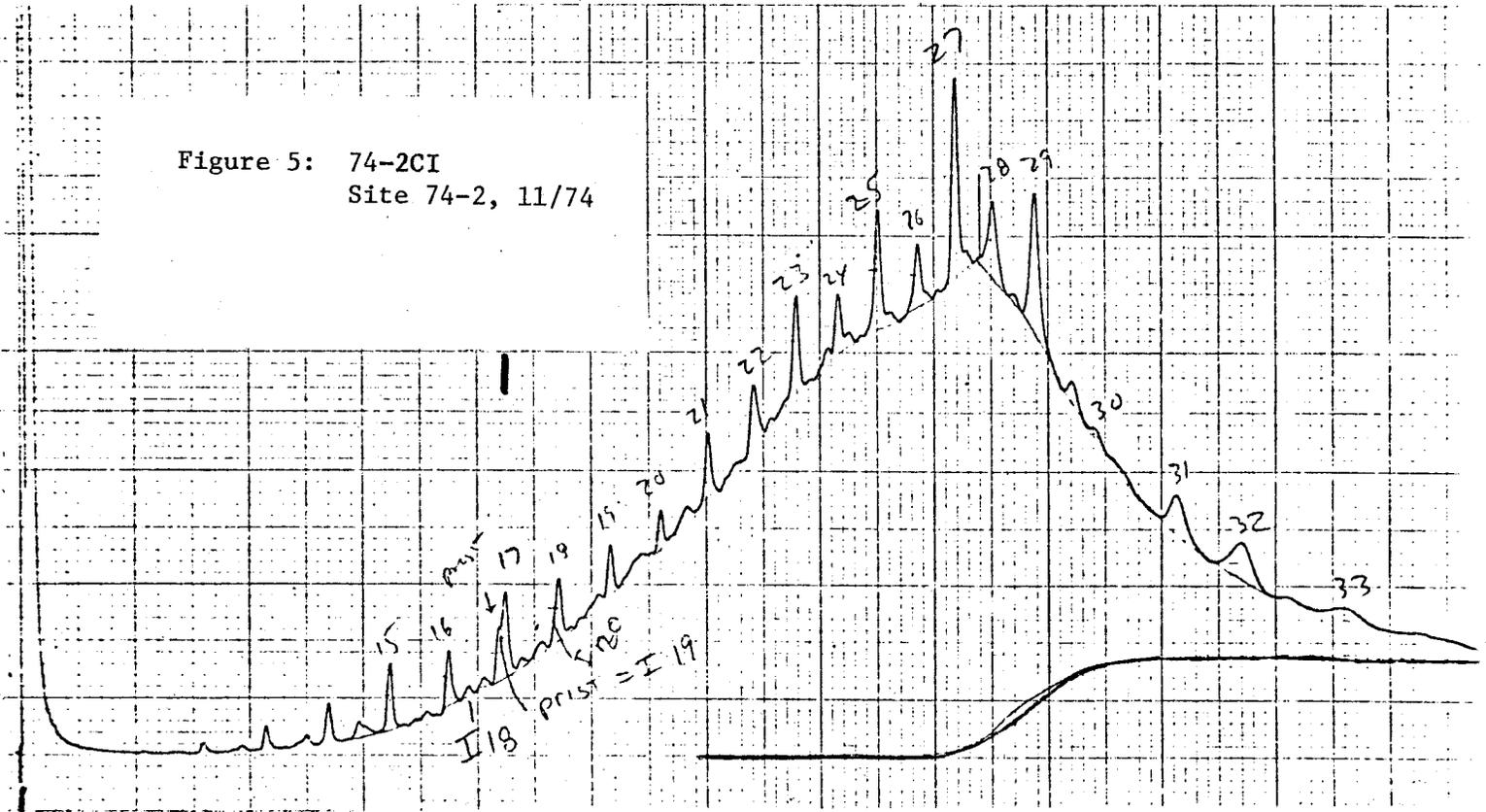


Figure 6: 74-3BI
Site 74-3, 11/74
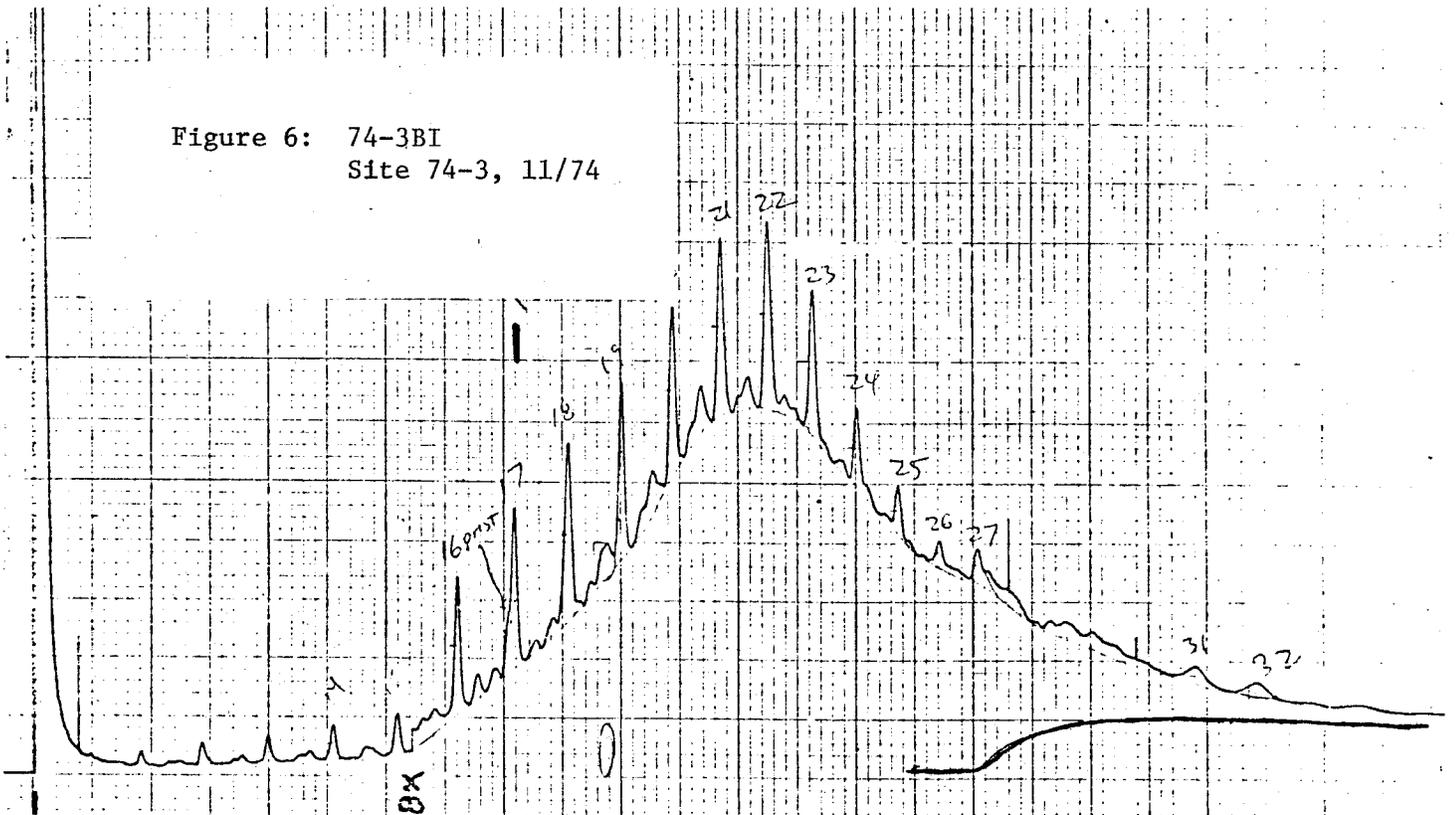
Figure 7: 74-4BI
Site 74-4, 11/74
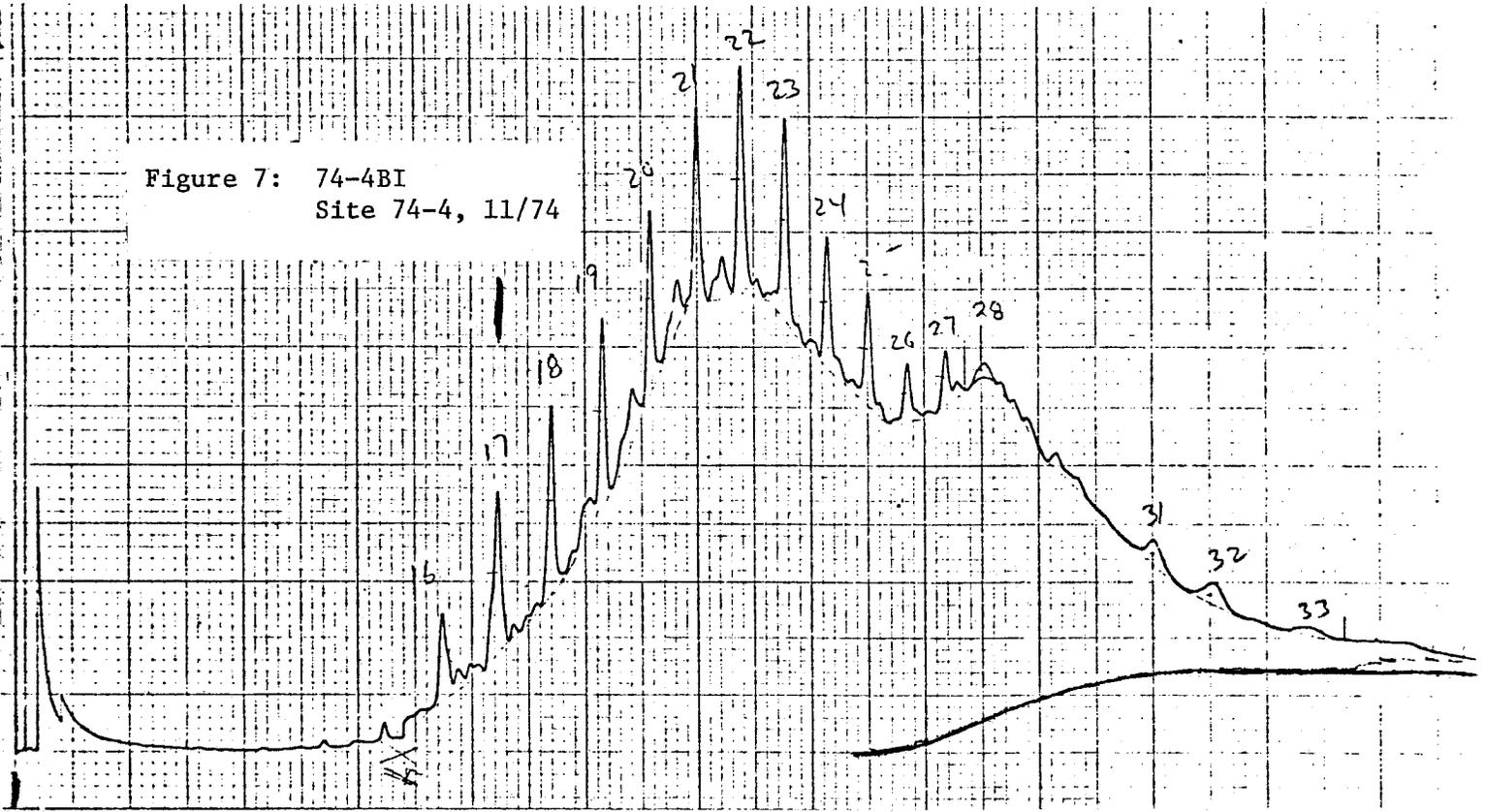


Figure 8: 74-5AI
Site 74-5, 11/74
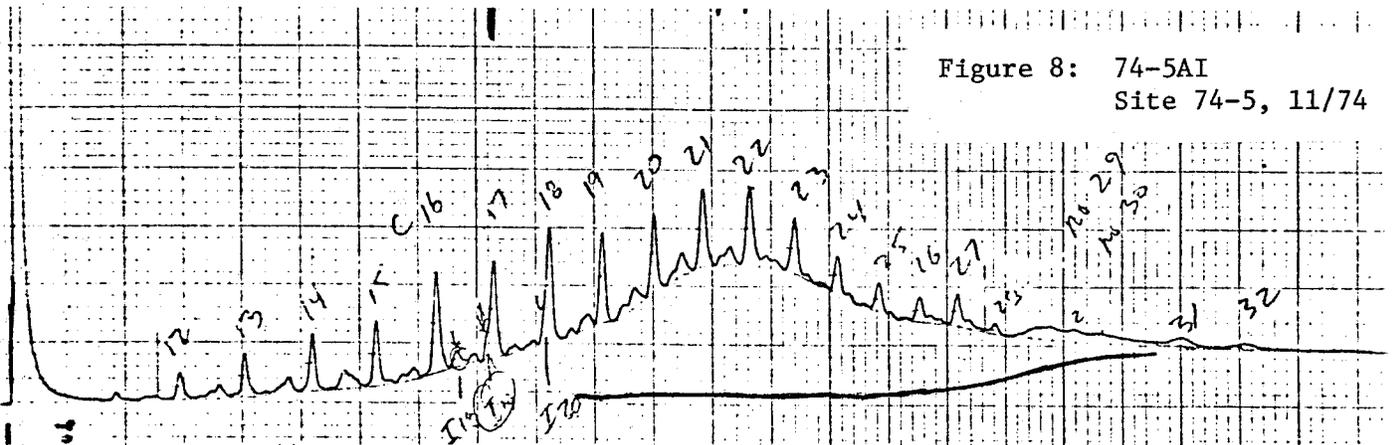
Figure 9: 75-61A
Site G-2, 1/75
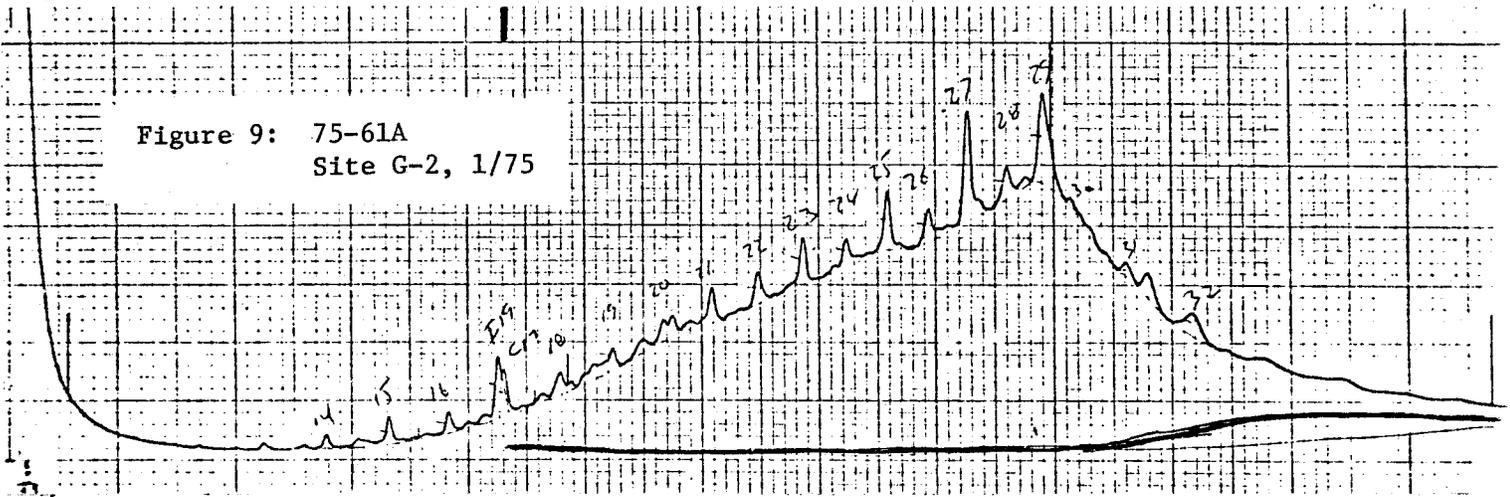


Figure 10: DB-1
Site DB-1, 10/73

Figure 11: DB-2
Site DB-2, 10/73

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Figure 12: DB-3
Site DB-3, 10/73



Figure 13: DB-4
Site DB-4, 10/73

Figure 14:   75-90AI
Site H-2, 1/75



Figure 15:   75-81AI
Site F-19, 1/75
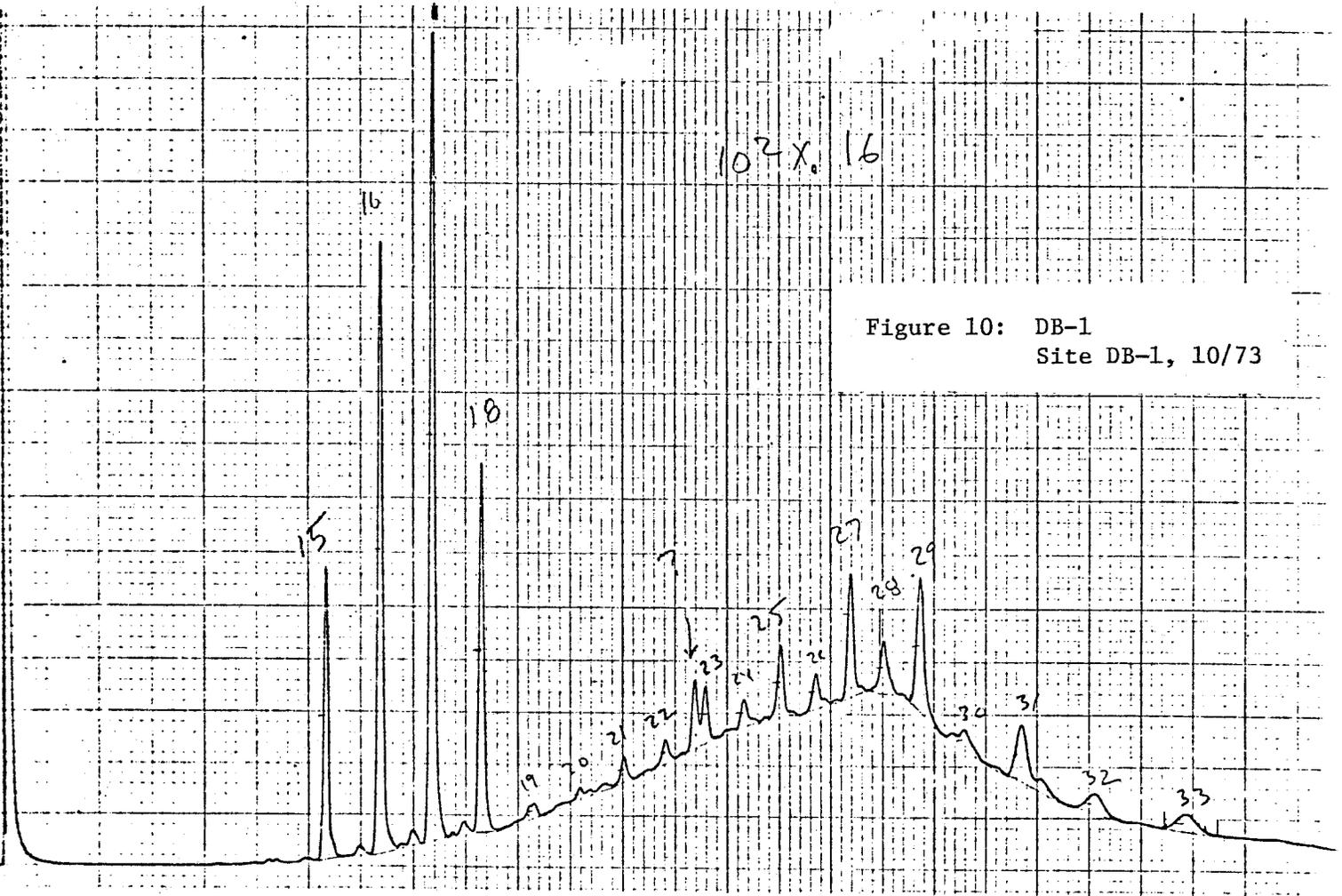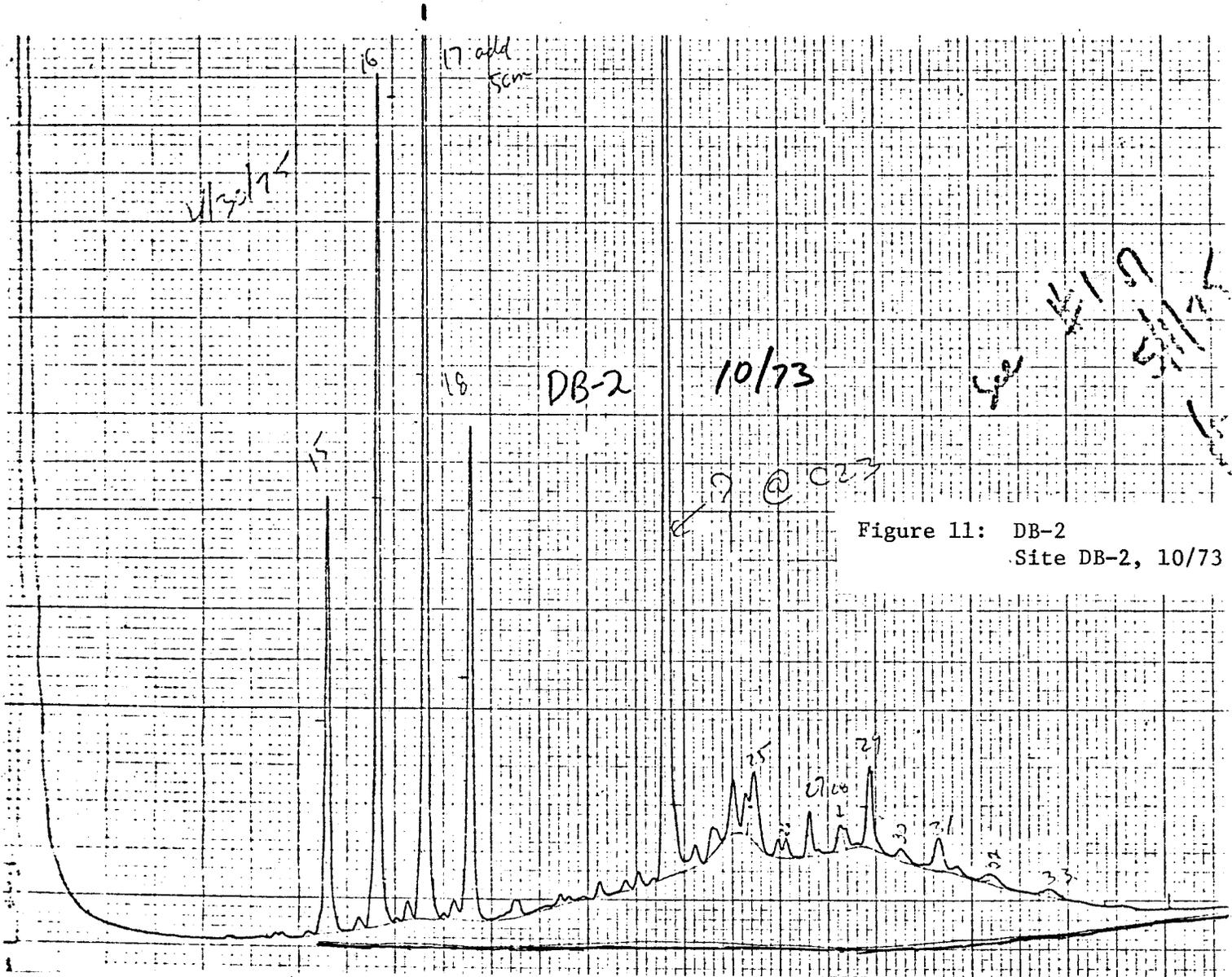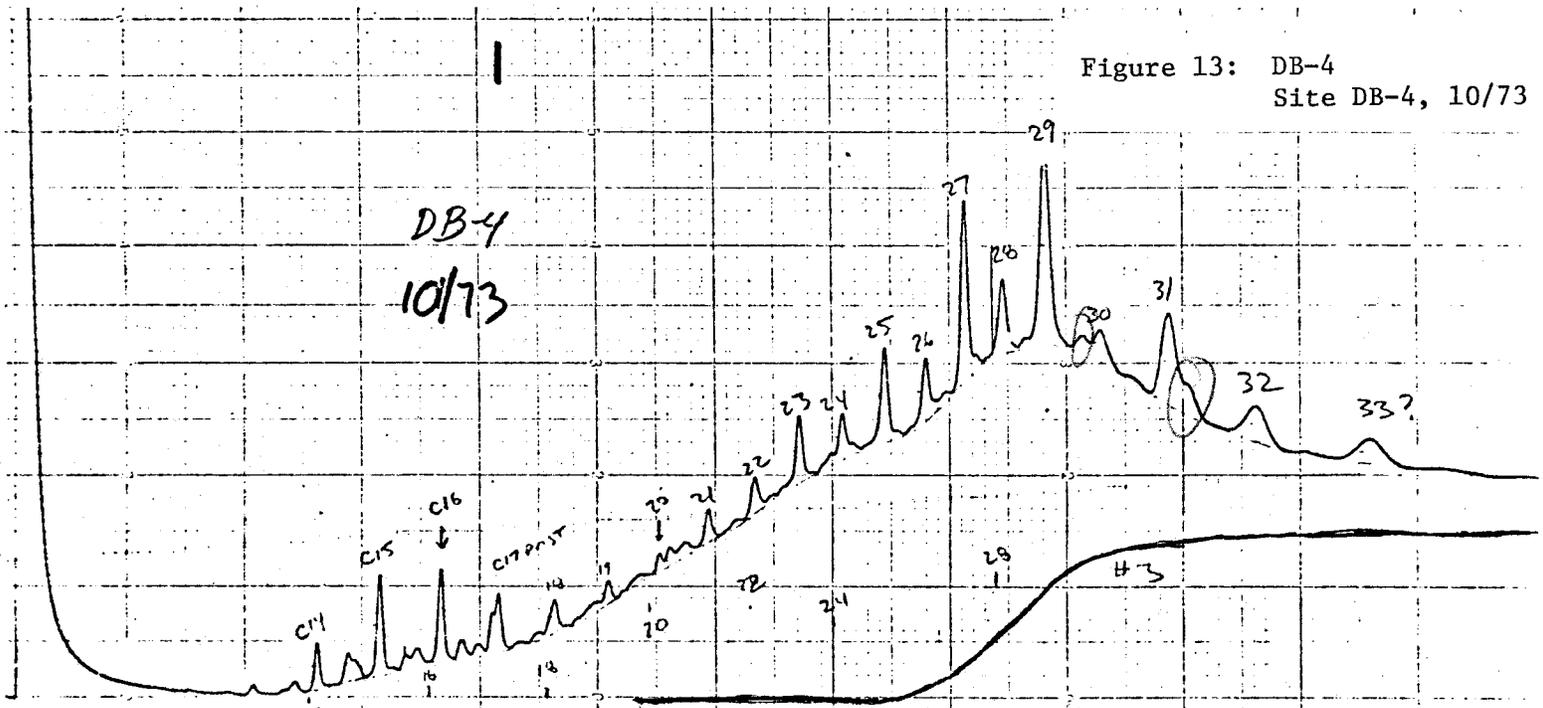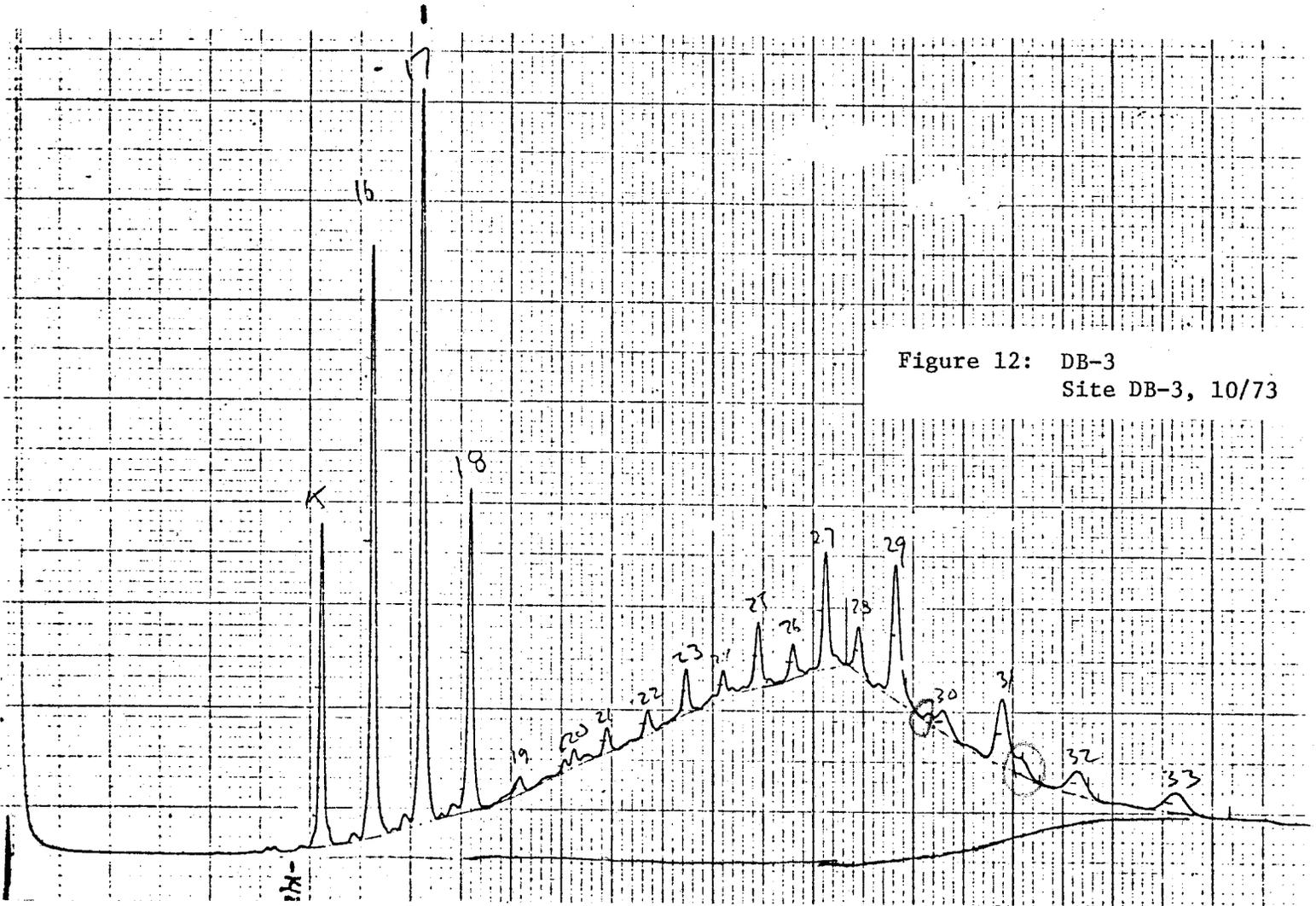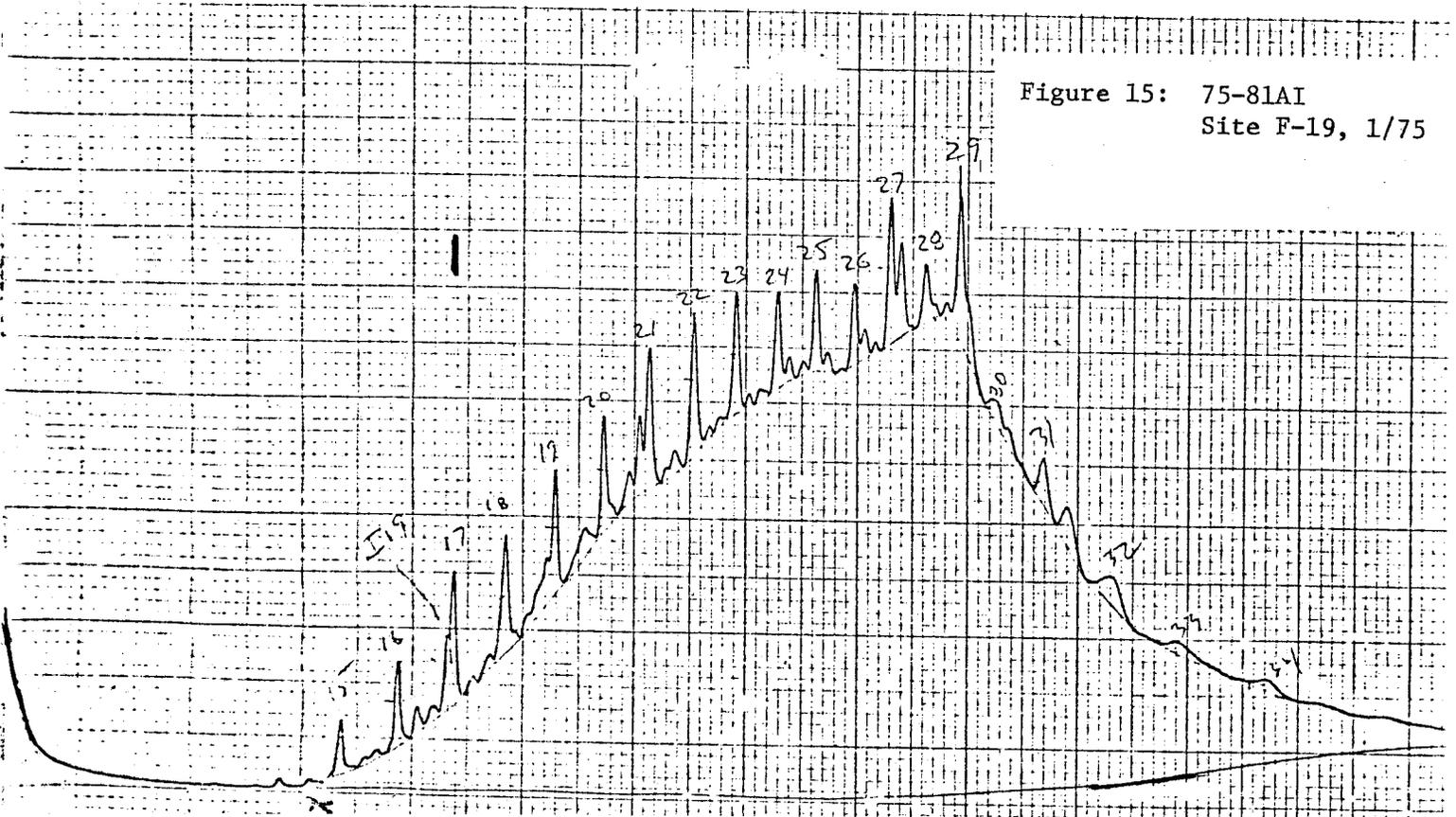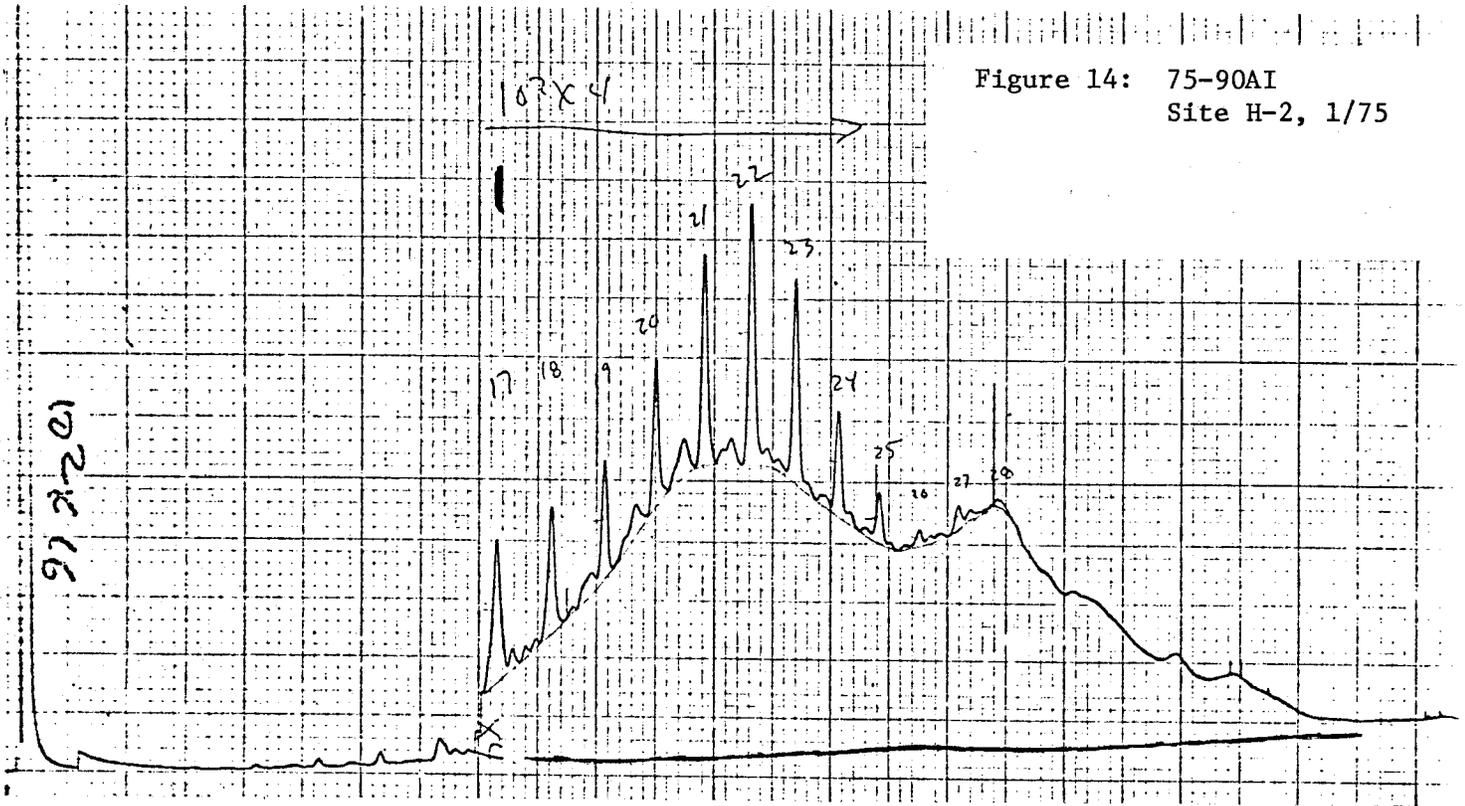
Figure 16: 75-89AII
Site F-18, 1/75
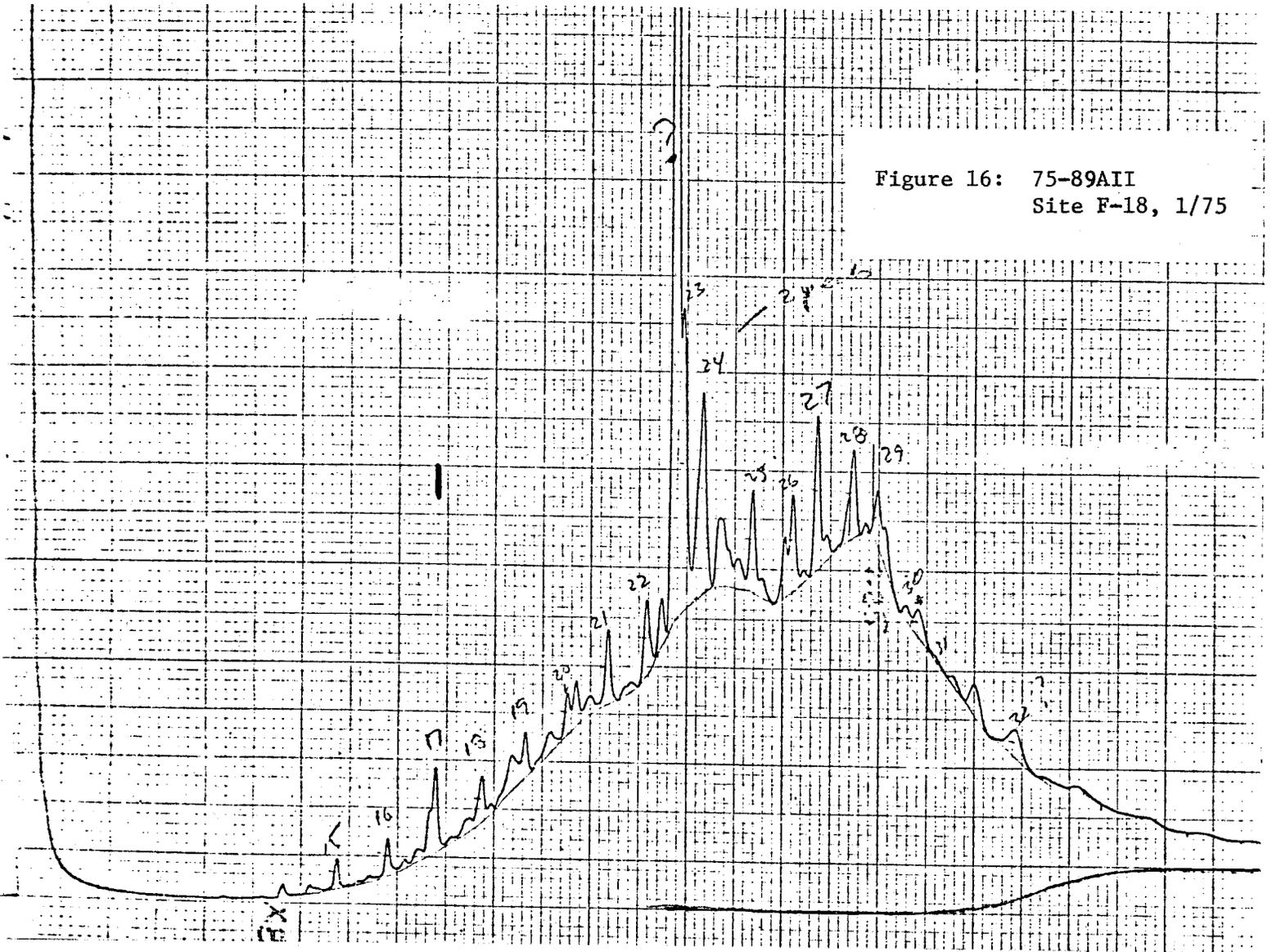


Figure 17: 75-92AI
Site H-4, 1/75
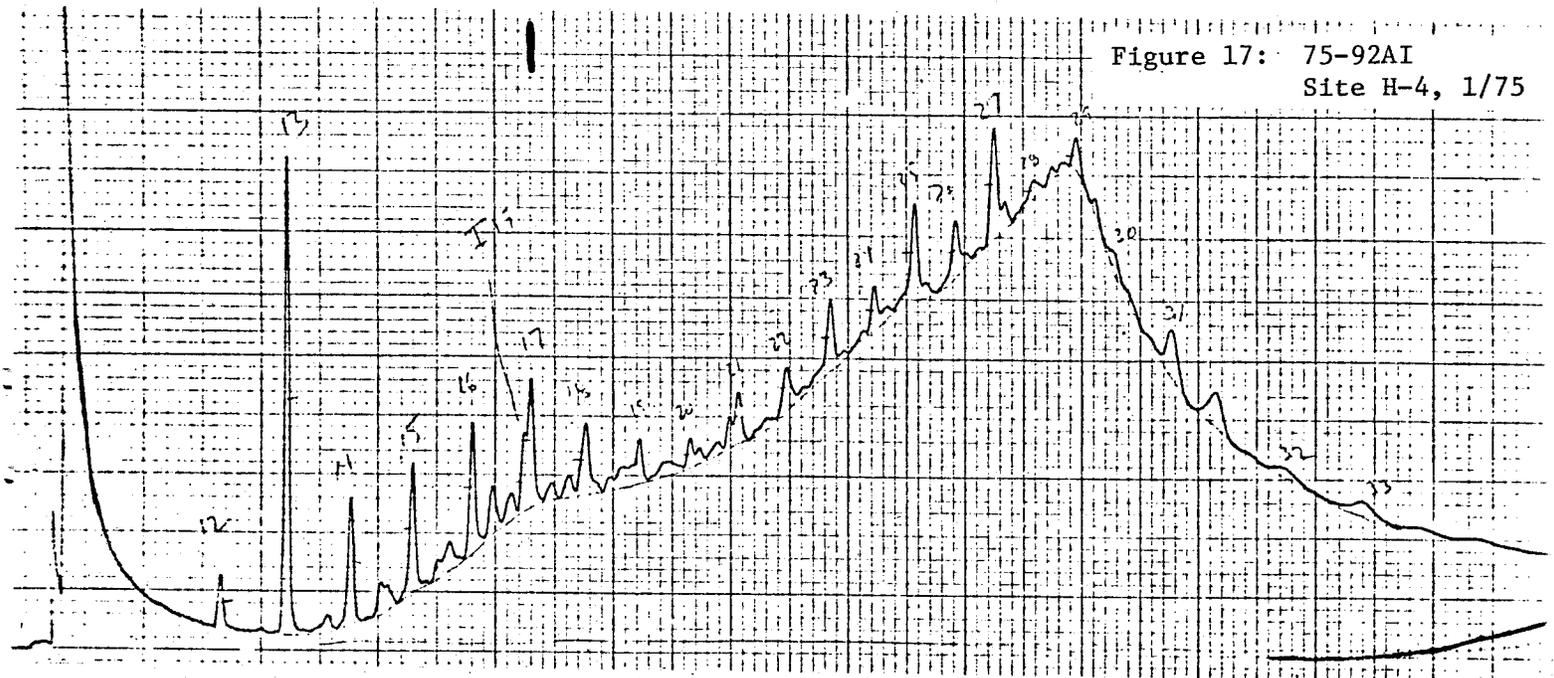
Figure 18: 75-75AI
Site F-20, 1/75

Figure 19: 75-78CI
Site F-11, 1/75



Figure 20: 75-95BI
Site H-7, 1/75
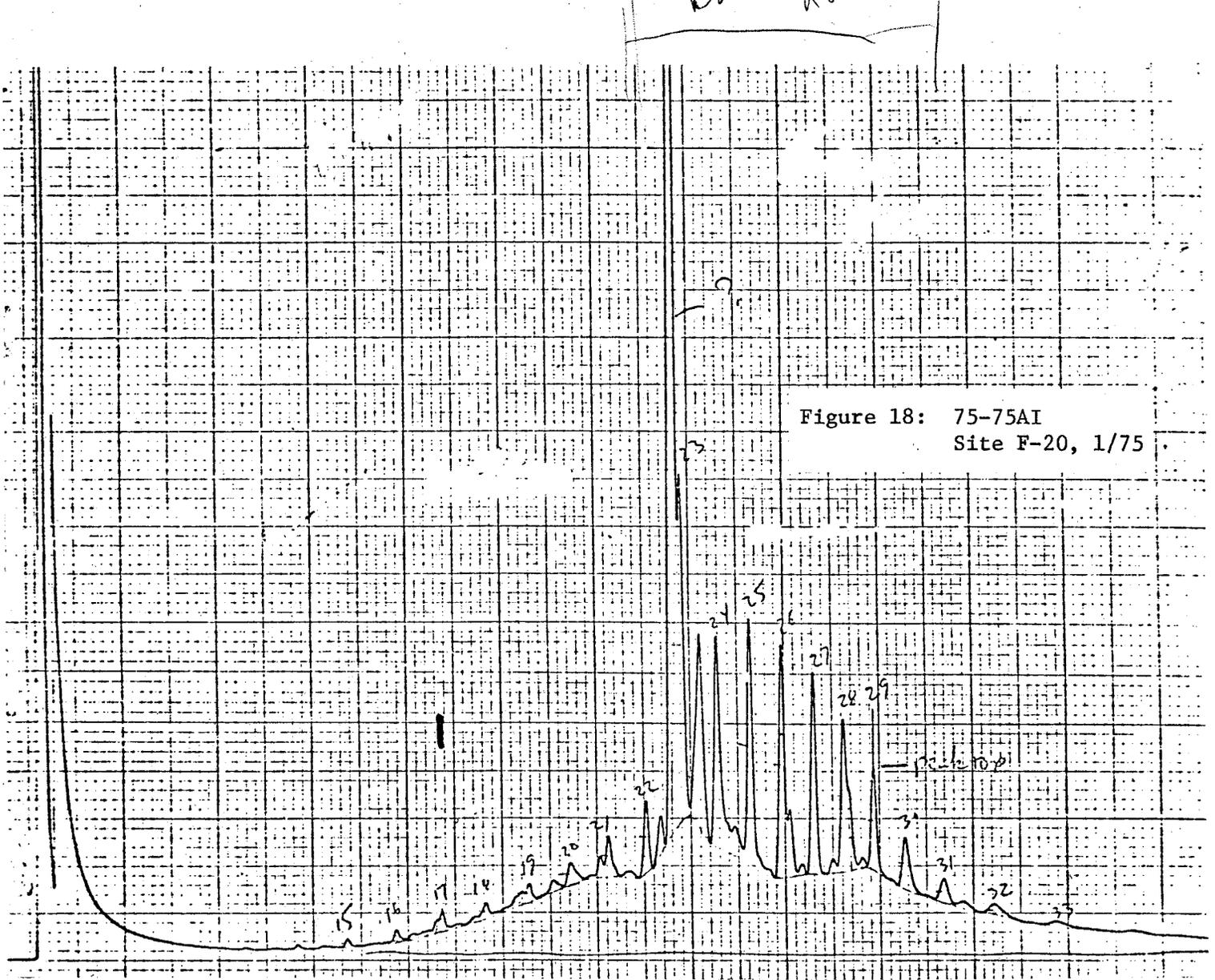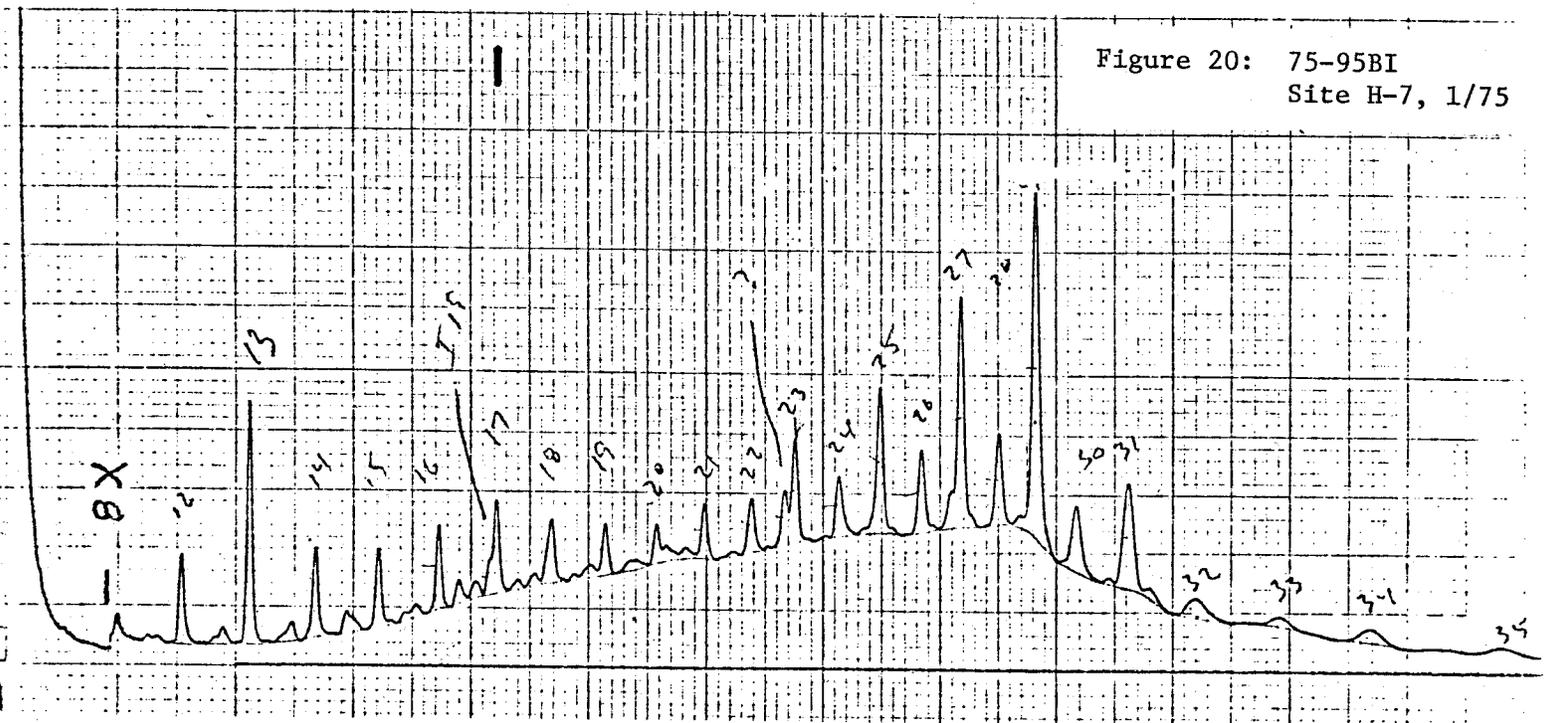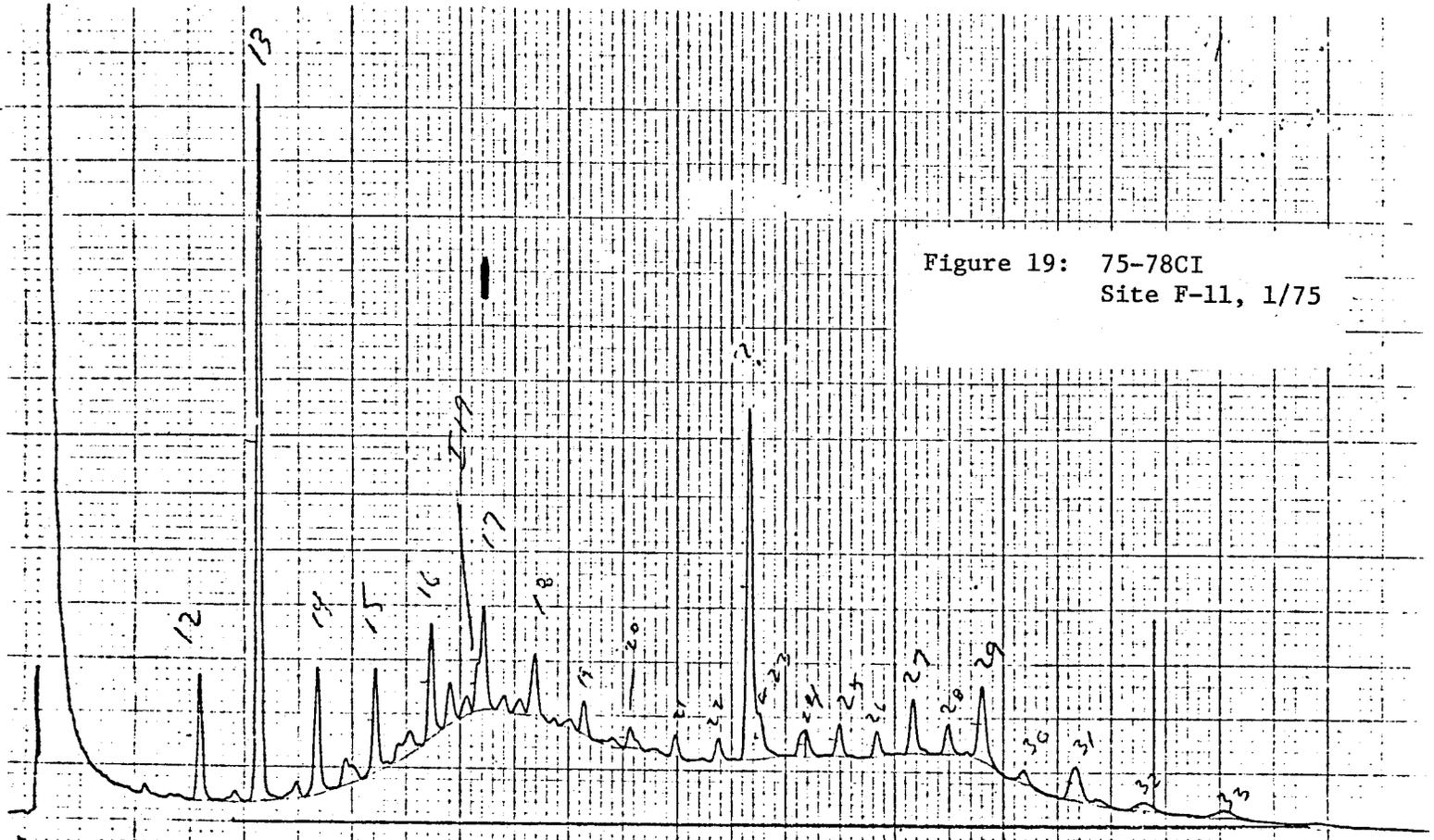
Figure 21:  HDB
Composite from Upper Bay,
12/72
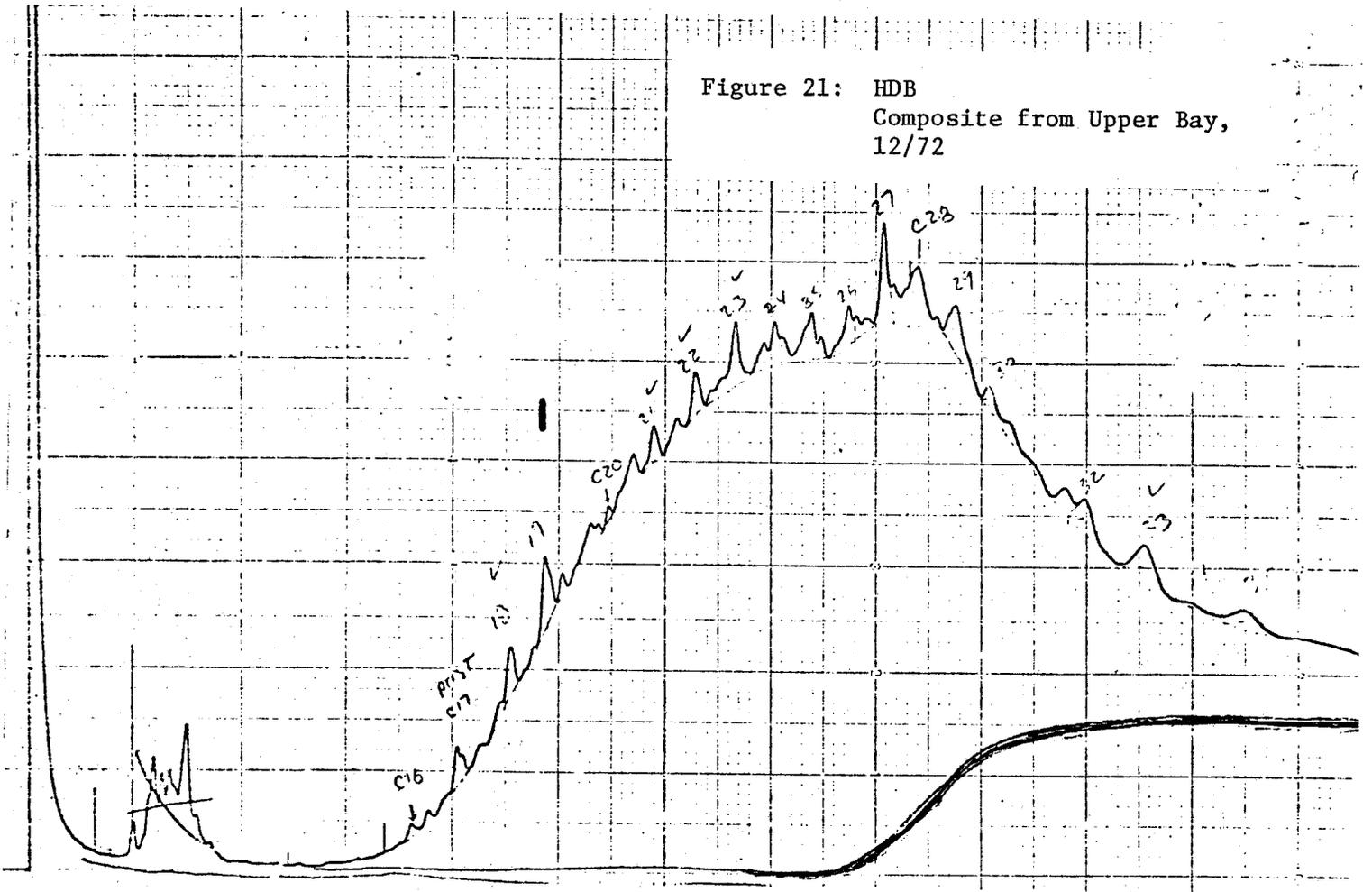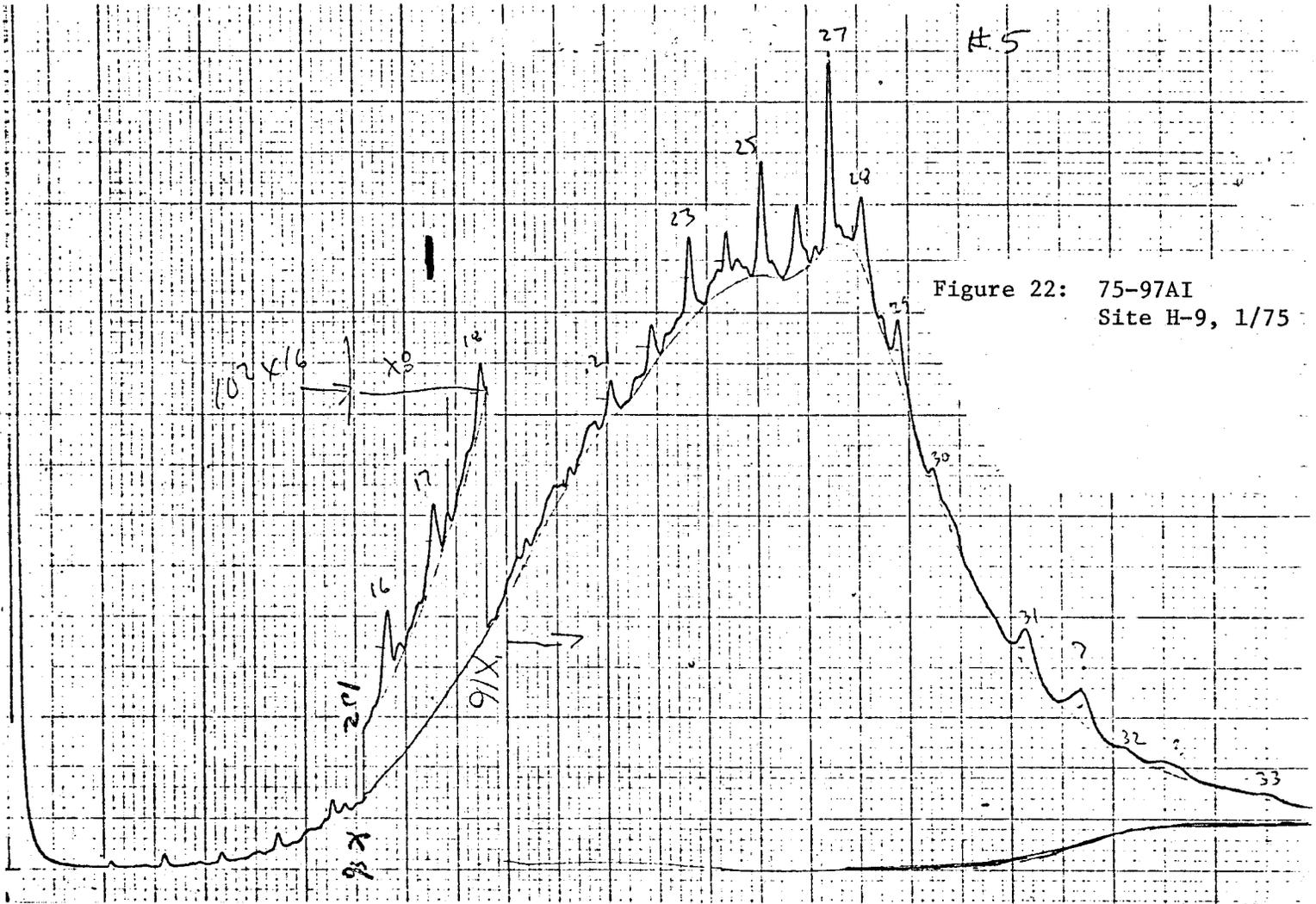
Figure 22: 75-97AI
Site H-9, 1/75

Figure 23: 75-126BI
Site AS-III, 4/2/75
(surface)

Figure 24: 75-36BII
Site D-4, 1/75

Figure 25: C-11-3I
4"-6" Depth, core at
AS-III, 1/75

check for vegprods
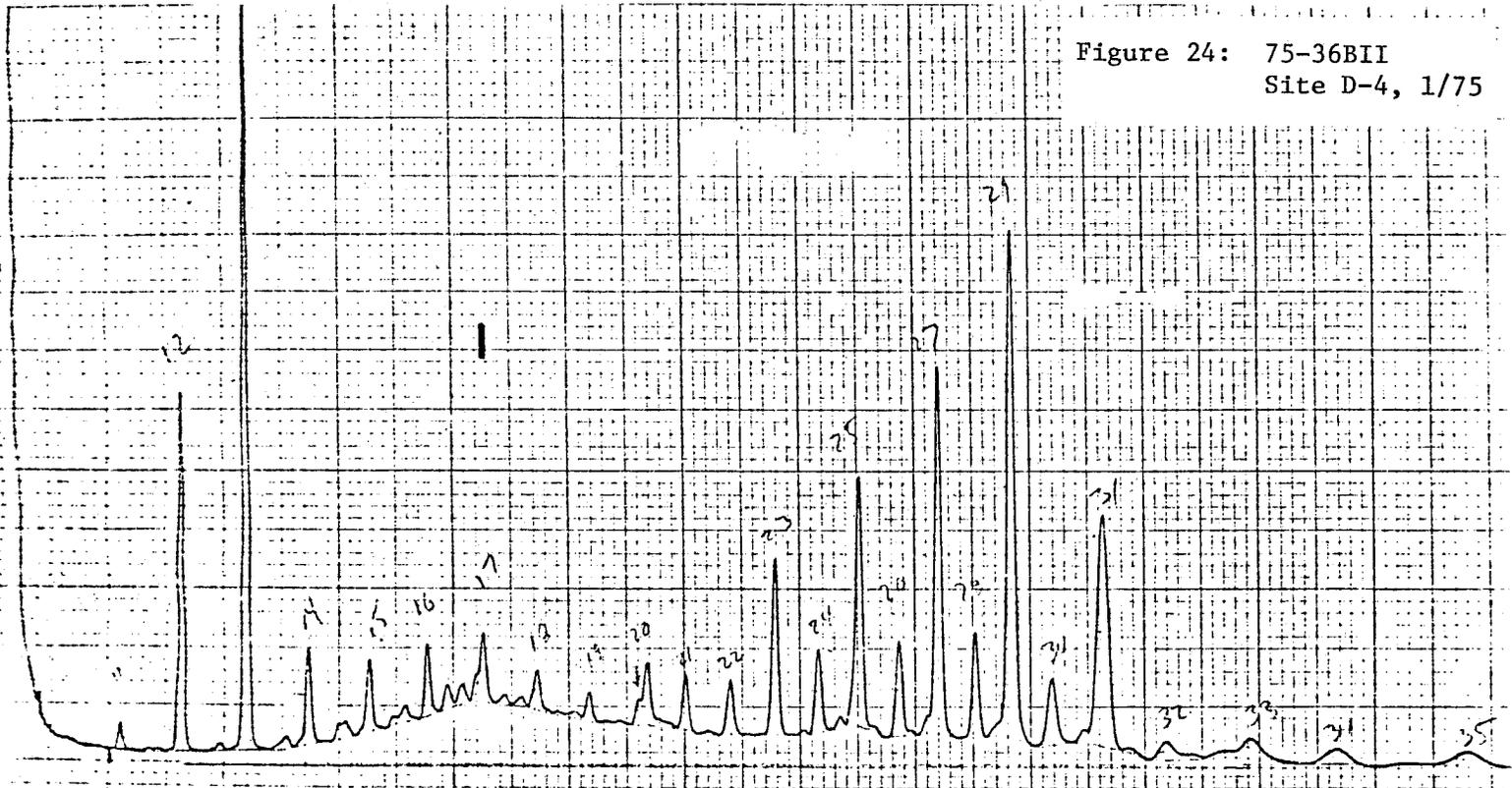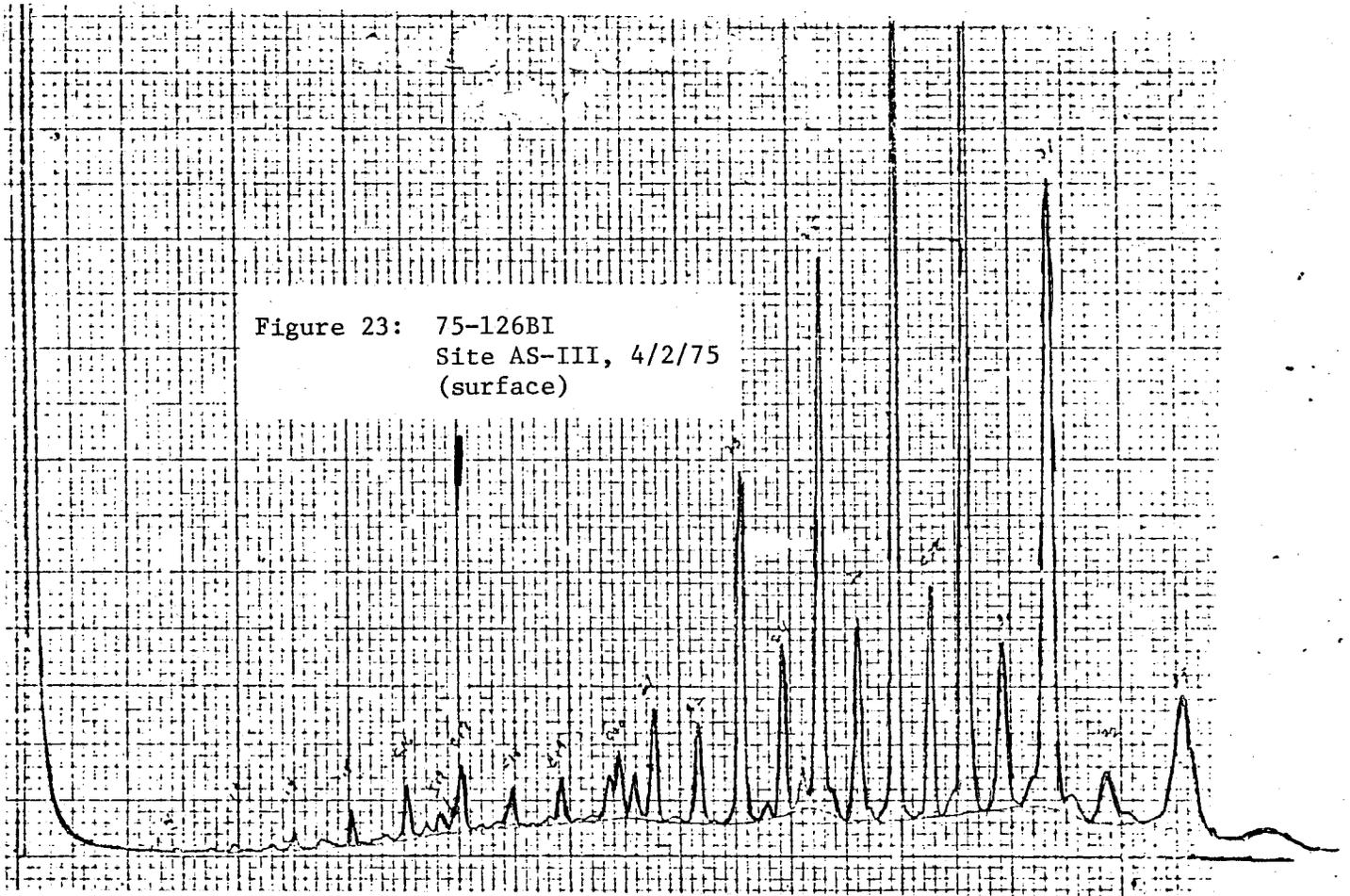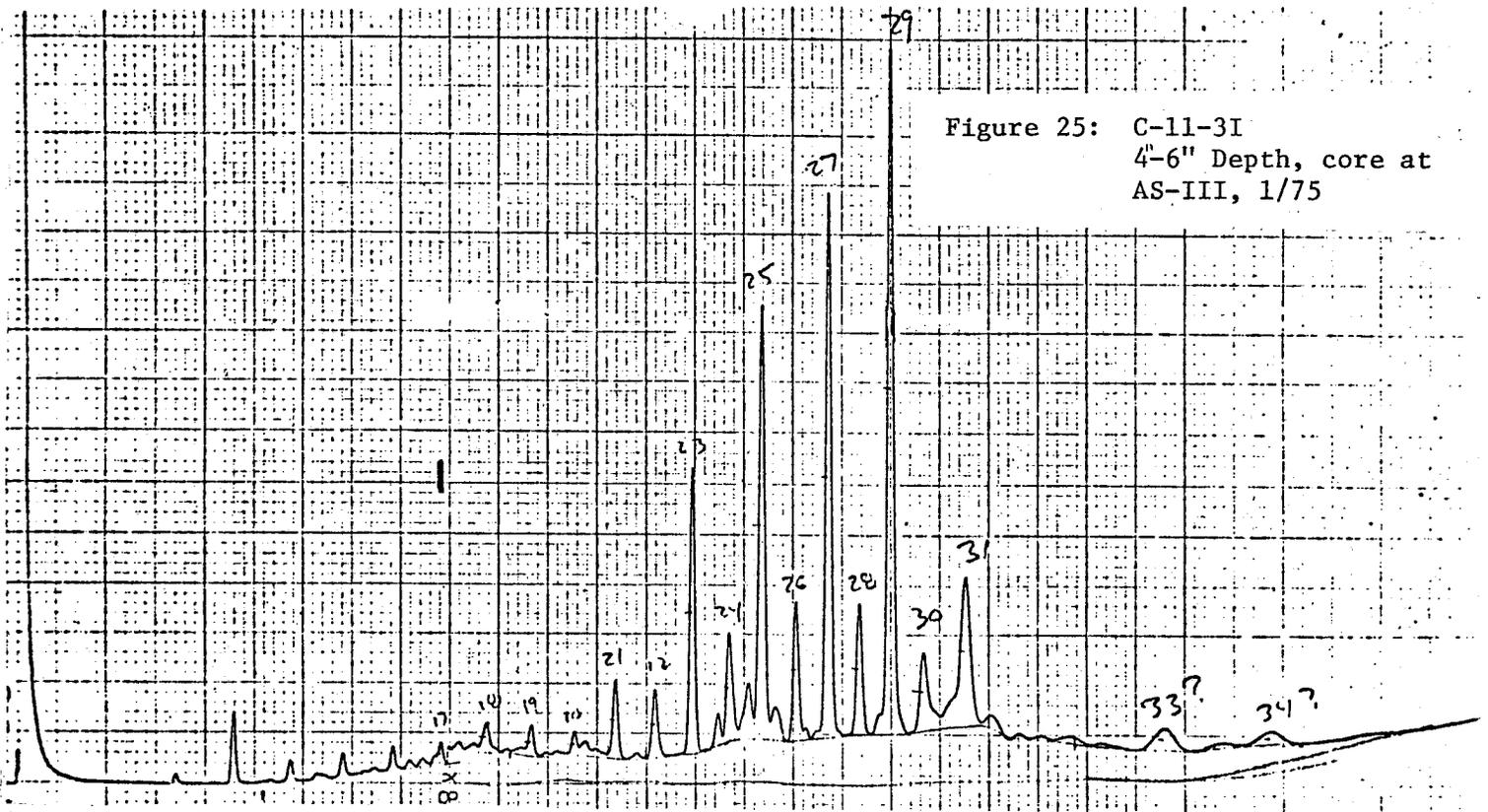


Figure 26:  C-11-13II
            24"-26" Depth, core at
            AS-III, 1/75
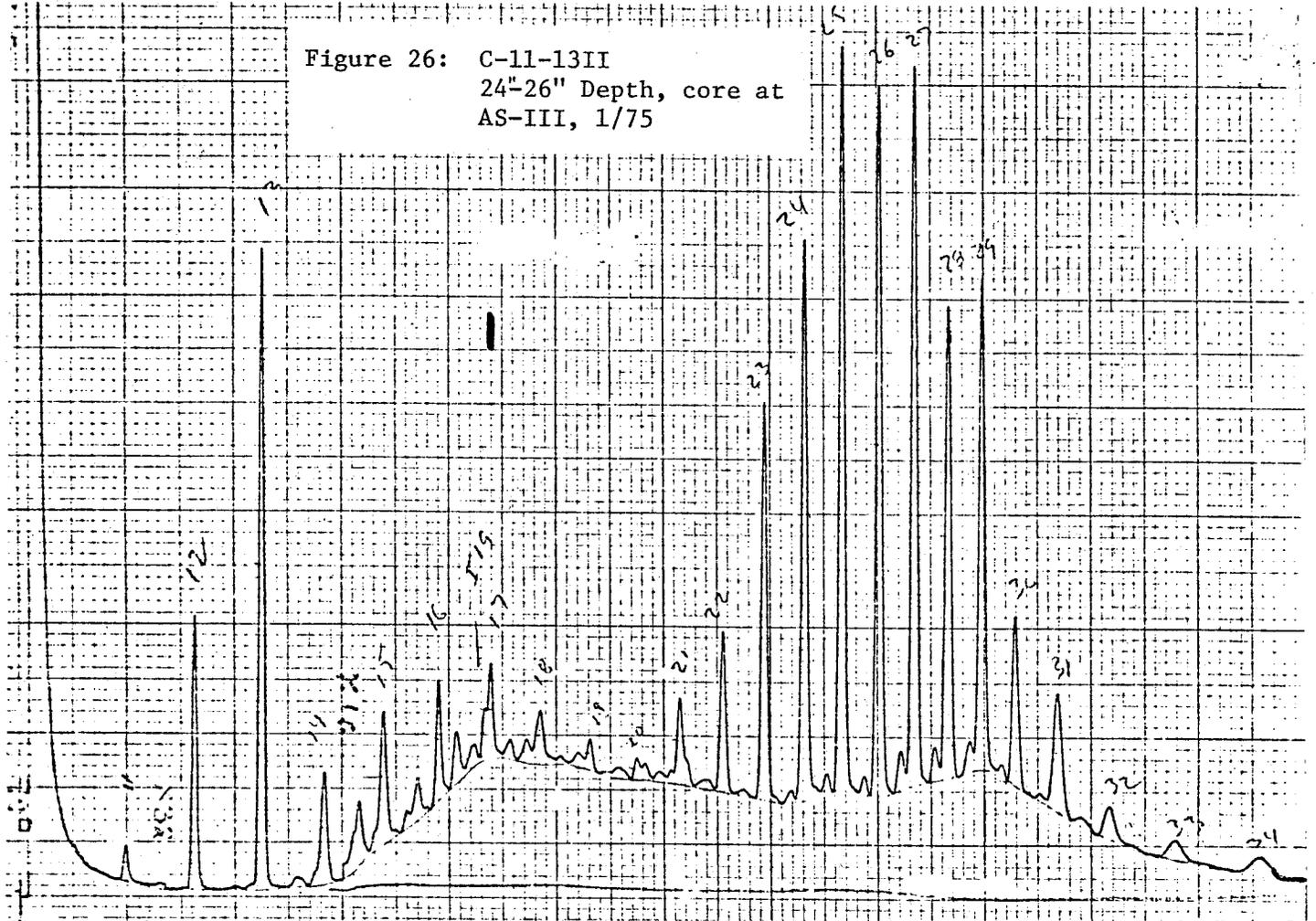
Figure 27: C-11-17I
32-34" Depth, core at
AS-III, 1/75

Figure 28: 75-25BI
Site C-6, 1/75

Figure 29: 75-1BII
Site A-1, 1/75



Figure 30: 75-104AII
Site A-1, 2/6/75

Figure 31: 75-27CI
Site C-8, 1/75
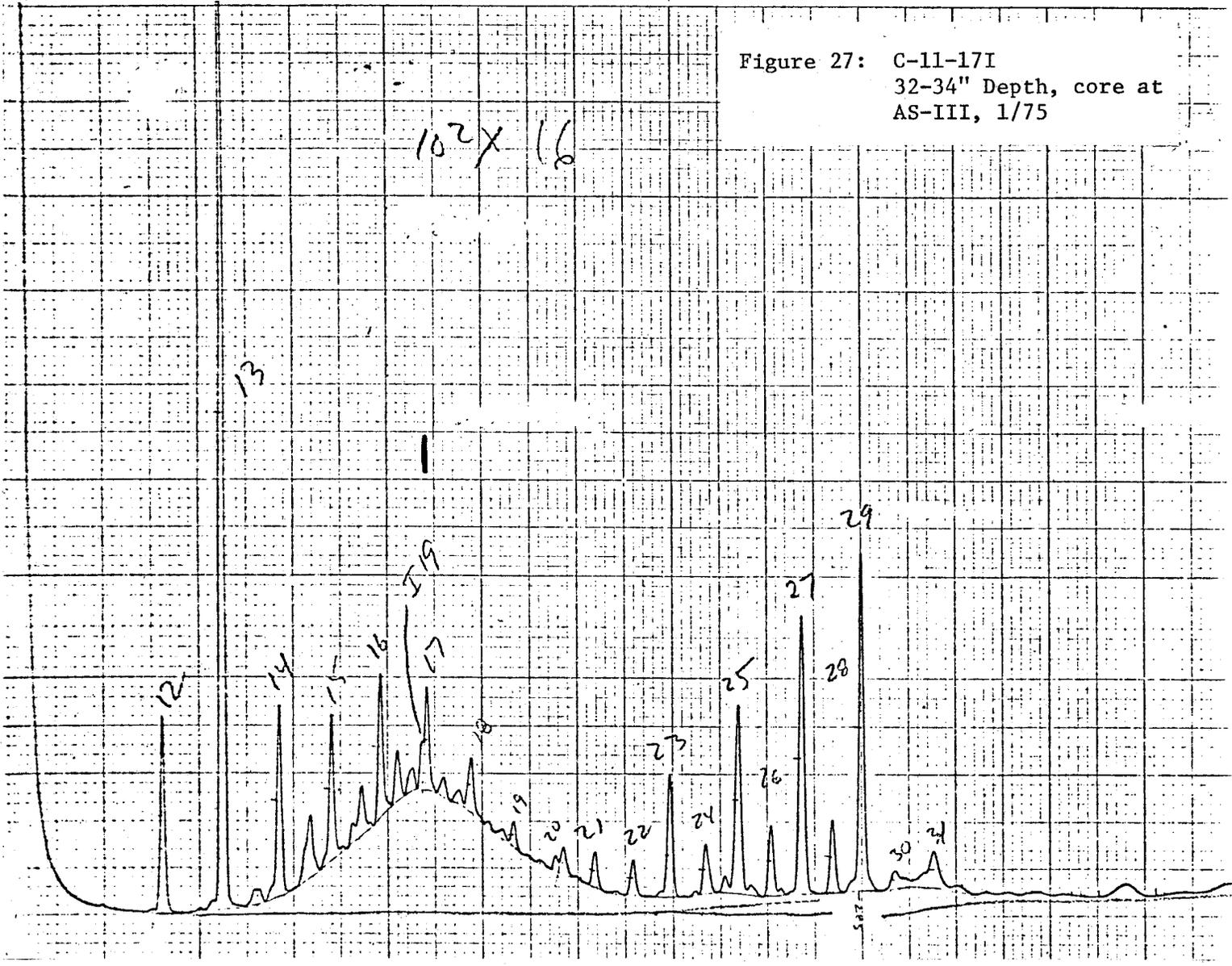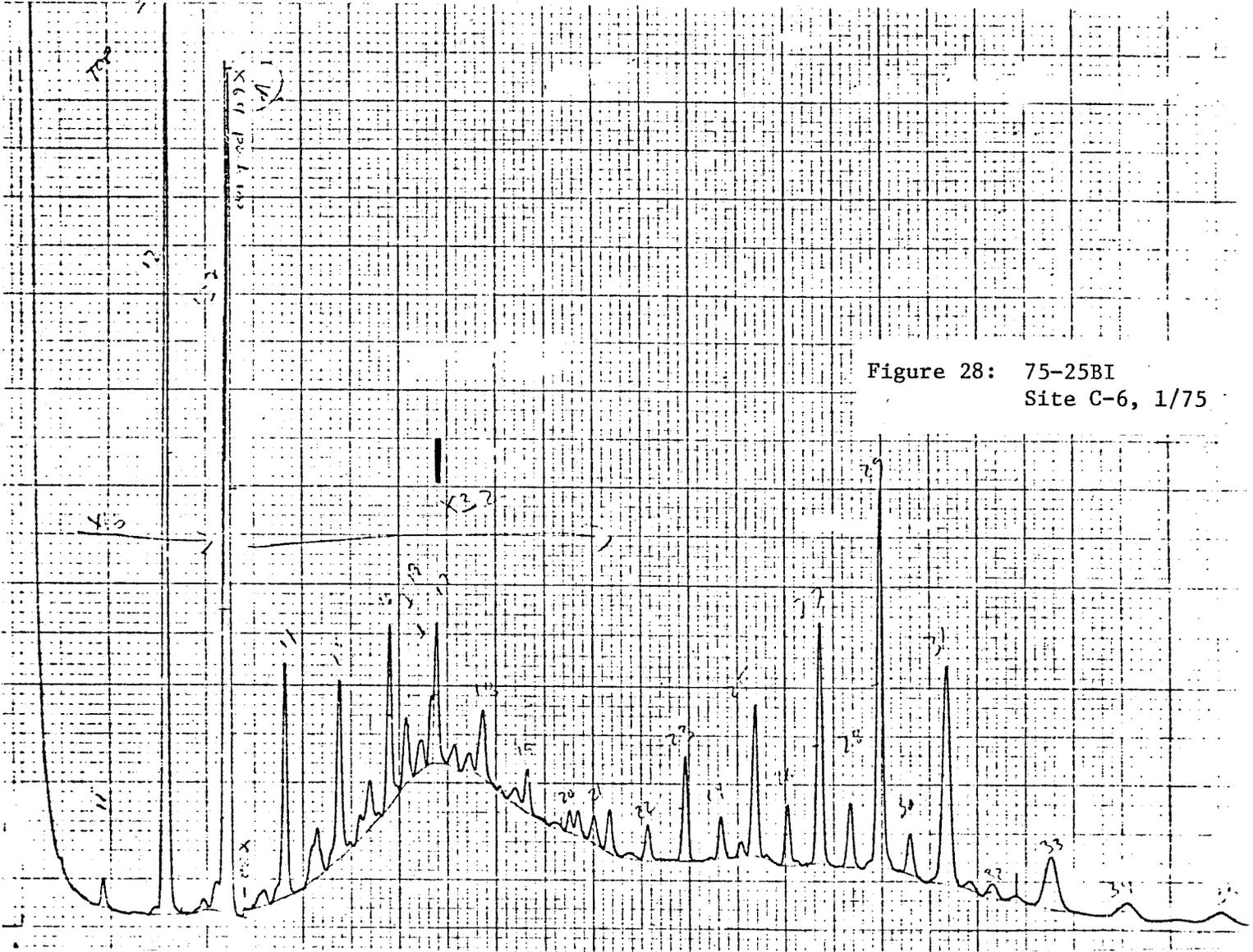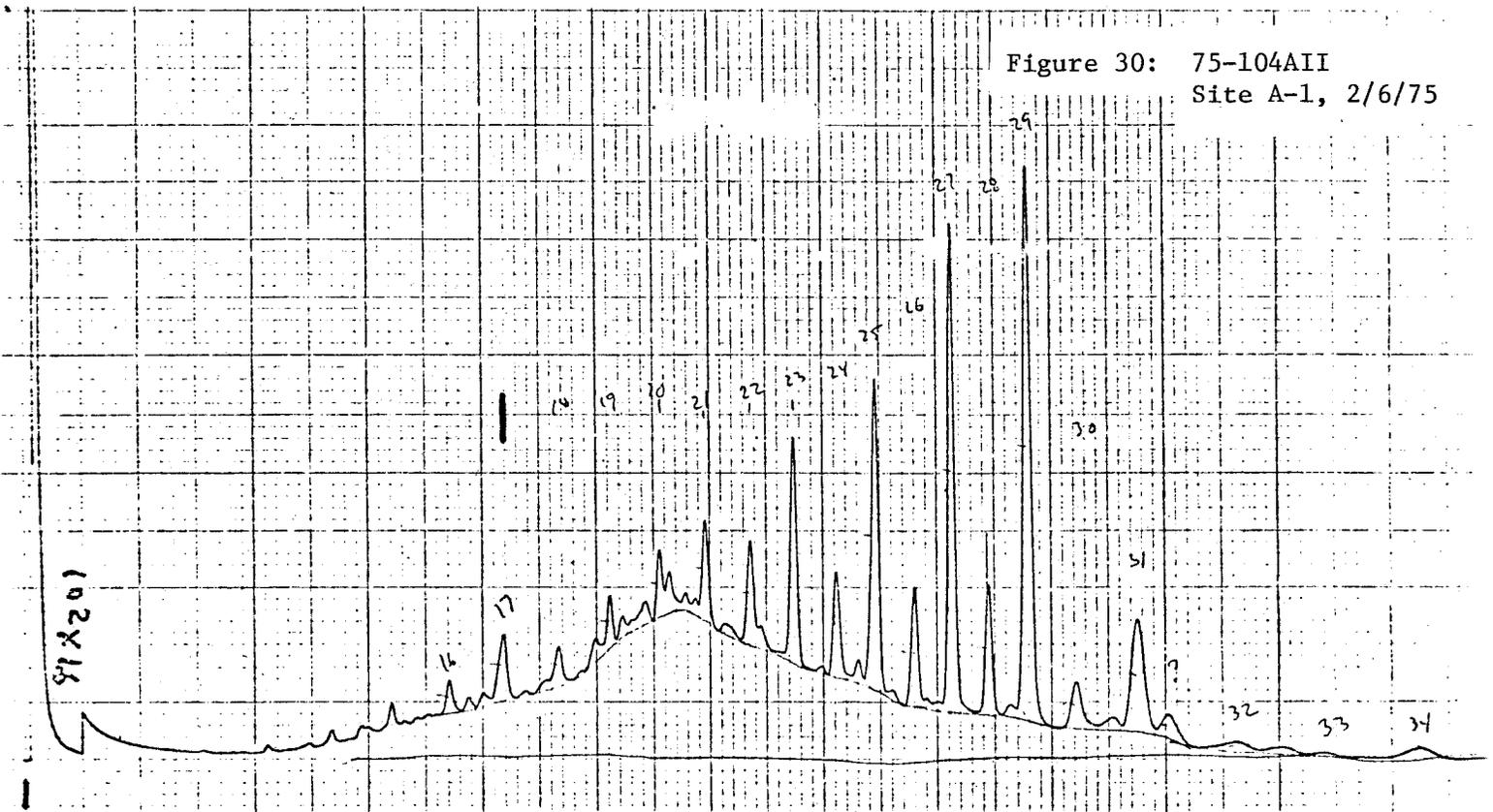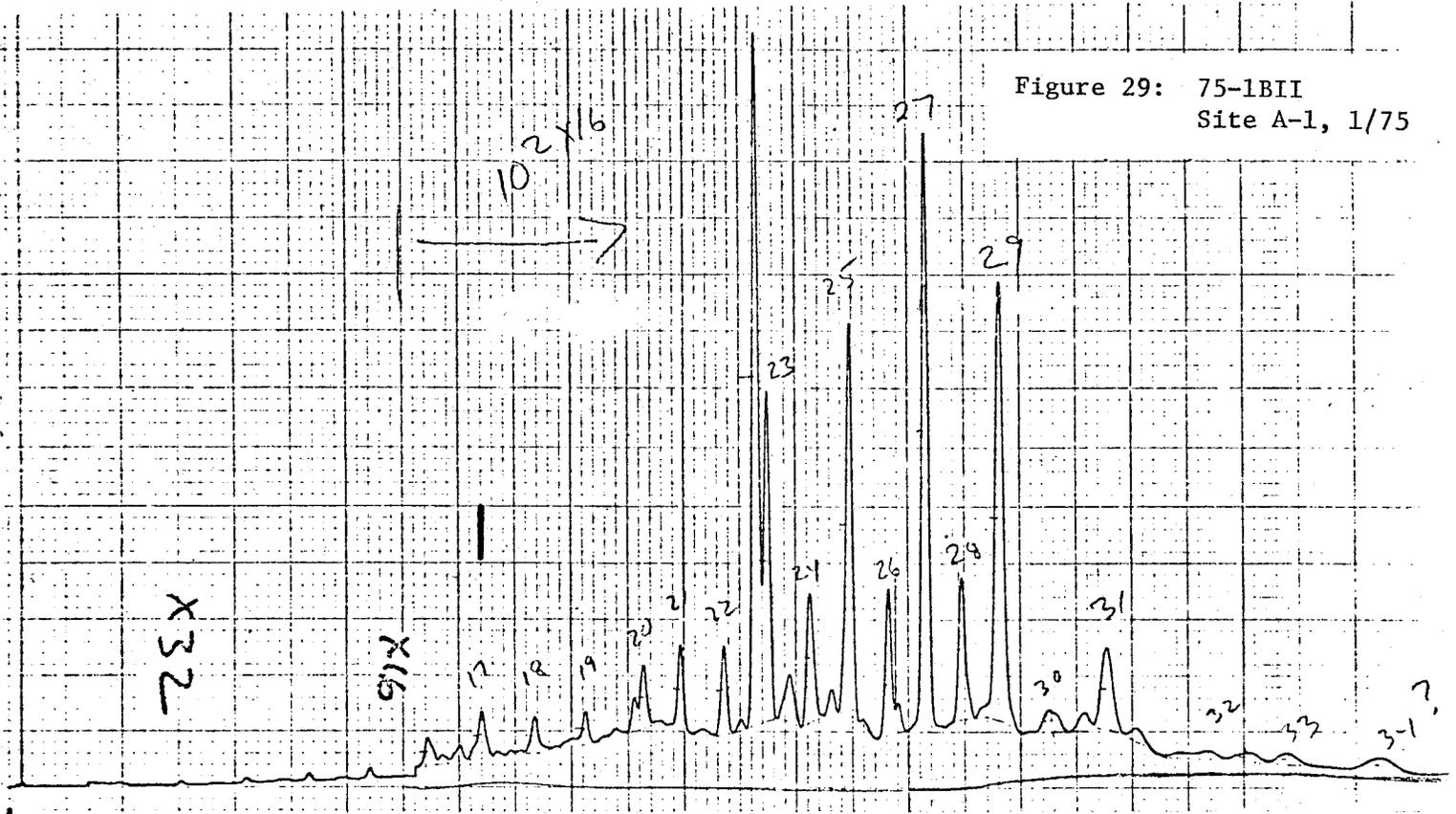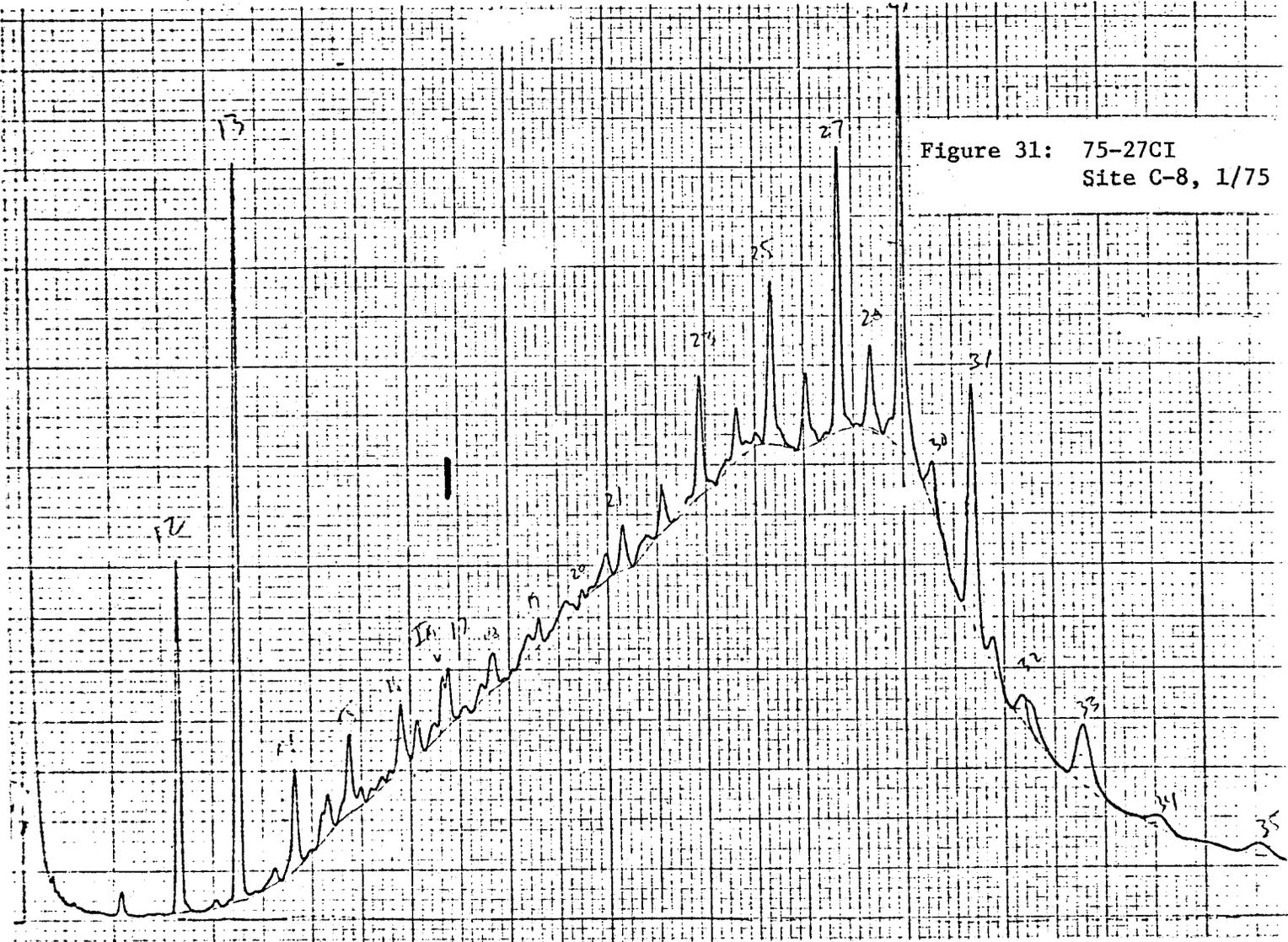
Figure 32: 75-102AI
Site C-8, 2/6/75

63
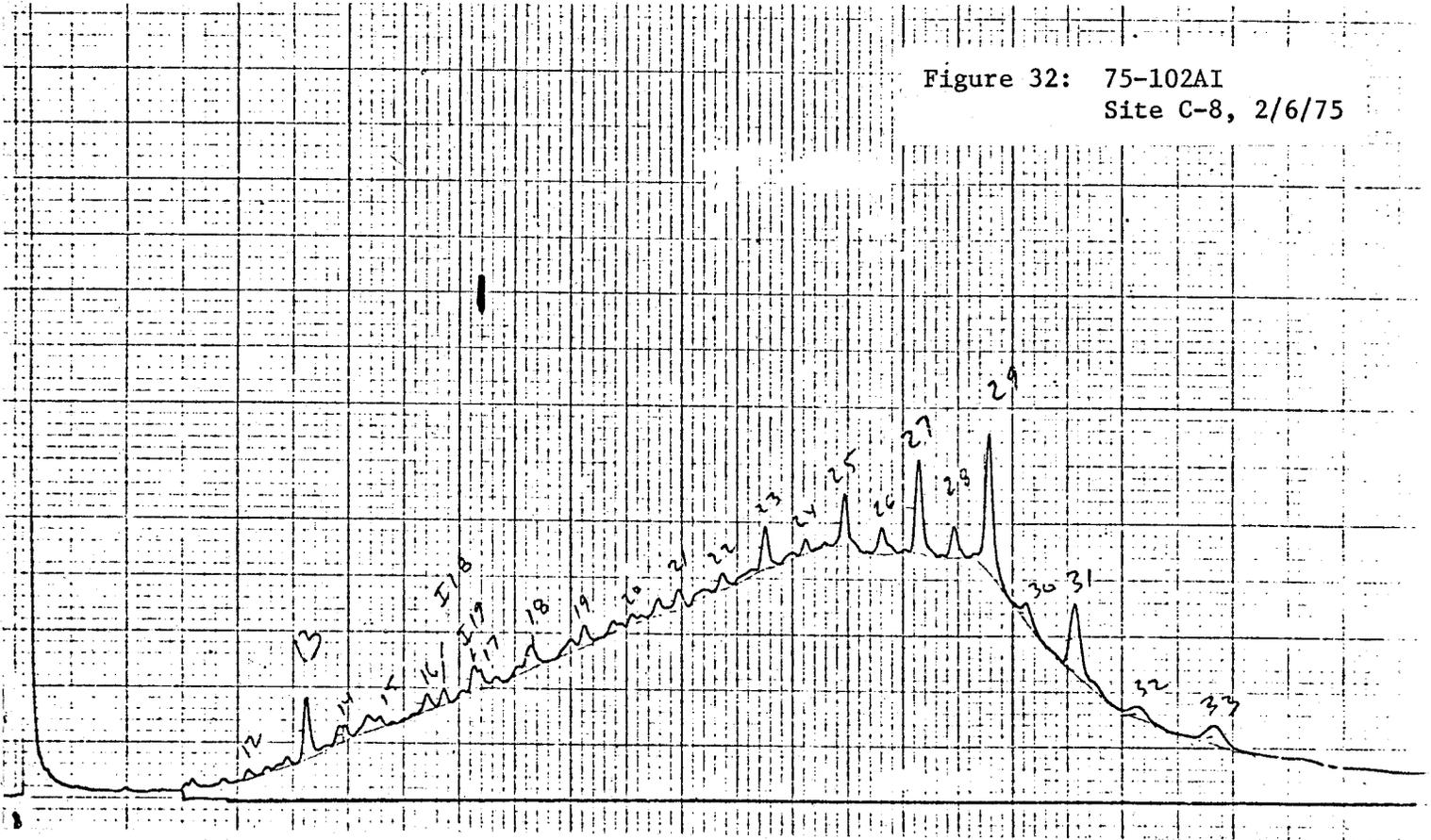


Figure 33:   75-27CI – Urea adduct
(cf. Fig. 31)

64
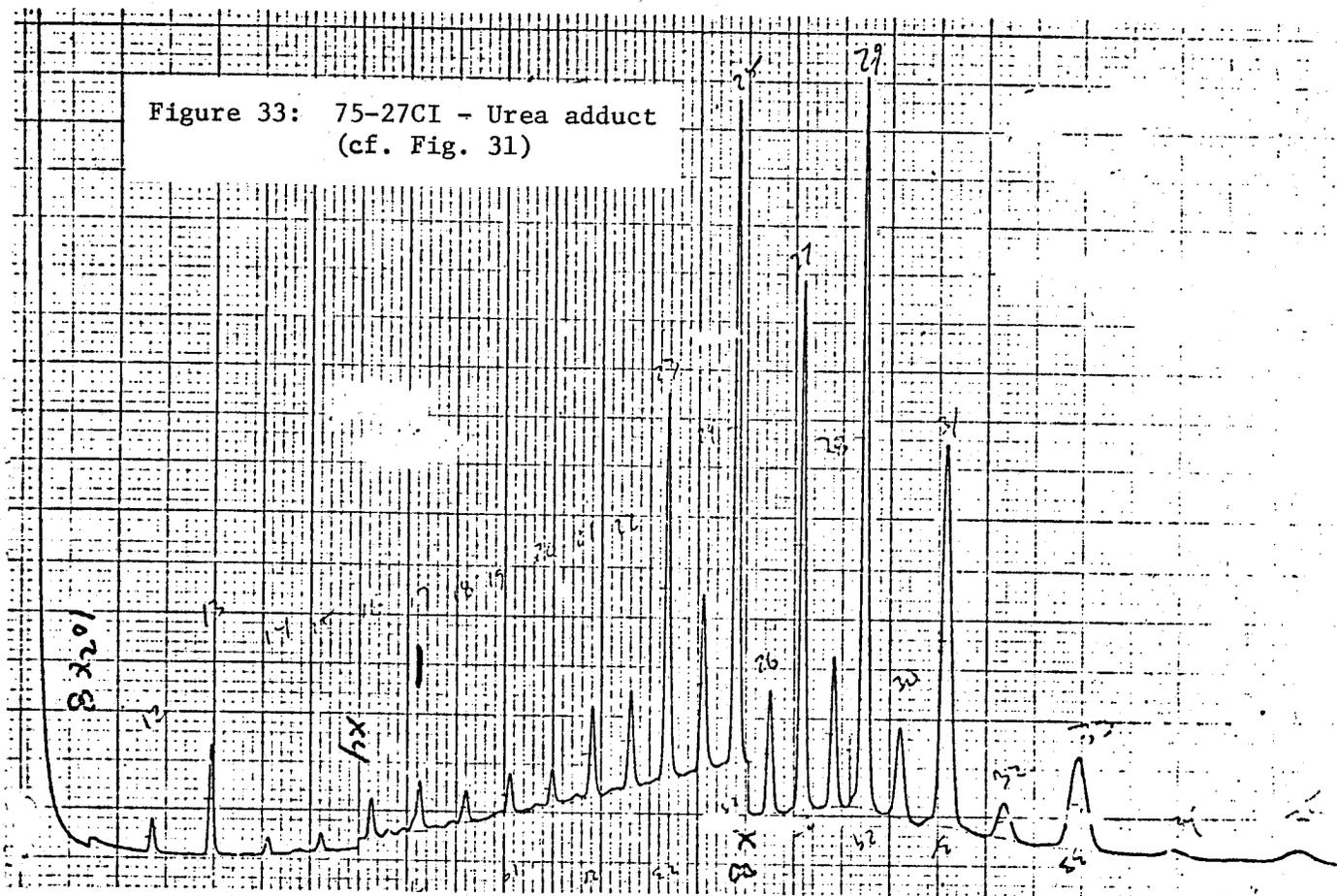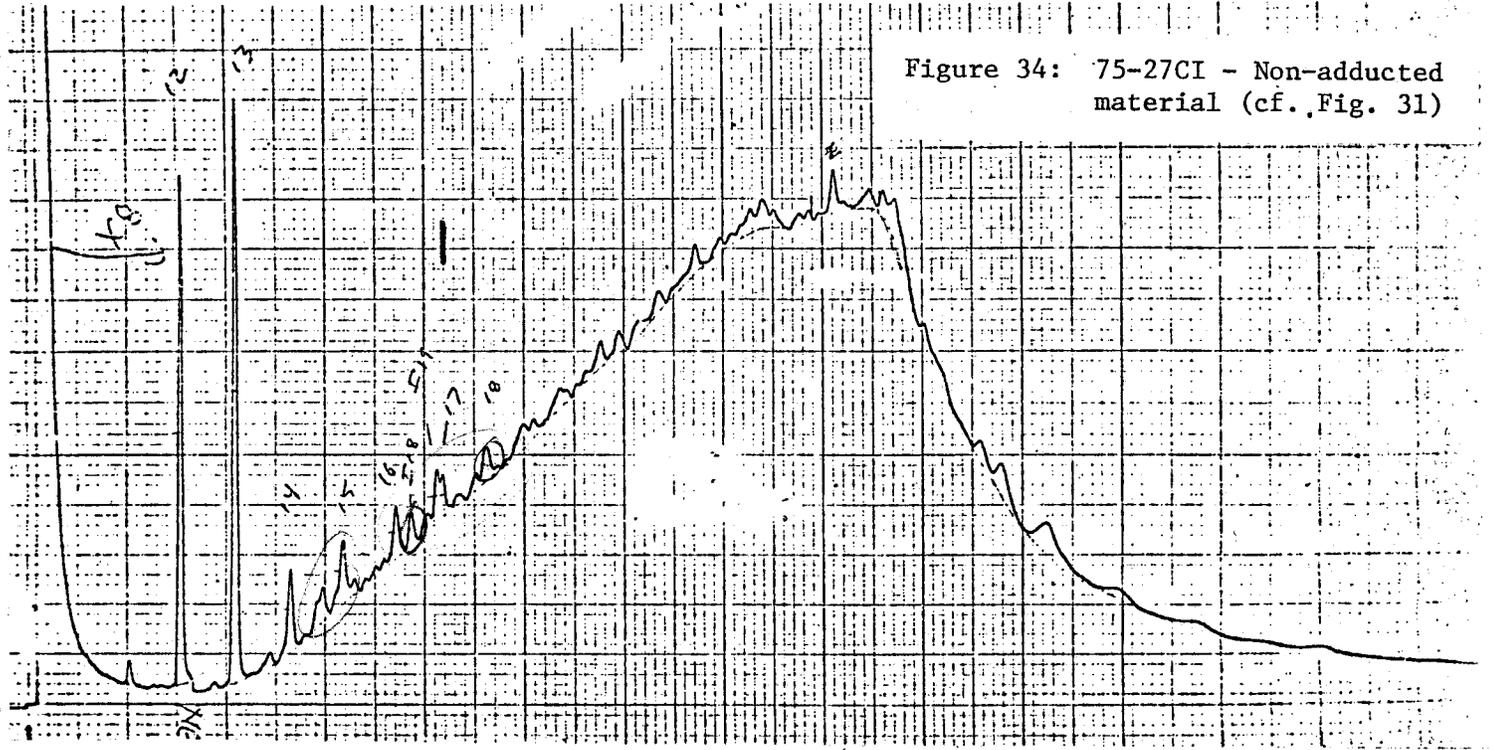


Figure 34: 75-27CI – Non-adducted material (cf. Fig. 31)

Figure 35: 75-106BI
Site A-3, 2/6/75



Figure 36: 75-5AI
Site AS-I, 1/75

Figure 37: 75-110BI
Site AS-I, 2/6/75

Figure 38: 75-16AII
Site B-8, 1/75

29/um
3.%
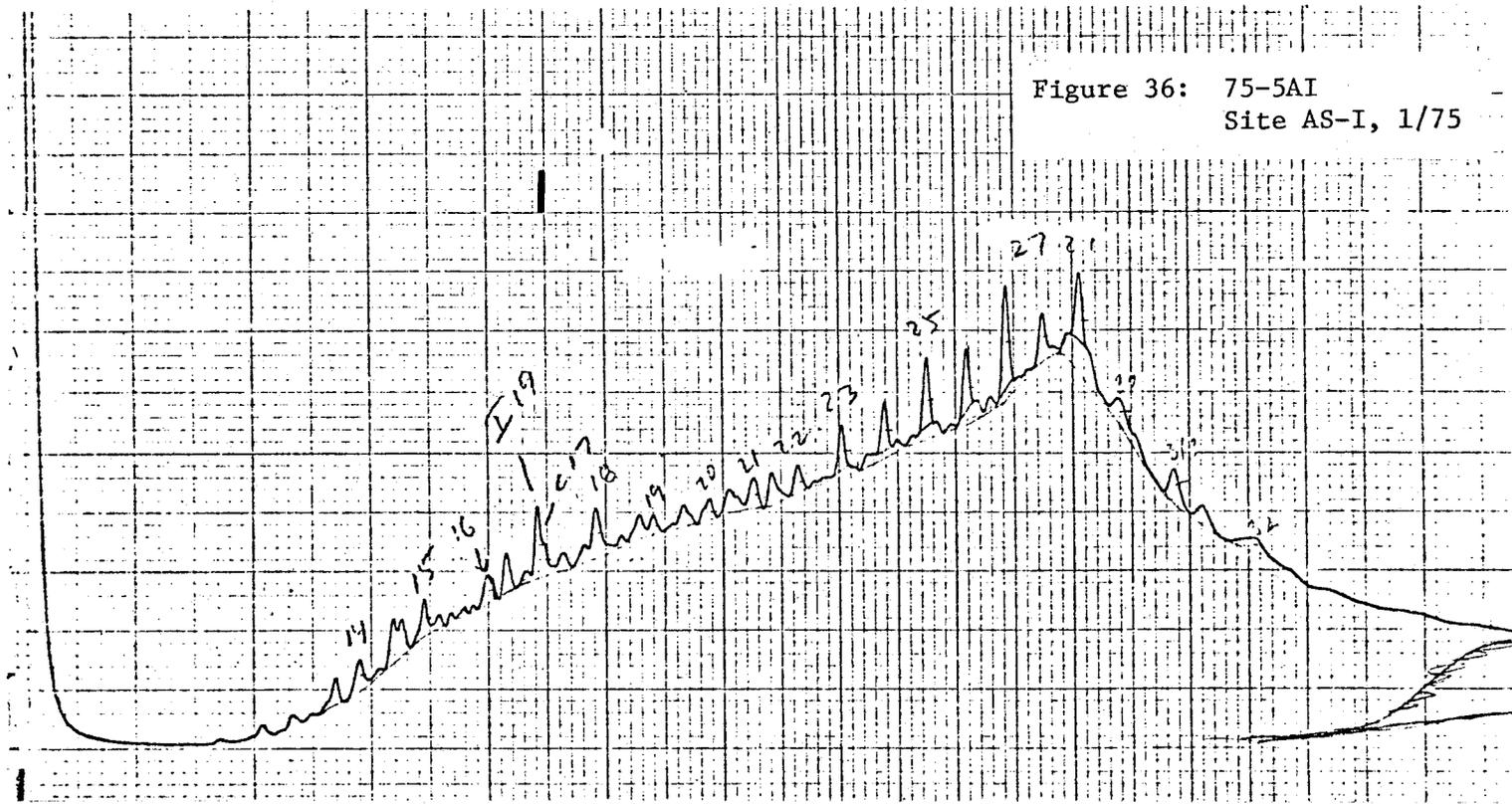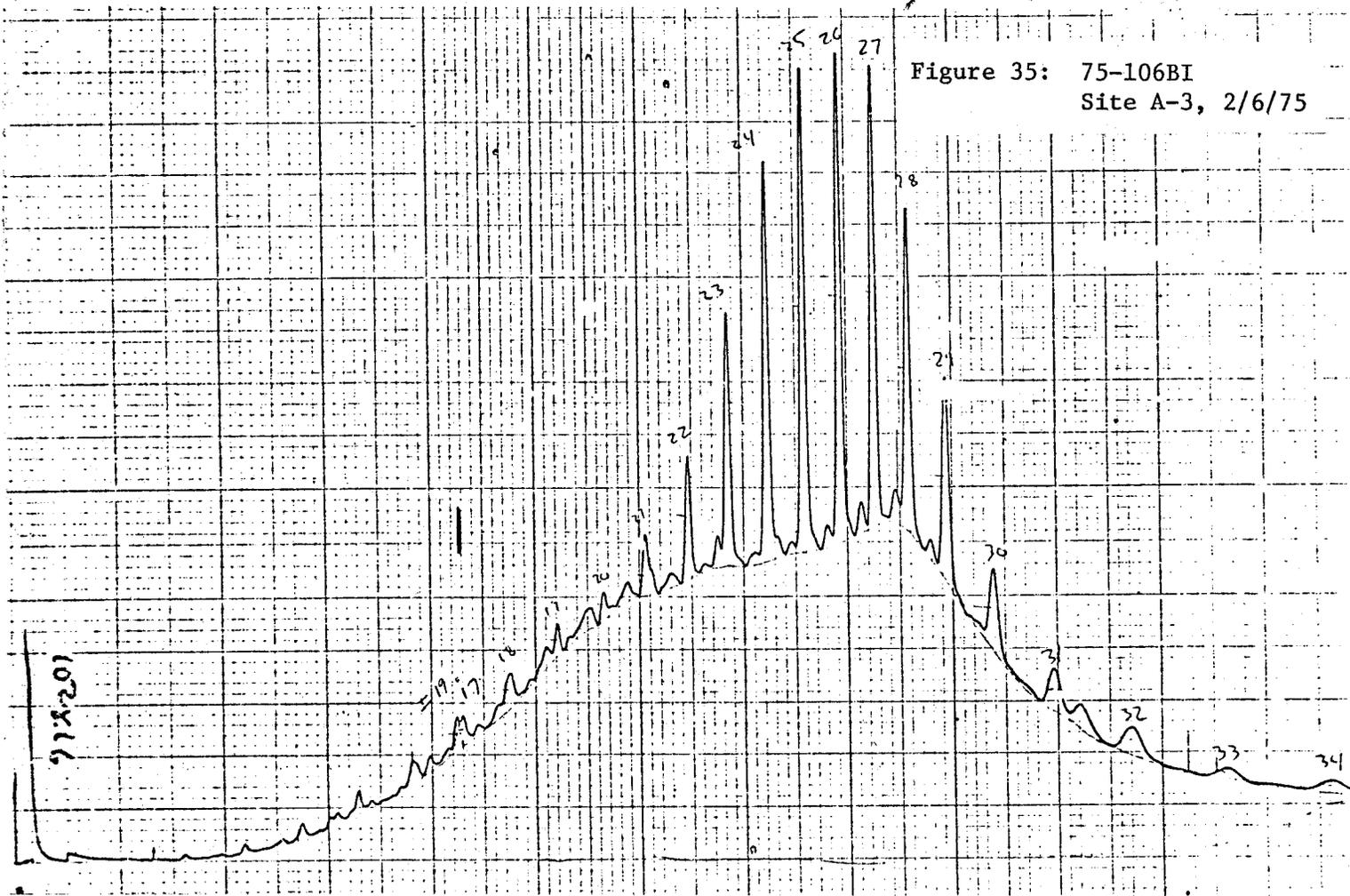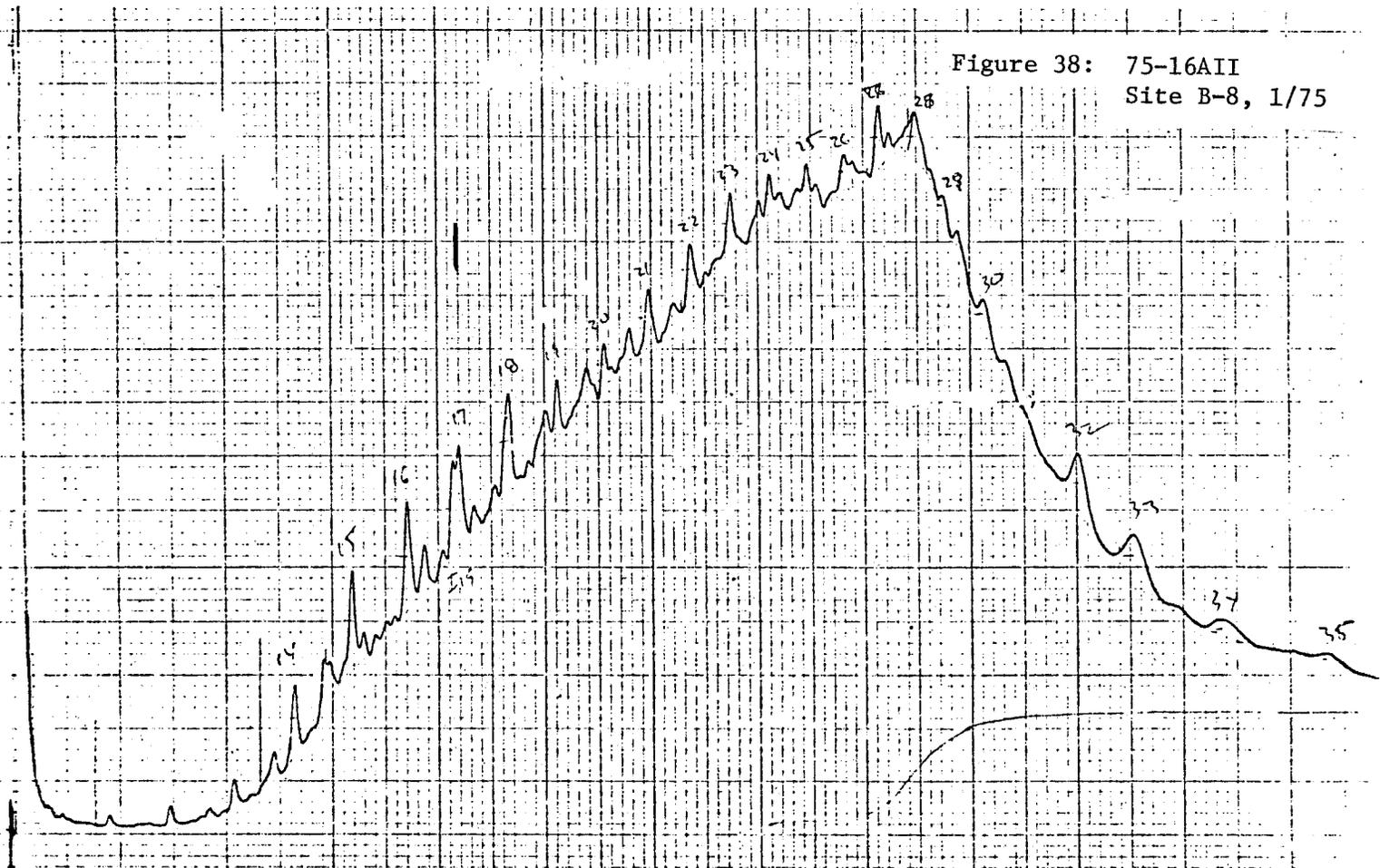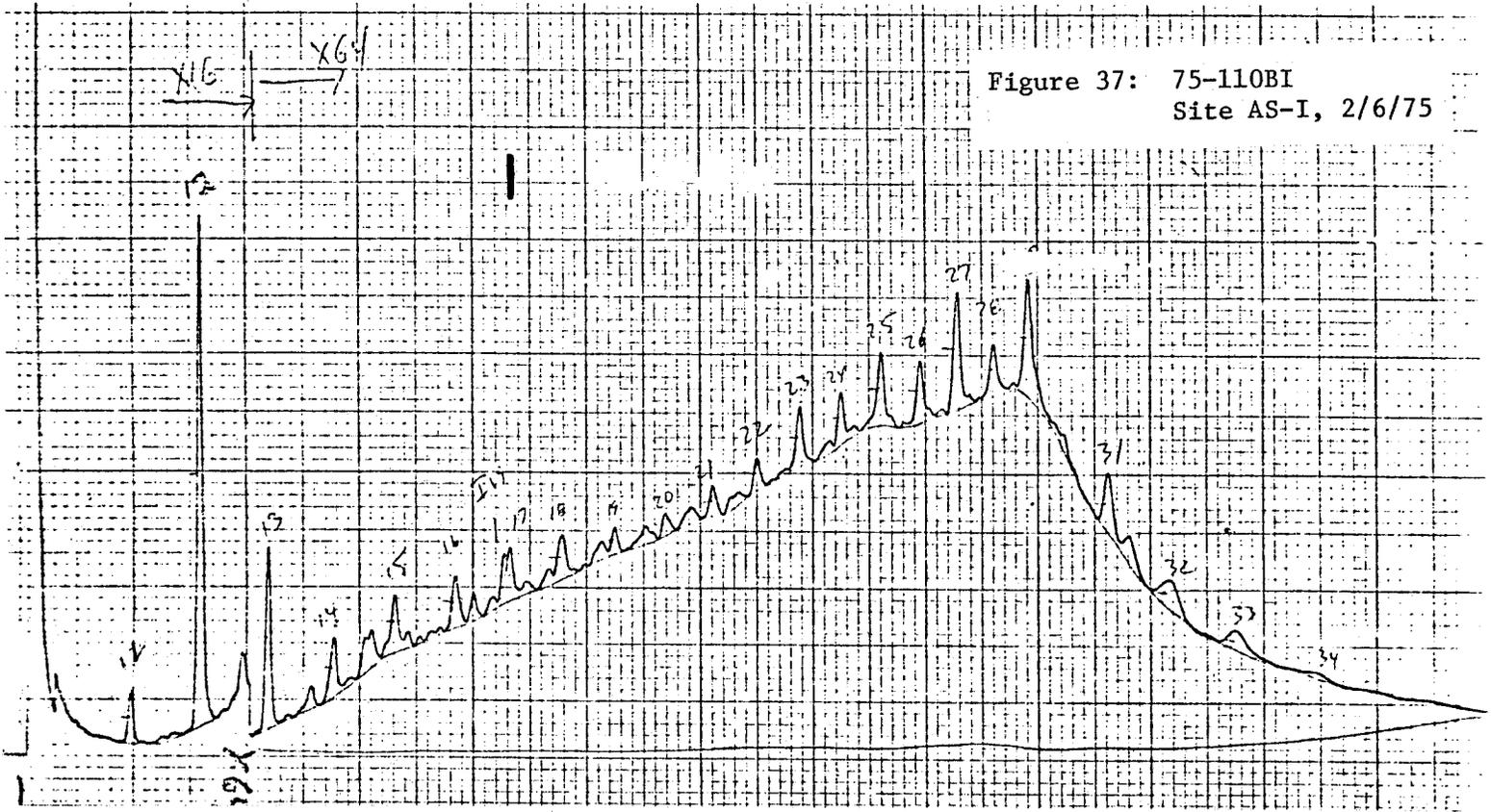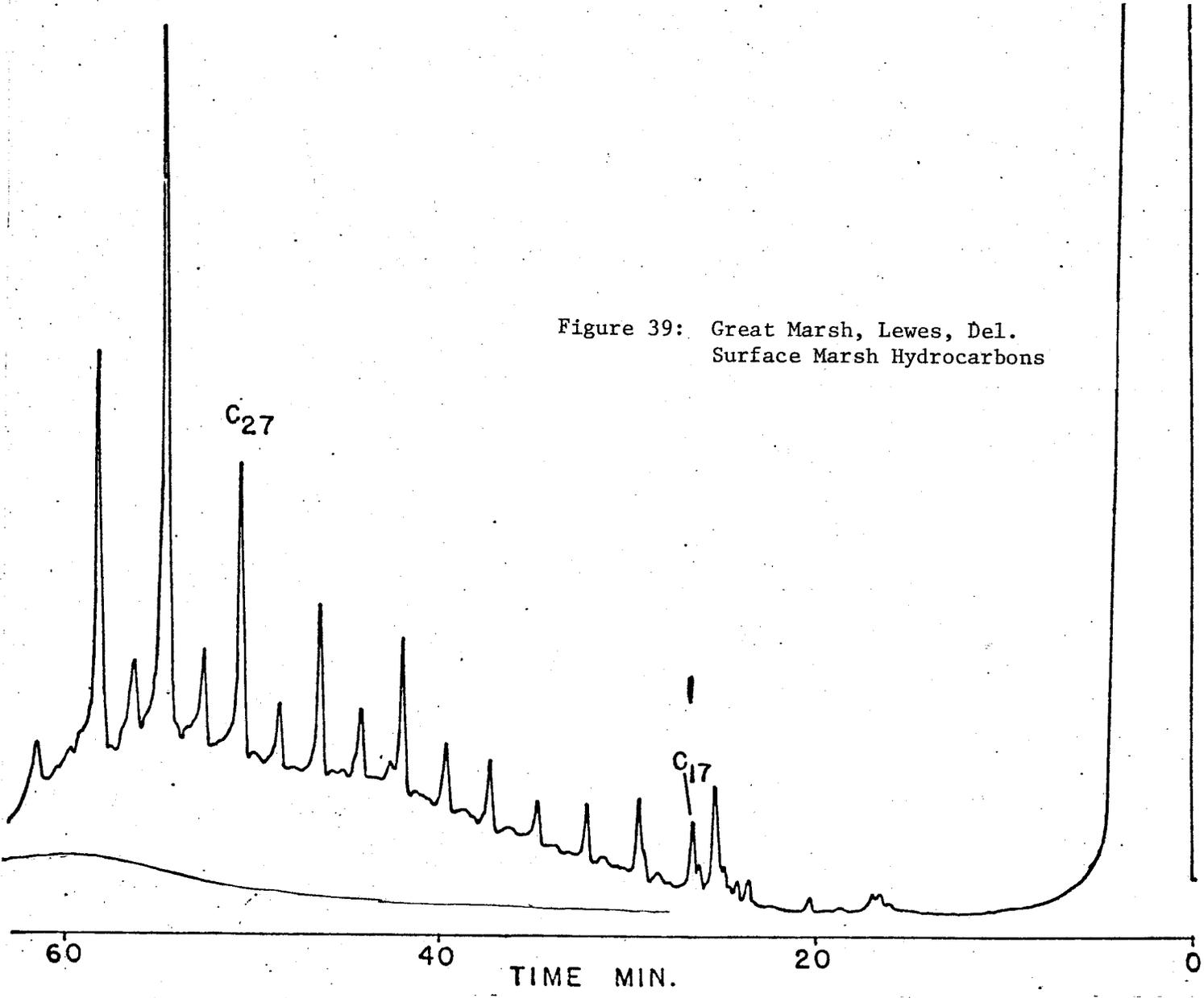


Figure 39:  Great Marsh, Lewes, Del.
Surface Marsh Hydrocarbons

$C_{27}$

$C_{17}$

60            40            20            0

TIME  MIN.

Figure 40: Soil Sample, Sussex County, Del.
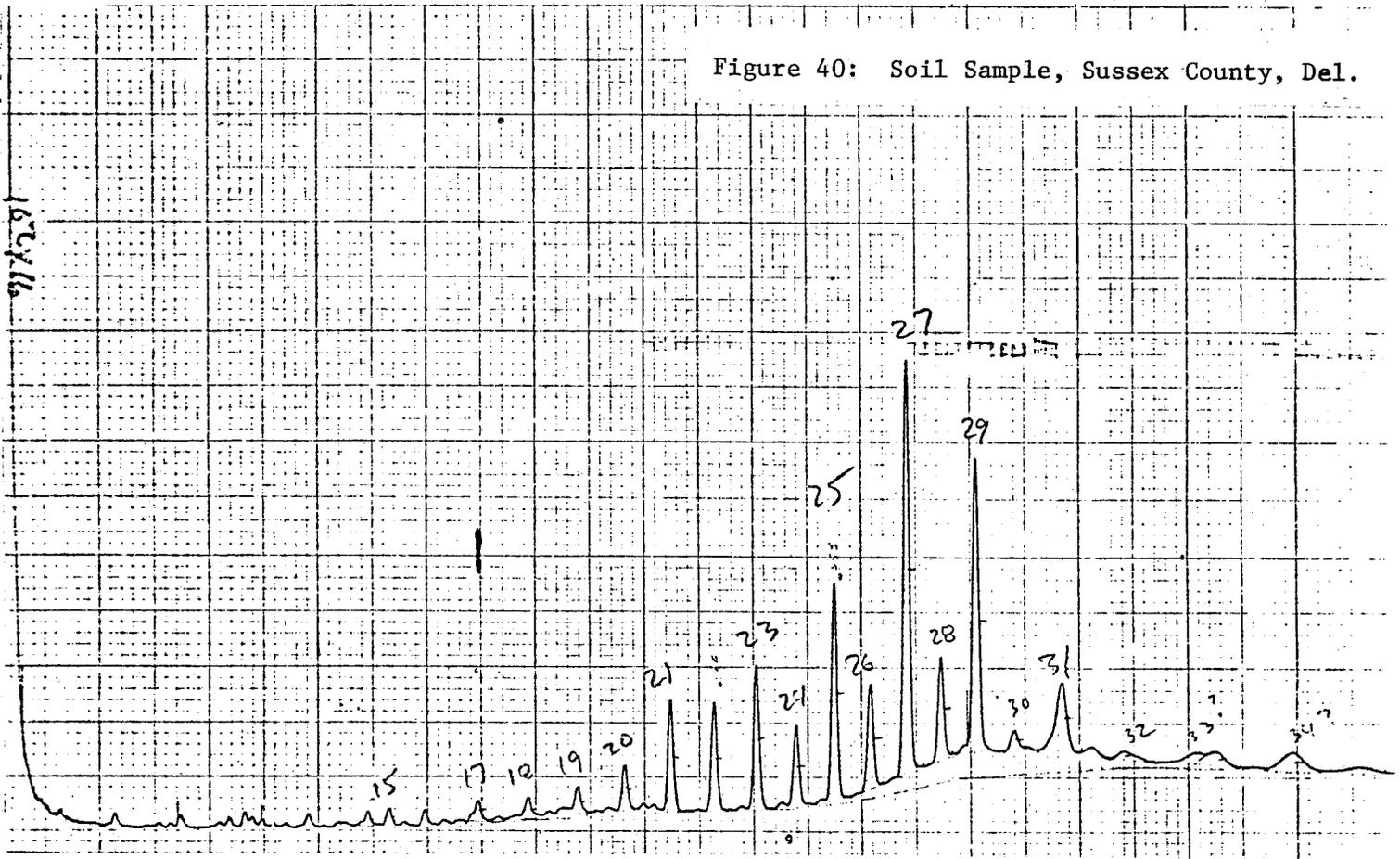


Figure 41: Great Marsh Core
180-200 cm
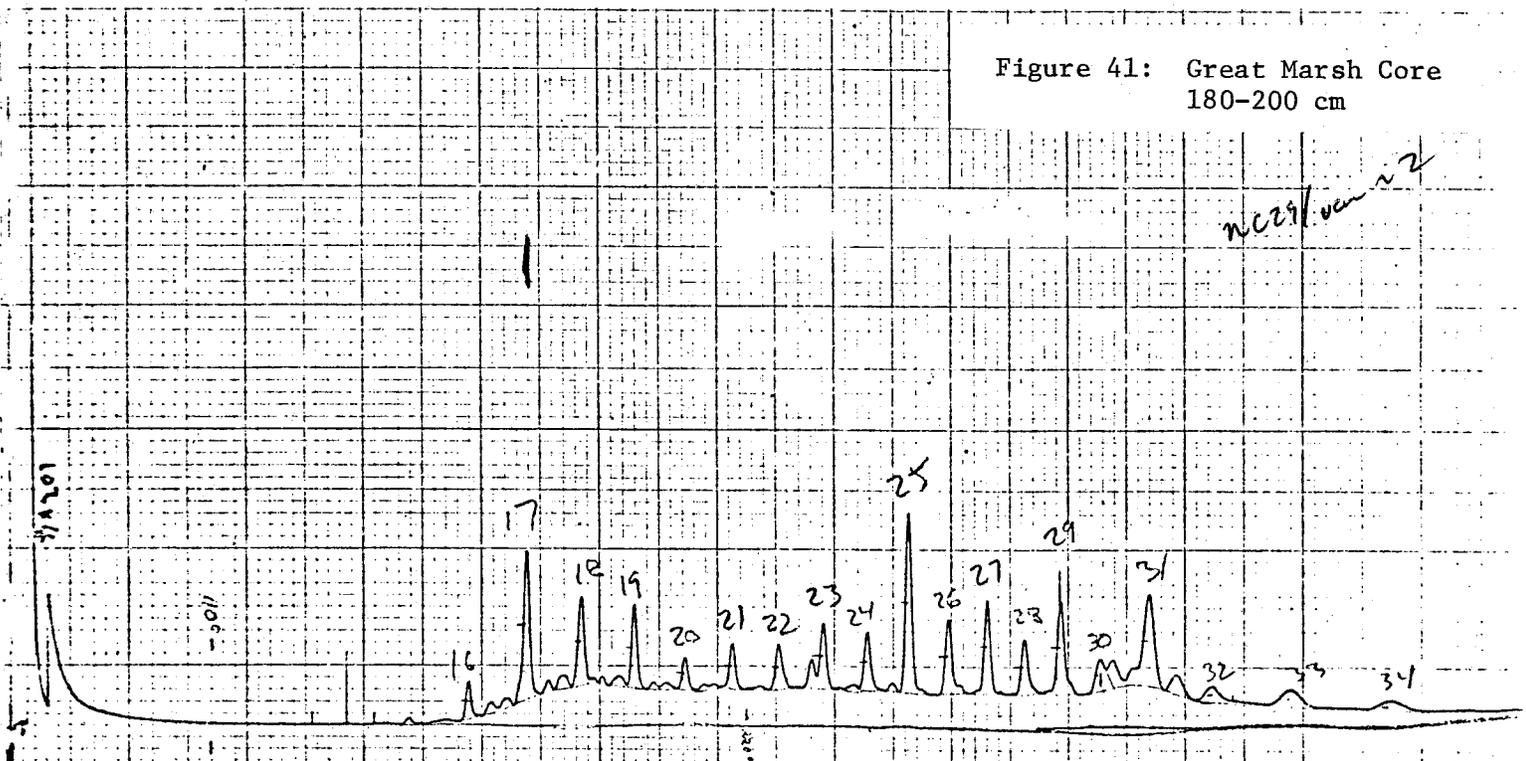
Figure 42:   Great Marsh Core
320-340 cm
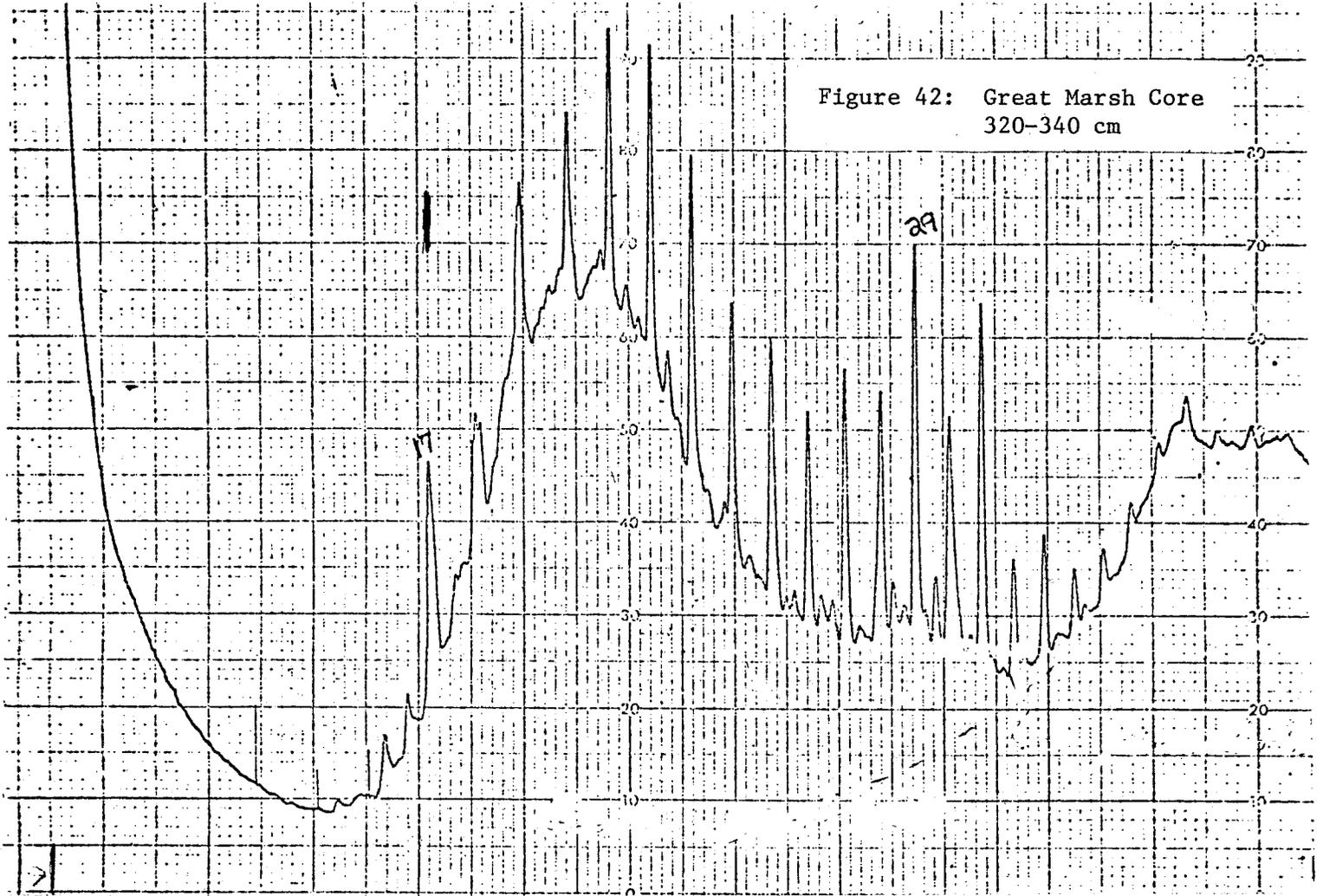
Figure 43: Suspended Particulate HC (Diatom Filter) AS-I, Jan. 1975
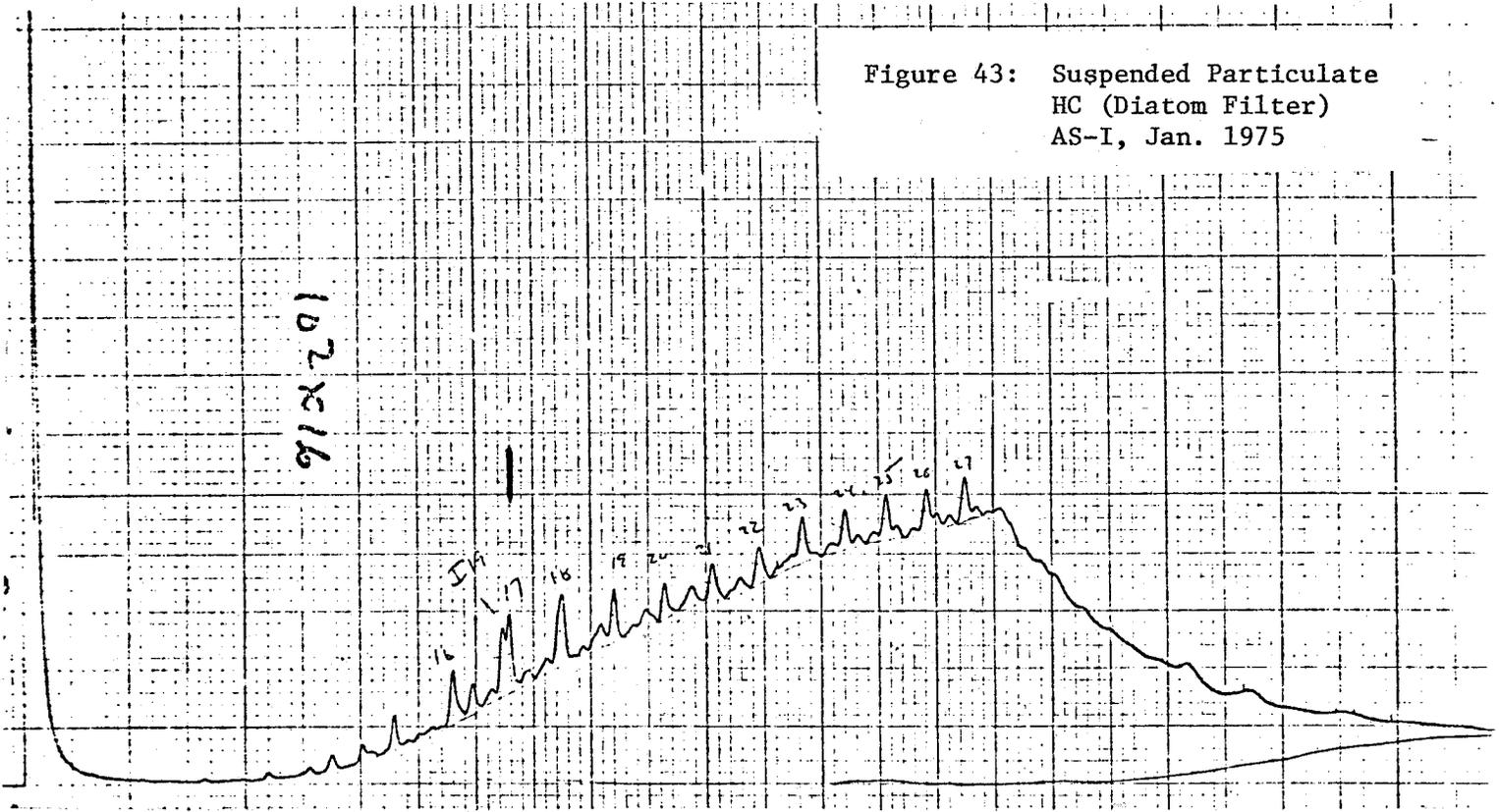


Figure 44: Suspended Particulate Hydrocarbons AS-III Jan. 1975
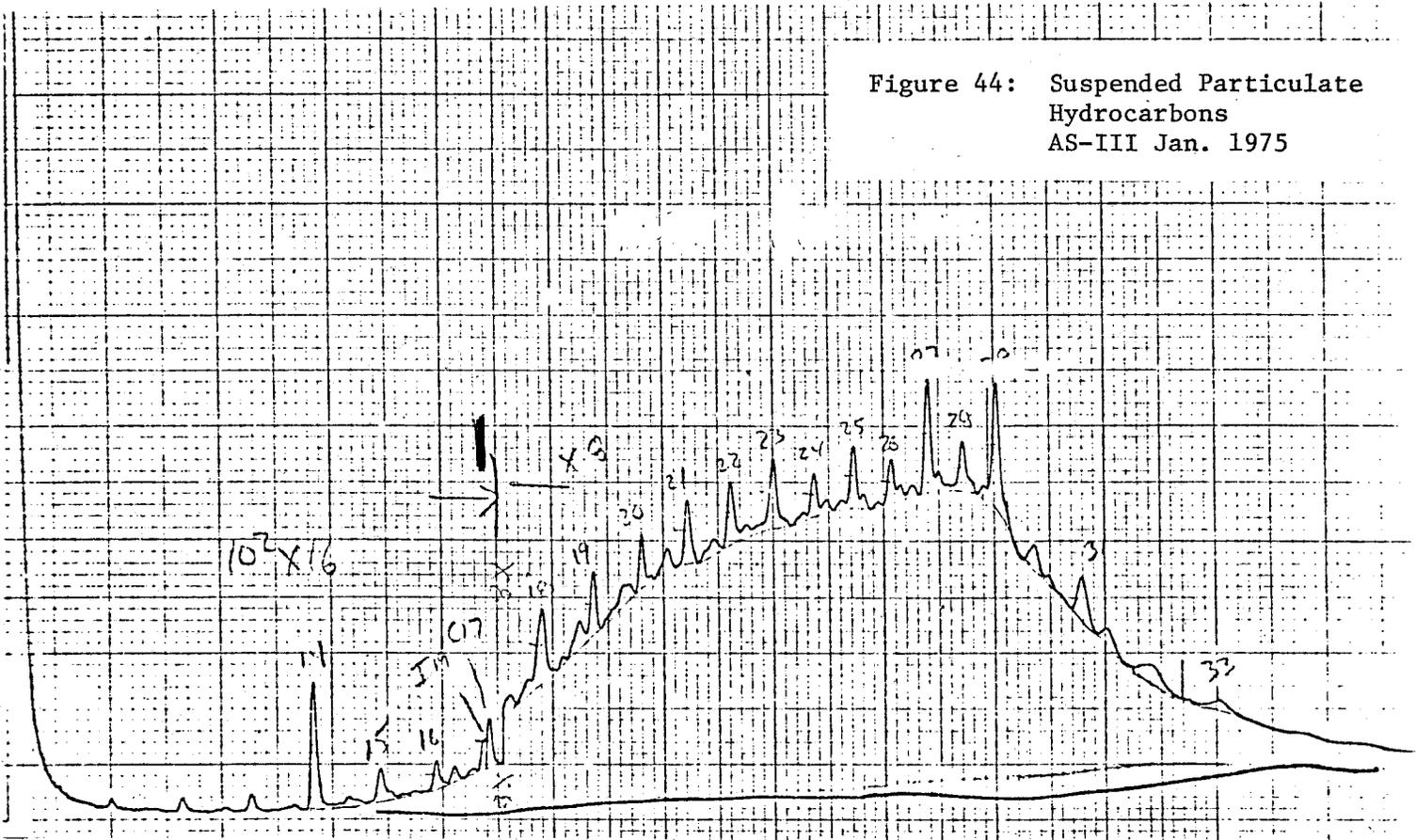
Figure 45: Suspended Particulate Hydrocarbons AS-IV Jan. 1975

72
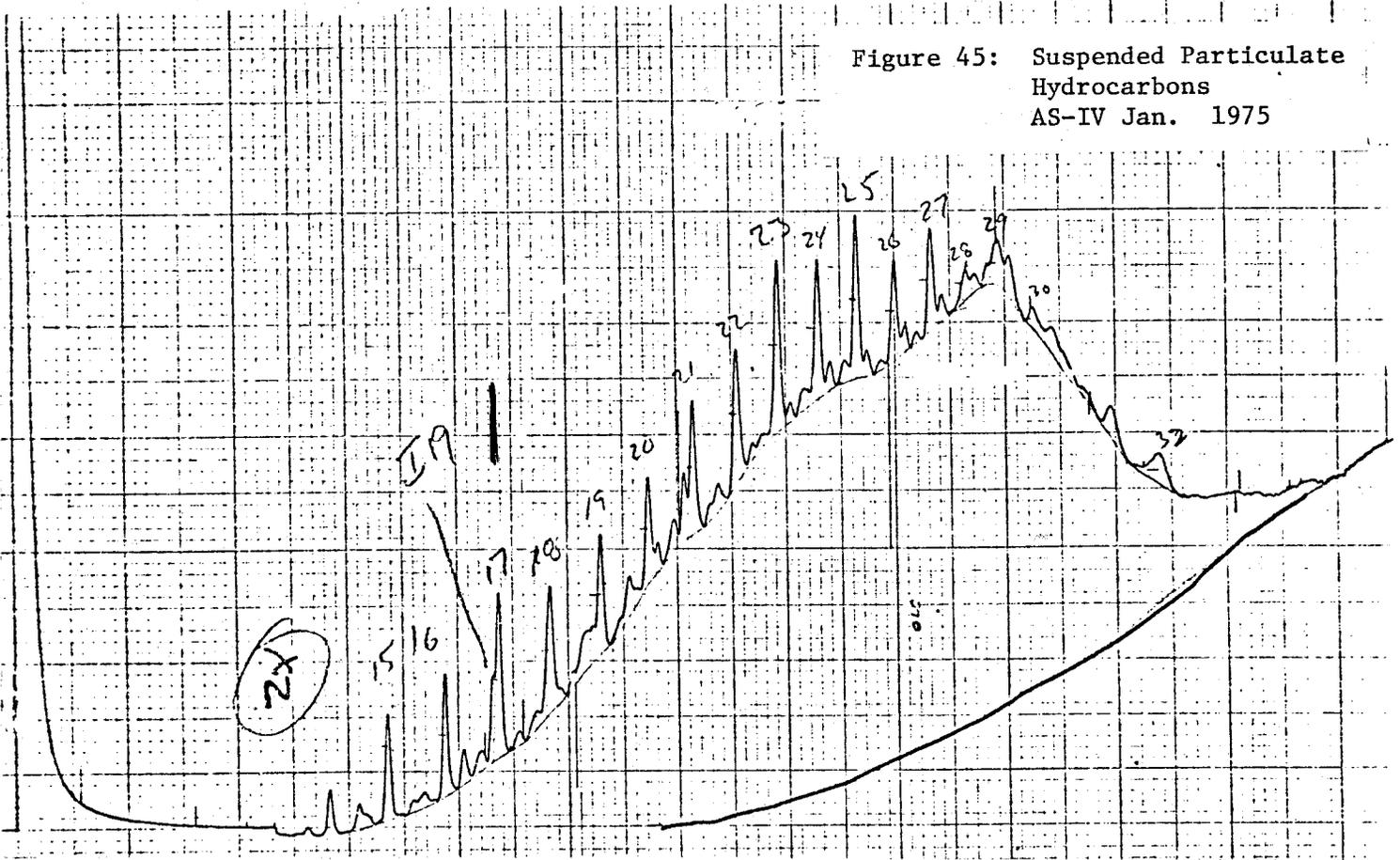


Figure 46: Suspended Particulate Hydrocarbons, AS-VI, 1/75
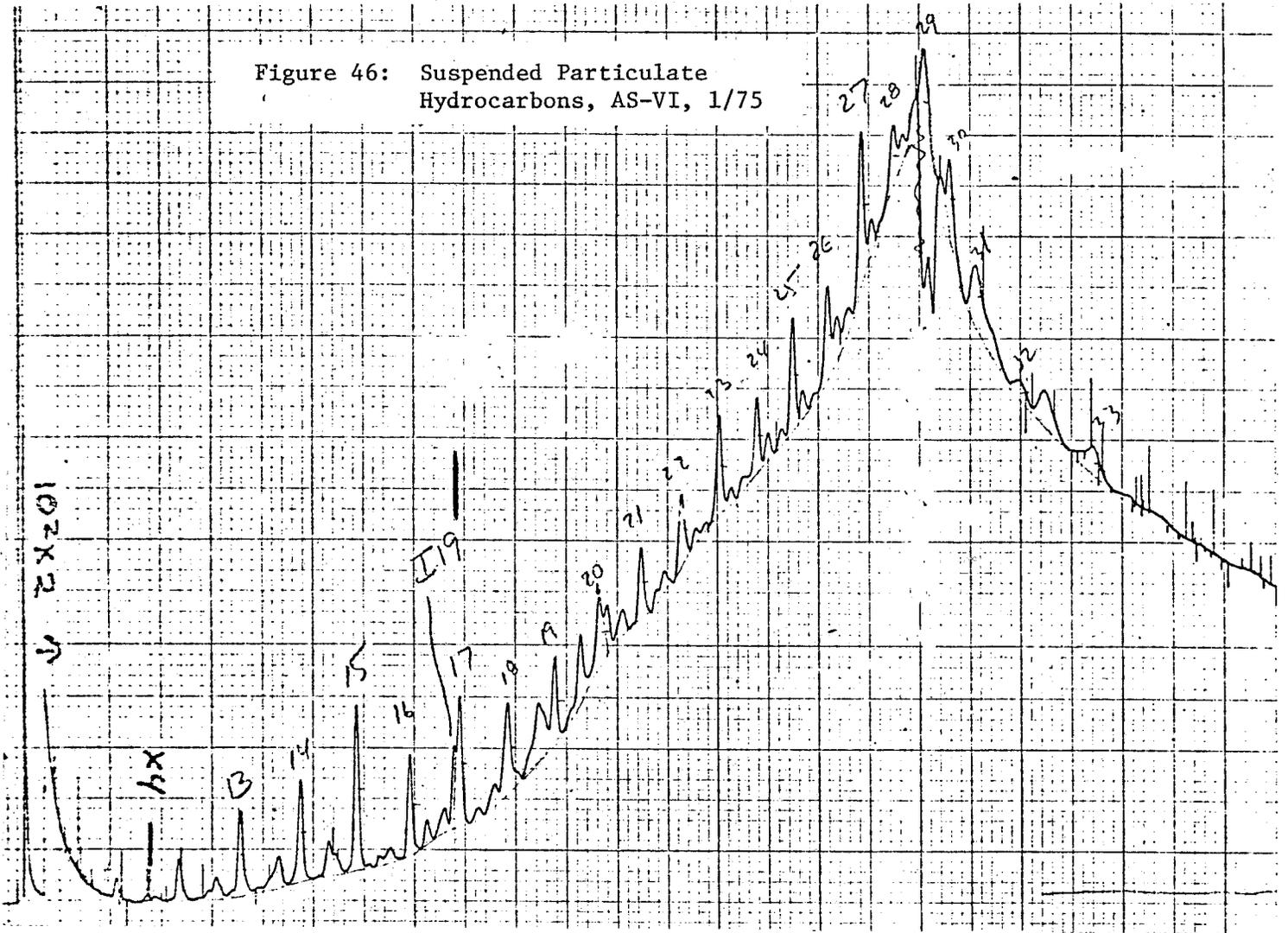
Figure 47: Suspended Particulate
Hydrocarbons
Continuous pumping
between Eddystone Pa.
and C & D Canal
Feb. 6, 1975
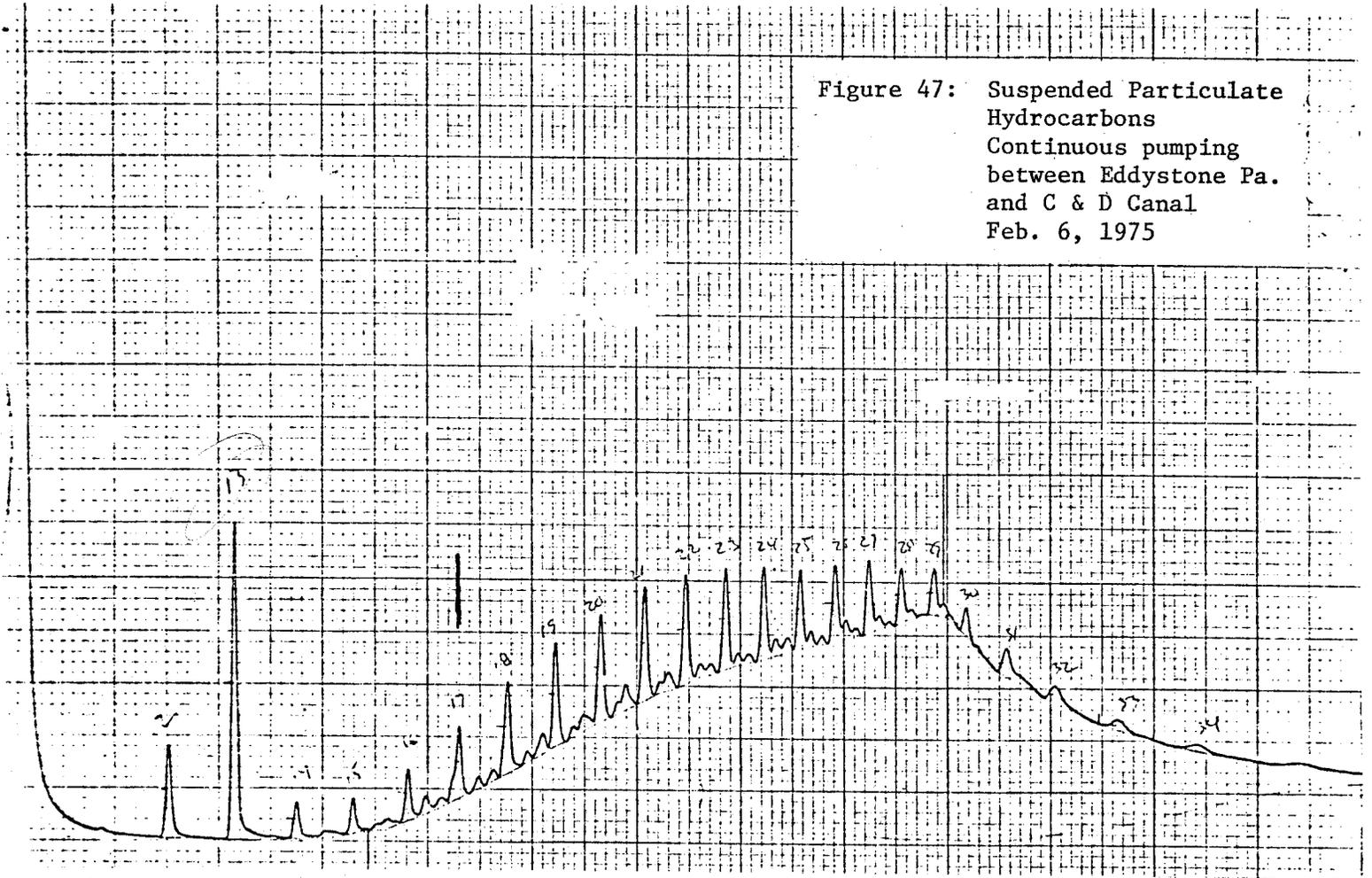
Figure 48: Suspended Particulate Hydrocarbon Material Site A-1 to AS-I, 2/6/75

75
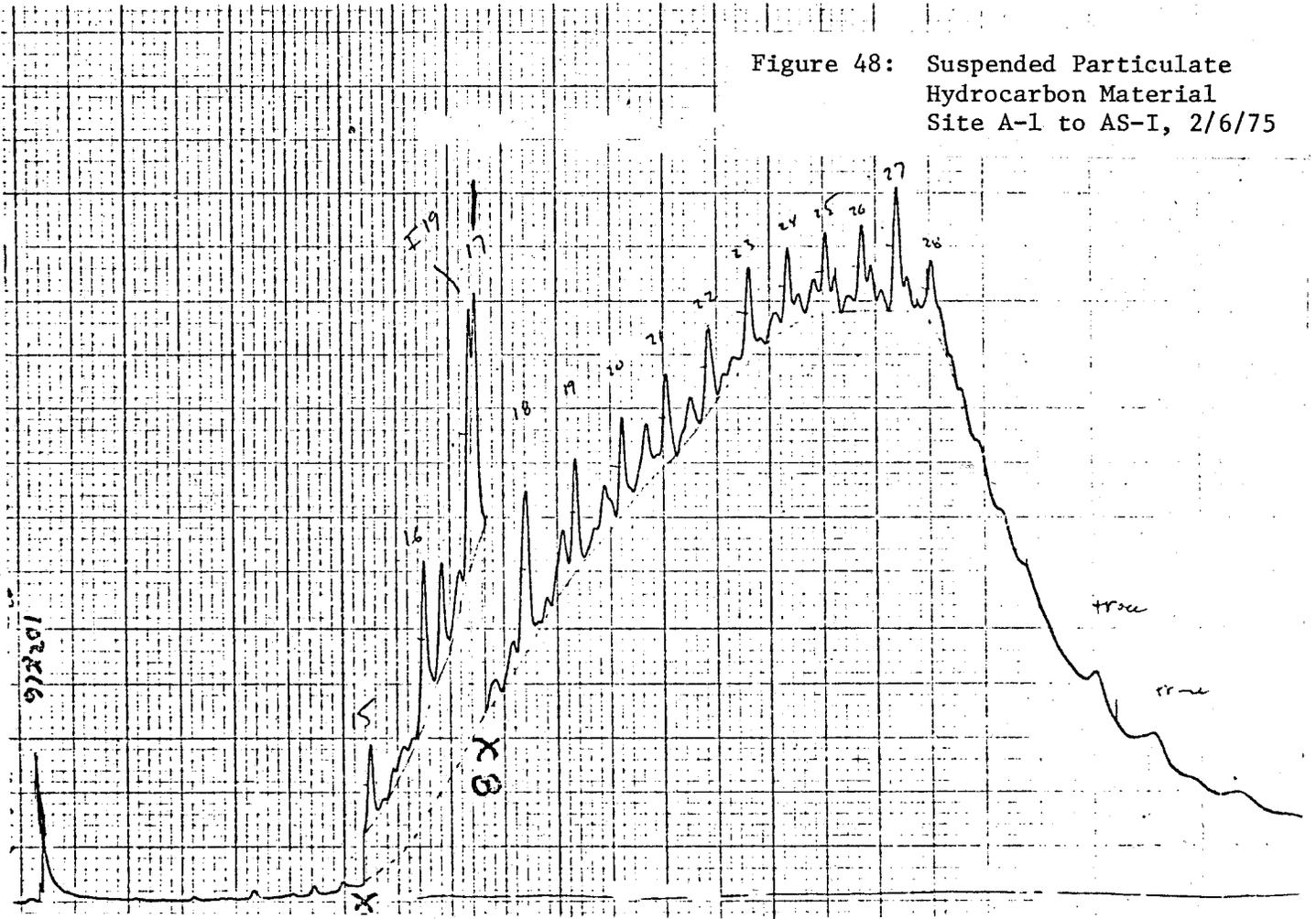


Figure 49:  Suspended Particulate Hydrocarbons
75-128
Sta. C-8 to A-1
4/2/75
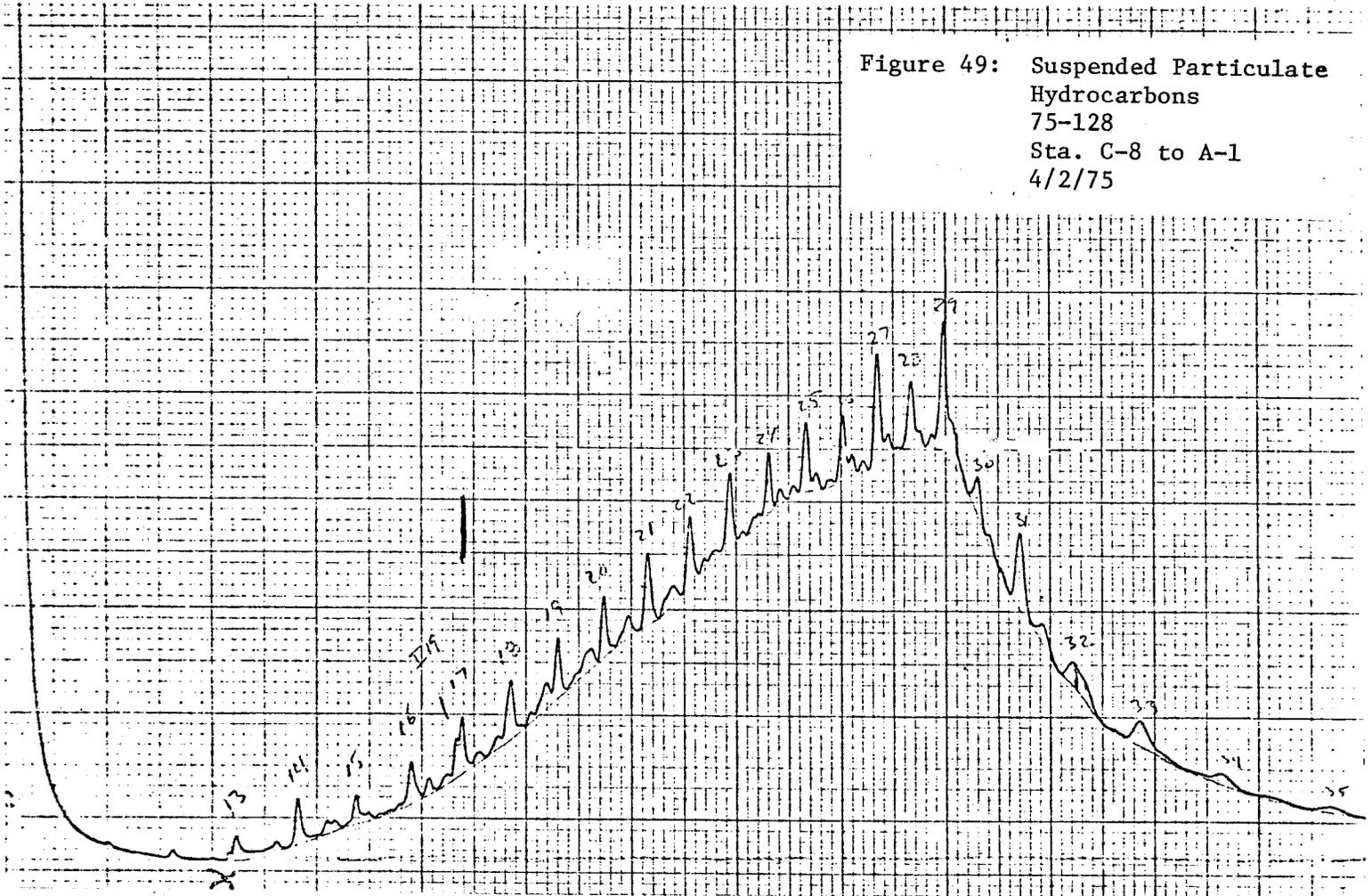
Figure 50: 75-135
Suspended Particulate
Hydrocarbons
Sta. A-3 to B-2
4/2/75
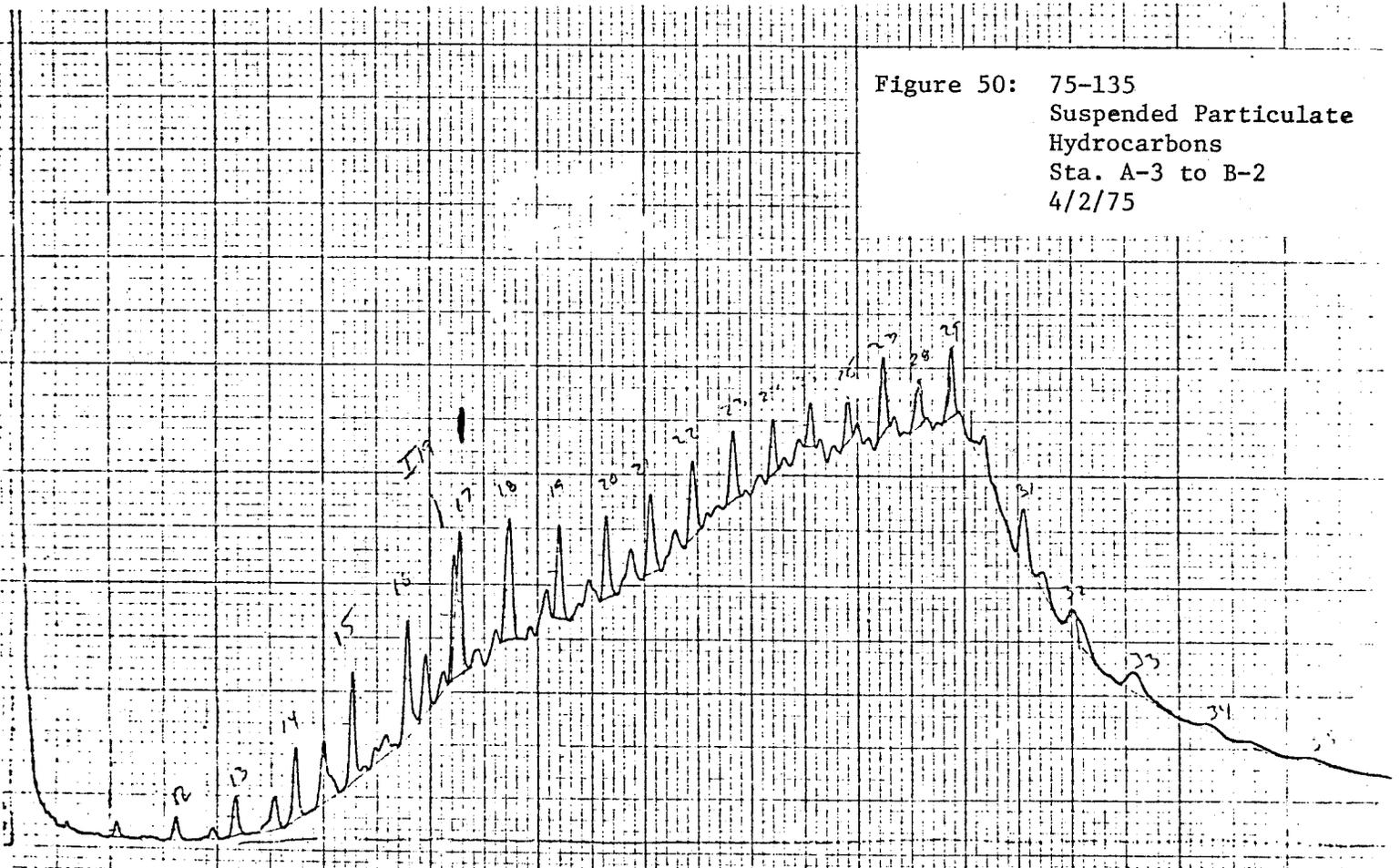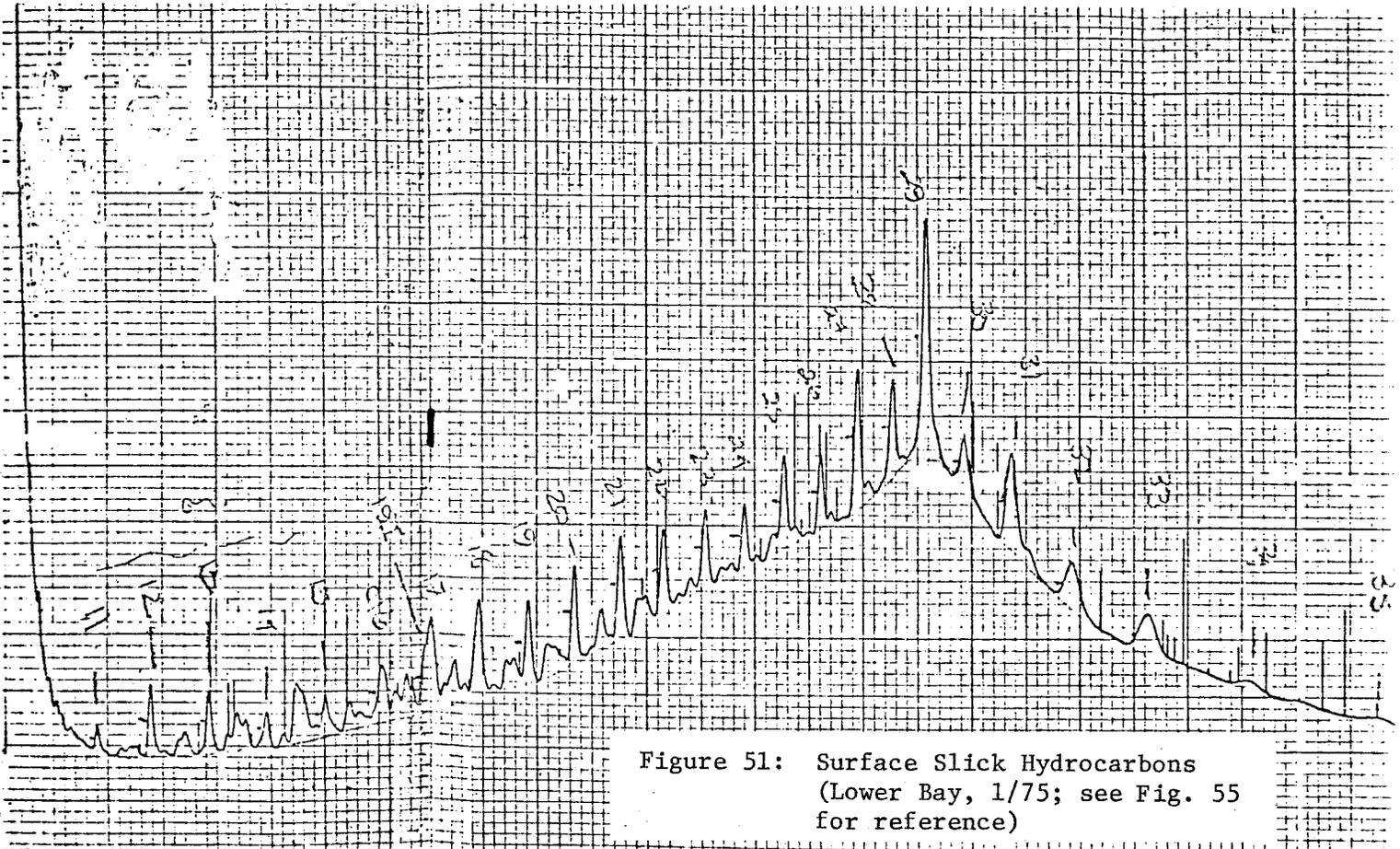
Figure 51: Surface Slick Hydrocarbons
(Lower Bay, 1/75; see Fig. 55
for reference)
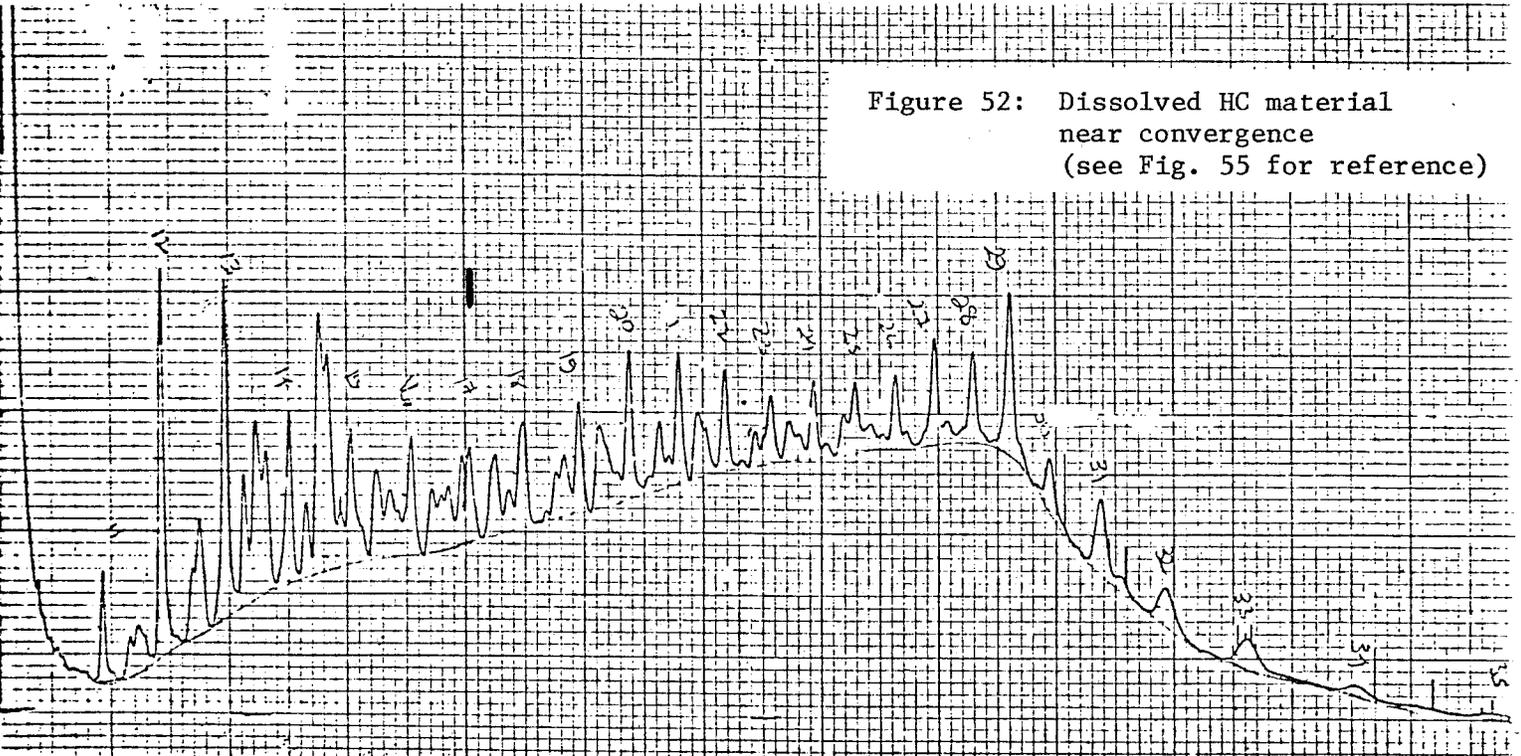
Figure 52: Dissolved HC material
near convergence
(see Fig. 55 for reference)

Figure 53: Dissolved HC material beneath convergence (see Fig. 55 for reference)



Figure 54: Dissolved HC material near convergence (see Fig. 55 for reference)

West

East

surface slick
(Fig. 51)

1 meter

color change

light color

dark color

Depth, m

0

1

Fig. 52
S= 19.346 o/oo

Fig. 53
S= 19.302 o/oo

Fig. 54
S= 19.054 o/oo

2

3

4

39° 09.8'N
75° 17.5'W
Front north of lightering area
moving west to east; samples taken
during ten-minute period, Jan. 1975

Approx. bottom
topography

Figure 55:   Spatial relationship of four samples  (Figures 51-54)
taken for dissolved hydrocarbons. (Fiest, pers. comm.)

APPENDIX

APPENDIX

Since the initial preparation of this report, several more post-Corinthos samples have been processed and these results are presented here with only a short summary discussion.  Duplicate analyses of some of the samples previously presented are also included here.  Since the gas chromatographic analyses of many of these samples has not been completed, the new quantitative information presented here is primarily the information determined by weighing the extracts.  All data presented in the body of the report for locations of interest here are presented again for the purpose of easy comparison with new results.

Table A-I presents these results by location and date:  amounts of saturated hydrocarbon material are given for all samples, and, where applicable, comments about the chromatograms are also given.

Station AS-III is the southernmost of the stations that has been monitored.  As mentioned in the main report, a visible "tar" contamination was observed in sediment samples taken at this location in late April, 1975.  Such contamination was not found in sediments taken early in April, 1975, at this location.  Thus, it could be inferred that some "event," perhaps transport of Corinthos oil, affected this area in mid-April, 1975.  The chromatograms of samples from this location confuse this picture somewhat; while all samples from a core taken in January, 1975 and a surface grab in early April, 1975 show small amounts of saturated hydrocarbons and no unresolved complex mixtures, the surface grab at this location in January, 1975, shows significantly greater amounts of saturated hydrocarbons and a large unresolved complex mixture.  Aside from this one sample, however, all other observations from stations farther upstream are consistent with the hypothesis that contaminated sediments were being transported downstream in such a manner that they "arrived" at stations A-1 and C-6 by early April and "arrived" at station AS-III, at least, by late April, 1975.

Perhaps the most convincing evidence for the above statement is the suite of samples from station A-1.  It appears that there was a slight increase in the amount of saturated hydrocarbon material in

sediments at this location by February 5, 1975, when sample 75-104 was taken. However, a dramatic increase is seen by early April (75-131A); the amount of material in the samples has increased, and perhaps more significantly, the chromatogram of 75-131A shows a large unresolved mixture, whereas none of the other samples from this location have shown such a mixture. The difference between 75-131A and C is also significant: the A sample represents the top 3-5 cm of sediment, while the C sample represents sediment about 10-15 cm deep within the grab. Both the amounts and chromatographic appearance of the C samples suggest less contamination than in the surface sample.

Station C-6 also shows the above phenomenon: between January and early April (and probably between early February and early April) significant amounts of saturated hydrocarbon material "arrived" at this location, and the chromatographic difference between the January and April samples is dramatic. The January samples show the pattern of little or no complex mixture and a large CPI value: the April samples show a large unresolved complex mixture (high-boiling) and a low CPI value (less than 1.5).

Since all data for these sediments have not yet been obtained, unequivocal interpretation of the results is not possible at this time. Nevertheless, it is important to see how hydrocarbon abundances can vary in sediments at certain localities over a short period of time. Though such an organized effort at monitoring in the lower bay has not been attempted, a few samples that have been taken over a long span of time in the lower bay do not reflect these rapid temporal changes. Thus the results presented here must be considered as being indicative of the movement of one (or more) spill events in the upper estuary. Since the exact chemistry of the spilled oil from the Corinthos incident has not been defined, the results given here cannot yet be correlated to this one particular spill, but the likelihood of correlation is quite obvious, since this has been the one major spill of significance during the winter and spring of 1975 (to the authors' knowledge). Such a correlation has obvious implications for those with the responsibility of assessing the impact of upstream refinery activities on the downstream regions of the river and bay.

Table A-I

Summary of Sediment Analyses related to Corinthos Spill

| Station | Sample # | Date Taken | Sat. HC-VW | Sat. HC-GC | Comments |
|---------|----------|------------|------------|------------|----------|
| AS-I | 75-5AI | 1/6/75 | 97.2 | 131 | Low CPI |
|  | AII | 1/6/75 | 321 | 199 | Large UCM |
|  | 75-5BI | 1/6/75 | 139 | | |
|  | BII | 1/6/75 | 115 | | |
|  | 75-110AI | 2/5/75 | 655 | | |
|  | AII | 2/5/75 | 722 | | |
|  | 75-110BI | 2/5/75 | 965 | 468 | " |
|  | BII | 2/5/75 | 904 | 492 | " |
|  | 75-136AI | 4/2/75 | 2173 | | |
|  | AII | 4/2/75 | 1983 | | |
| A-1 | 75-1AI | 1/6/75 | 18.4 | | |
|  | AII | 1/6/75 | 32.8 | | |
|  | 75-1BI | 1/6/75 | 17 | 24 | No UCM, |
|  | II | 1/6/75 | 25 | 12.7 | large CPI |
|  | 75-1CII | 1/6/75 | 16.7 | | |
|  | 75-104AI | 2/5/75 | 91.7 | 42.6 | Small UCM, |
|  | AII | 2/5/75 | 539 (?) | 41.0 | large CPI |
|  | 75-104BI | 2/5/75 | 48.4 | | |
|  | BII | 2/5/75 | 46.8 | | |
|  | 75-131AI | 4/2/75 | 145 | | Large UCM, |
|  | AII | 4/2/75 | 101 | | low CPI |
|  | 75-131CI | 4/2/75 | 69 | | Moderate UCM |
|  | CII | 4/2/75 | 70 | | moderate CPI |
| C-6 | 75-25BI | 1/8/75 | 163 | 58 | Slight |
|  | BII | 1/8/75 | 387 | 36 | lower boiling UCM, |
|  | 75-103AI | 2/5/75 | 157 | | CPI = 4.5 |
|  | AII | 2/5/75 | 179 | | |
|  | 75-130AI | 4/2/75 | 442 | | Large UCM |
|  | AII | 4/2/75 | 499 | | high boiling CPI ≅ 1.5 |
| C-8 | 75-27CI | 1/8/75 | 338 | 209 | High Boiling |
|  | CII | 1/8/75 | 197 | 138 | UCM, low CPI |
|  | 75-102AI | 2/5/75 | 263 | 139 | "  " |
|  | AII | 2/5/75 | 194 | 198 | "  " |
|  | 75-129AI | 4/2/75 | 140 | | |
|  | AII | 4/2/75 | 171.5 | | |
| AS-III | C-11BI | 1/8/75 | 291 | | High boiling |
|  | BII | 1/8/75 | 317 | | UCM, low CPI |
|  | C-11-3I | 1/8/75 | 31.6 | 20.4 | No UCM, CPI ≅ |
|  | 3II | 1/8/75 | 70.4 | 20.5 | 4.5 |
|  | 75-126BI | 4/1/75 | 36.1 | | No UCM, |
|  | BII | 4/1/75 | 14.7 | | CPI > 4 |
|  | 75-140 | 4/29/75 | Sample visibly contaminated with "tar"-not yet analyzed | | |

Appendix:  Figures 1 through 4

The following figures are included in this discussion
for comparison with "pre-Corinthos" chromatograms pre-
sented in the body of the report.  Information pertaining
to these and other samples taken after the Corinthos
spill is found in Table A-1; chromatographic conditions
for these determinations were identical to those reported
for all other samples.

Appendix Figure 1: 75-136AII,
Site AS-I, 4/2/75
(cf. Figs. 36, 37)



Appendix Figure 2: 75-131AII,
Site A-1, 4/2/75
(surface sediment –
cf. Figs. 29, 30)
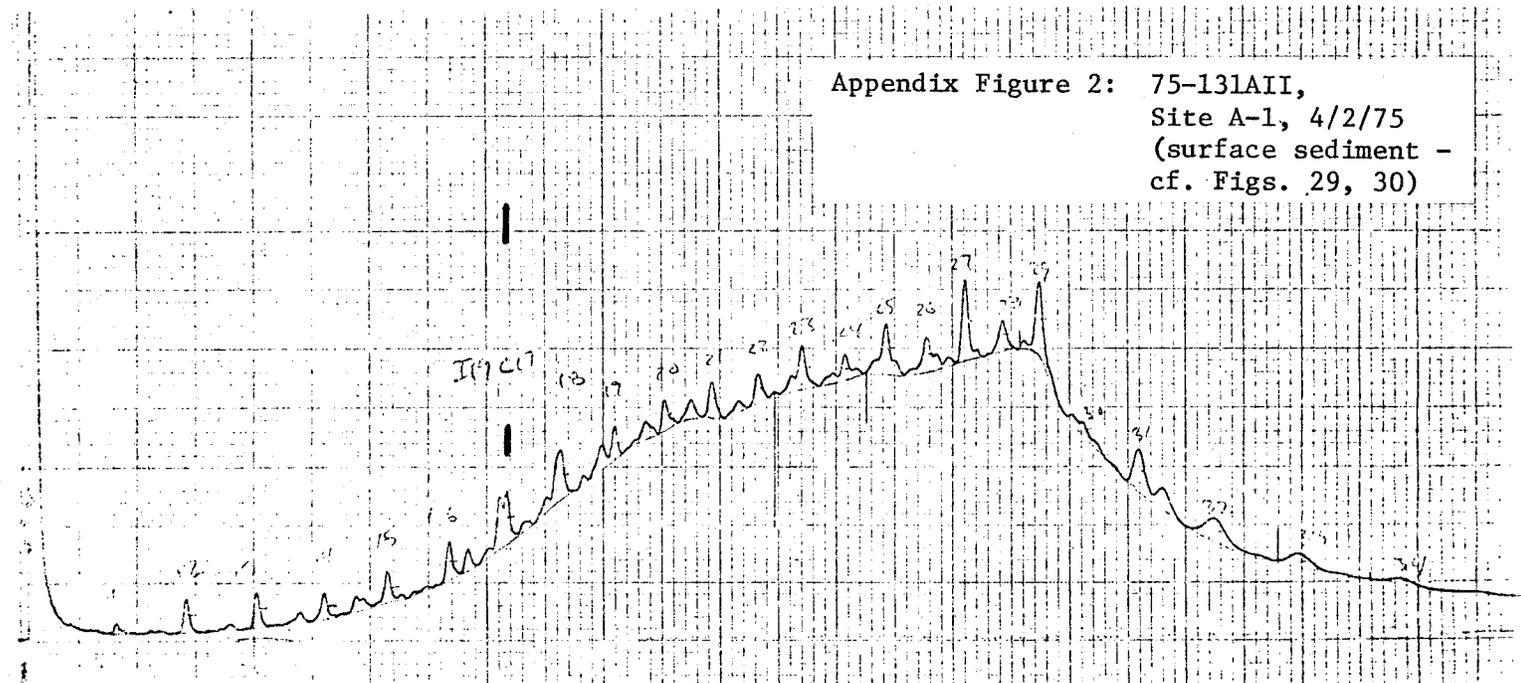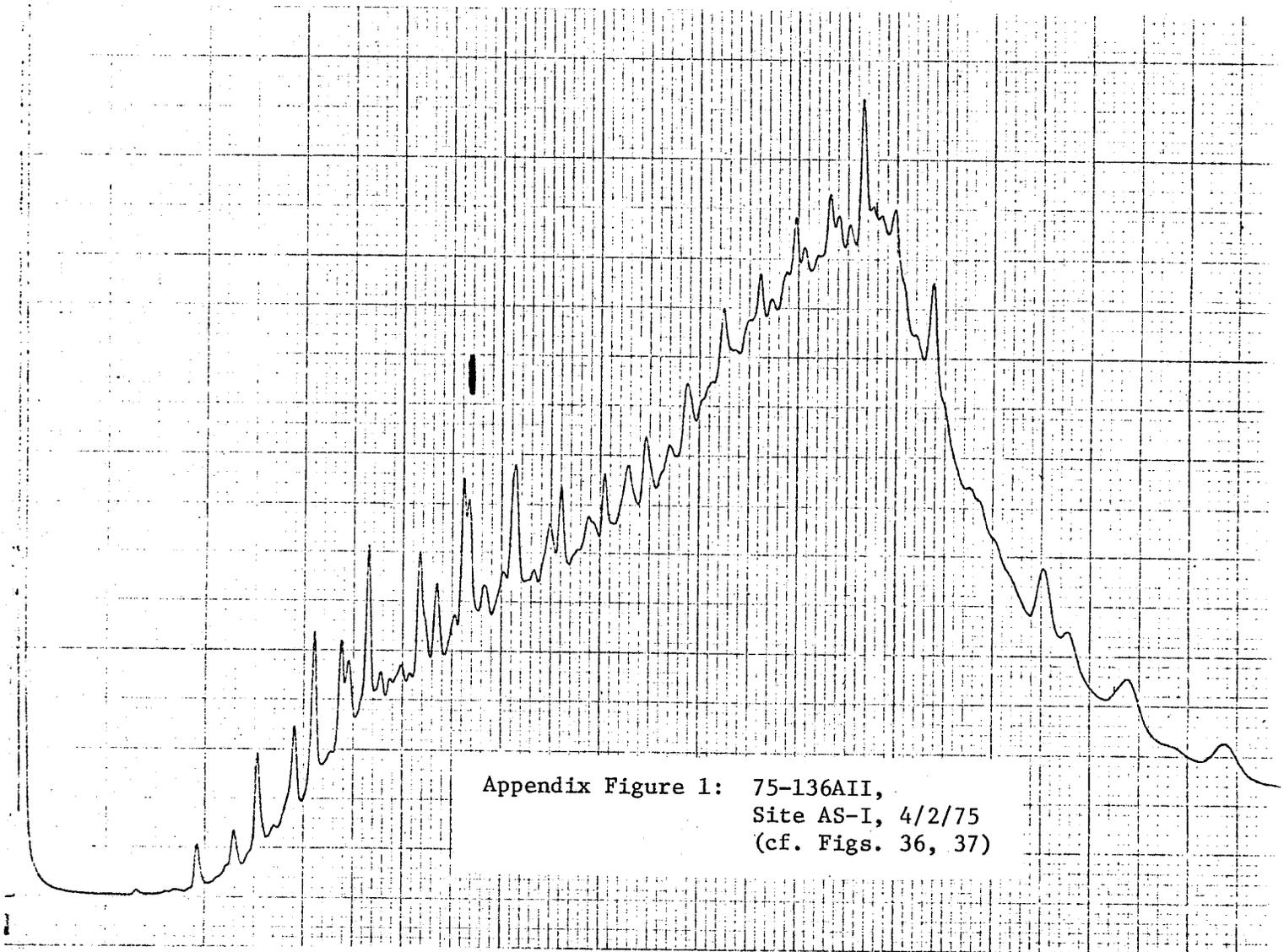
Appendix Figure 3: 75-131CII, Site A-1, 4/2/75 (approx. 10 cm deep — cf. Figs. 29, 30)
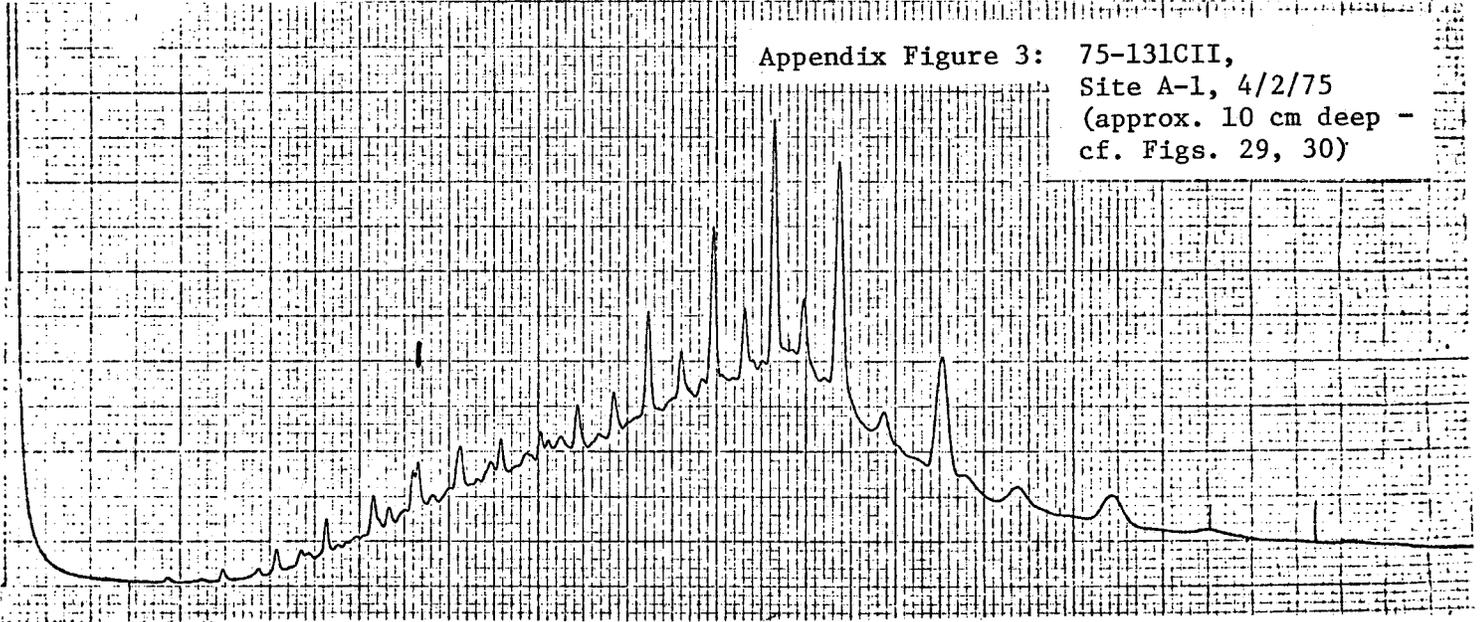
Appendix Figure 4: 75-130AII,
Site C-6, 4/2/75
(cf. Fig. 28)