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BASELINE STUDIES OF PETROLEUM HYDROCARBONS IN WINYAH BAY

Final Report to NOAA, Coastal Energy Impact Program
Grant No. CEIP82-08/20361, January, 1983

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1983

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REFERENCE Grant No. NA-79-AA-D-CZ025 308(c) planning funds

Request for utilization of unexpended funds:

Federal amount	$ 10,719
Non-federal	2,467
Total	13,186

The original grant award designated $46,461 in 308(c) planning funds for an oil spill impact study for the City of Myrtle Beach. For various reasons, the city declined to take on the project and it was subsequently awarded to the state Department of Parks Recreation and Tourism at a reduced amount. A request was made in January, 1981 to reprogram these unused funds for use in conjunction with our new CEIP award (referenced below) for a study of baseline hydrocarbon concentrations in Winyah Bay. A full application was submitted for the study in conjunction with the new award, but for only half the funds necessary to complete the examination in Winyah Bay. The reprogramming request was denied on September 8th, one month after the new applica had been approvedby NOAA. This being the case , we would like to split the Winyah Ba hydrocarbon study into two phases, one to be funded through these unused monies for a time period of August 15, 1981 to January 31, 1982; and the next phase to begin Feb. 1 and run through August 15, 1982 and funded through the new grant award. Each phase shall have a seperate contract and work tasks as shown below:

Phase I (August 15, 1981 - Jan. 31, 1982) The first phase of the project will be devoted to methods development for extracting and measuring oil concentrations by fluorescer evaluating sampling and analytical techniques, and sample collection in the Bay itself. samples will be extracted with dichloromethane by rolling the collection jugs on a jar mill for several hours. The extracting solvent will be seperated, concentrated a flash evaporator, and analyzed by fluorescence spectroscopy against a #2 Fuel oil standard. A selected number of samples will also be examined for petroleum residues by gas chromatography using a Dexsil 300 column and flame ionization detection.

Budget for Phase I

Graduate Assistants, 7.25 person months	$ 4,226.00
Fringe	8.00
Fluorimeter	2,450.00
Jar Mill	1,220.00
Supplies	1,000.00
Overhead @34.7%, excluding equipment	1,815.00
Total	$10,719.00
Non-federal share	2,467.00
Total Phase I	$13,186.00

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EXECUTIVE SUMMARY

Petroleum hydrocarbons were measured in the surface water (top 20 cm) of Winyah Bay and the Sampit River on 10 sampling dates between October, 1981 and November, 1982. Analyses were carried out by fluorescence spectroscopy (FS) and packed-column gas chromatography (GC). Oil residues measured by FS as South Louisiana crude oil (SLC) equivalents averaged 3.3 µg/L in the industrialized portion of the Sampit River near Georgetown, 0.8 µg/L in the upper Sampit River, and 0.5 µg/L in Winyah Bay. One sample containing slick material showed 100 µg/L total hydrocarbons. The residue had GC characteristics of both a fuel oil and a lubricating oil. The oil concentrations in the open bay are very low, and are more typical of continental shelf waters than industrialized estuaries. Three samples from Charleston Harbor (June, 1982) showed oil residues approximately 10-20 times above those in Winyah Bay.

The effect of cleanup on hydrocarbon analysis by FS was investigated for 59 samples from Winyah Bay and Charleston Harbor. Alumina column chromatography removed about 90% of the fluorescent materials from water extracts and saponification with alcoholic KOH removed an additional quantity of fluorescing compounds equivalent to 0.7 µg/L SLC. Accurate analysis by FS thus requires rigorous cleanup procedures to remove extraneous fluorescing compounds.

GC and FS analyses were carried out on 26 samples to compare the two techniques. For oil concentrations below 5 µg/L, FS results expressed as SLC equivalents agreed within a factor of 2-3 with those obtained by GC. Quantification of water extracts by FS against a lubricating oil or fuel oil standard gave poorer agreement with GC results. However for two high-level samples (30-100 µg/L), GC and FS analyses agreed more closely when FS results were expressed as lubricating oil equivalents.

INTRODUCTION

The pressure of development near South Carolina estuaries during the 1980's is likely to result in increased pollutant inputs to coastal waters. For example, future development plans for Winyah Bay (Georgetown County, SC, Figure 1) include construction of a refinery and dredging a deeper channel to allow heavier ship traffic up the bay. Either of these activities will probably cause additional petroleum discharges to the bay. Careful documentation of baseline oil concentrations in coastal waters is essential if we are to be able to assess the impact of further development on South Carolina estuaries.

Petroleum contamination of the ocean is generally measured by three methods: Tows with a neuston net are used to determine the distribution of tar lumps in the water column; dissolved oil and oil associated with small particles is extracted from seawater with an organic solvent and measured by gas chromatography (GC) or fluorescence spectroscopy (FS).

The fluorescence of crude and refined petroleum products is mainly due to the presence of polycyclic aromatic hydrocarbons (PAH) and FS is a common technique for measuring oil in seawater (Keizer et al., 1977; Gordon et al., 1974, 1978; Law, 1981; Fogelqvist et al., 1982) and sediments (Levy et al., 1981; Hargrave and Phillips, 1975; Keizer et al., 1978; Wakeham, 1977). A major drawback of FS is that the aromatic content of petroleum products and crude oils varies substantially. If one knows the source of petroleum pollution, say a spill of no. 2 fuel oil, one can choose no. 2 fuel oil as a reference standard and the results obtained by FS will be accurate. In many cases however the sources of petroleum pollution may be unknown and the choice of a reference standard is arbitrary. In this situation, FS provides only an estimate of total hydrocarbon pollution. On the positive side, FS is much faster than GC, allowing many more samples to be processed per day.

A detailed mapping of oil distribution in an area can be carried out in a relatively short time. FS also provides a measure of aromatic hydrocarbons, the most toxic components of petroleum. Mutagenicity in Salmonella strains has been correlated to the fluorescence intensity of sediment and sludge extracts (Litten et al., 1982). The objectives of this study were to survey Winyah Bay for petroleum hydrocarbons in the water column and to compare FS and GC for monitoring petroleum residues in coastal regions receiving chronic oil discharges from a variety of sources.

EXPERIMENTAL

Sampling Locations

The study area was Winyah Bay and the adjoining Sampit River (Figures 1 and 2). The upper Sampit River is clean and undeveloped, but sources of pollution increase near Georgetown. International Paper Company discharges into the river in Georgetown, and Georgetown Steel Company is located on the turning basin, near the entrance to Winyah Bay. Shrimpers and other boats also dock in the turning basin and contribute to chronic petroleum input to the river. Other sources of petroleum to the bay include a recently opened marina near the Highway 17 bridge (Figure 1) and storm runoff from streets and highways. Since most of the pollution sources and the proposed refinery site are in the upper bay - Sampit River area, we concentrated our sampling effort above and below the turning basin of the river and in the upper bay above Hare Island. During the fall of 1982 we also collected a few samples in the lower bay (Figure 2). Salinities measured with a refractometer during the sampling periods ranged from 0-11 parts-per-thousand (ppt) in the Sampit River and upper bay (stations 1-10) and 6-32

ppt in the lower bay (stations 11-14).

Sample Collection and Extraction

Water samples were collected from the bow of a 4.6-m Boston Whaler, while the boat was moving forward, by holding a glass jug about 10-20 cm below the surface. The bottles used for this work had teflon-lined caps and previously contained chromatographic analysis grade solvents. The unfiltered water samples (3.1-3.8 L) were extracted by adding 350-400 mL dichloromethane and rolling for three hours or longer on a jar mill. This water volume proved sufficient for FS analysis. Extracts from two bottles (6.2 - 7.6 L) were combined for GC analysis, allowing hydrocarbons to be detected at a 2:1 sample:blank ratio for oil concentrations above 0.3 - 0.9 µg/L. During February and March, 1982 we attempted to lower this detection limit by extracting larger volumes of water. Samples of 18-19 L were extracted in glass carboys by adding 1200-1800 mL dichloromethane and mixing for 24 hours with a teflon-coated stirring bar and a magnetic stirrer. This failed to reduce the detection limit because the blank values were proportionally higher, so we returned to the two-jug samples for GC work.

The dichloromethane was drawn off through a plug of glass wool and concentrated to 10-20 mL on a flash evaporator. Hexane (10 mL) was added and the extract was reduced to 2-3 mL on a flash evaporator or in a Kuderna-Danish apparatus. The extract was transferred to a 2-g column of activity grade III (6% added water) neutral alumina, and the column was eluted with 20 mL 30% dichloromethane-petroleum ether.

Figure 1

The Winyah Bay System showing major freshwater tributaries and placement of Georgetown and associated roads.

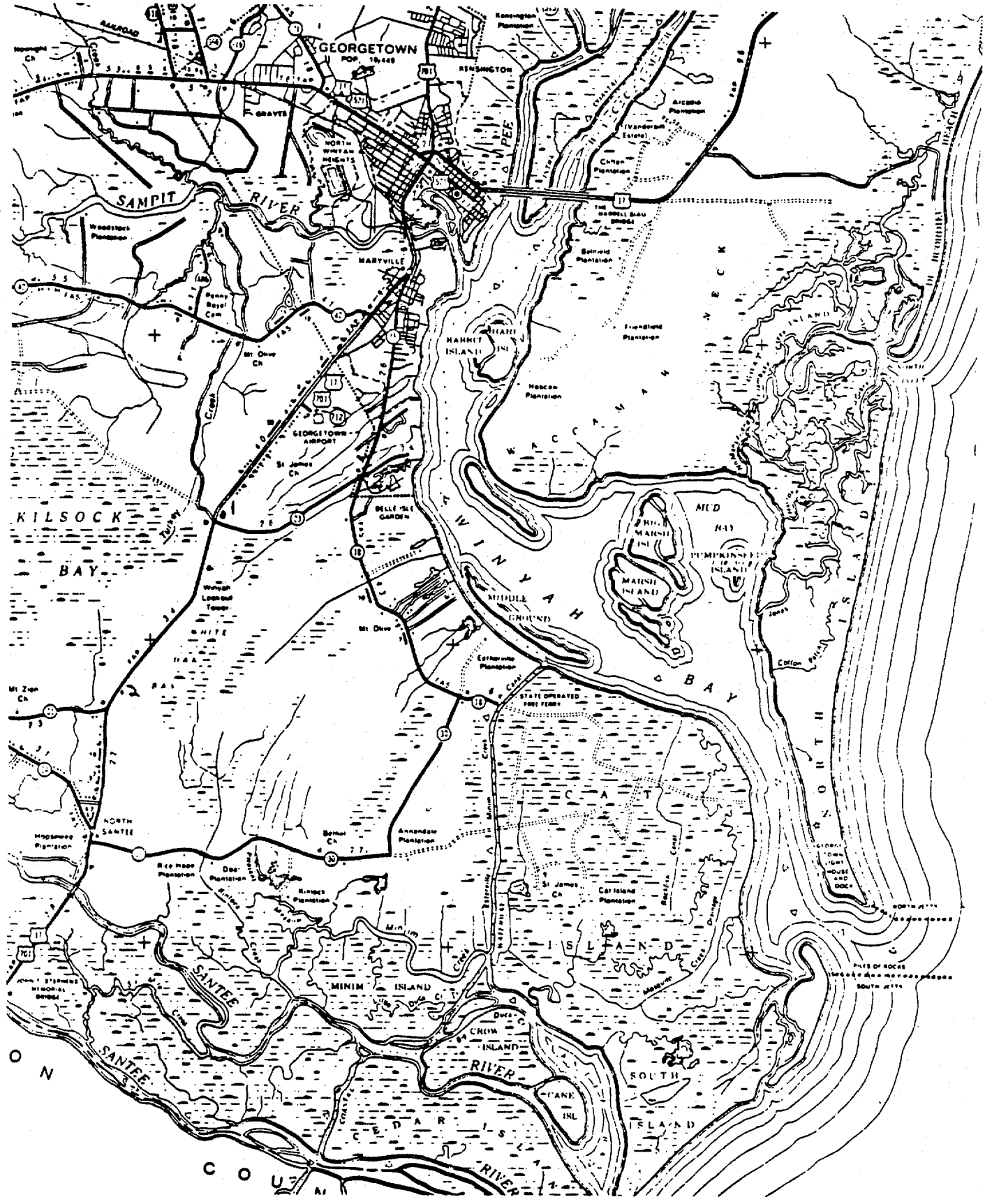

GEORGETOWN
KENSINGTON
GRAVES
NORTH WINYAH HEIGHTS
SAMPIT RIVER
MARYVILLE
Penny Royal Cem
Mt Olive Ch
GEORGETOWN AIRPORT
St James Ch
BELLE ISLE GARDEN
KILSOCK BAY
Winyah Lookout Tower
WHITE OAK BAY
Mt Zion Ch
NORTH SANTEE
Hopsewee Plantation
Rice Hope Plantation
Doar Plantation
Kinloch Plantation
Annandale Plantation
Bethel Ch
Mt Olive
Estherville Plantation
STATE OPERATED FREE FERRY
WINYAH BAY
MIDDLE GROUND
RABBIT ISLAND
HARI ISL
Hobcow Plantation
Friendfield Plantation
Bellfield Plantation
Clifton Plantation
Arcadia Plantation
Kensington Plantation
THE HARRELL SIAU BRIDGE
MUD BAY
BIG MARSH ISL
MARSH ISLAND
PUMPKINSEED ISLAND
Colfax Patch
NORTH ISLAND
CAT ISLAND
St James Ch
Cat Island Plantation
MINIM ISLAND
CROW ISLAND
CANE ISL
SOUTH ISLAND
SANTEE RIVER
CEDAR ISLAND
SANTEE RIVER
PILES OF ROCKS
SOUTH JETTY
NORTH JETTY
COUNTY

Figure 2

Sampling stations in the Sampit River and Winyah Bay. Station 4 is near International Paper, station 5 is about 200 m from Georgetown Steel, station 6 is in the fishing trawler docking area of the river, station 10 is inside the boundary of a small boat marina.

BLACK
R.
SAMPIT
R.
1
2
3
4
5
6
7
8
9
10
11
12
13
14

After alumina cleanup the samples were saponified to remove lipids before GC analysis. The extracts were reduced to about 1-2 mL in a Kuderna-Danish apparatus, and then blown down to less than 0.5 mL with a stream of nitrogen. A solution (1.0 mL) of 0.5 M KOH in 90% methanol-10% water was added and the sample was refluxed for 15-20 minutes. After cooling, 5 mL distilled water was added and the hydrocarbons were extracted with three 2-mL portions of petroleum ether. The combined extracts were diluted to 20 mL with 30% dichloromethane-petroleum ether for further examination by FS, and then concentrated to 100 μL or less for GC analysis.

Fluorescence Analysis

Fluorescence measurements were made in a 1-cm silica cell using a Perkin Elmer MPF-43A spectrofluorimeter. For quantitative work, the excitation (EX) and emission (EM) monochromators were set at 320 and 380 nm with 5-nm bandpasses. A sample of South Louisiana crude (SLC) API reference oil was used as a fluorescence standard. The relationship between fluorescence and SLC concentration was linear to about 0.5 μg/mL (Figure 3) and samples were diluted to fall within the linear range. The fluorescence values of several other crude and refined oils were also measured and expressed relative to that of SLC. The other oils were: API reference Kuwait crude (KC), API reference no. 2 fuel oil, EPA reference Venezuela bunker C (VBC), Quaker State Superblend 10W-40 lubricating oil (QS), and used automobile crankcase oil. Fluorescence measurements of these oils were made at concentrations of 0.4 - 2.0 mg/L, and were within the linear range for the respective oil.

Two types of fluorescence spectra were recorded for oil standards and water extracts. Conventional EM spectra were scanned while holding the EX wavelength constant, and synchronous spectra were obtained by scanning both the EM and EX monochromators simultaneously with a 10-nm offset. The synchronous mode provides more spectral detail and a better correlation between aromatic ring number and EM wavelength (Wakeham, 1977).

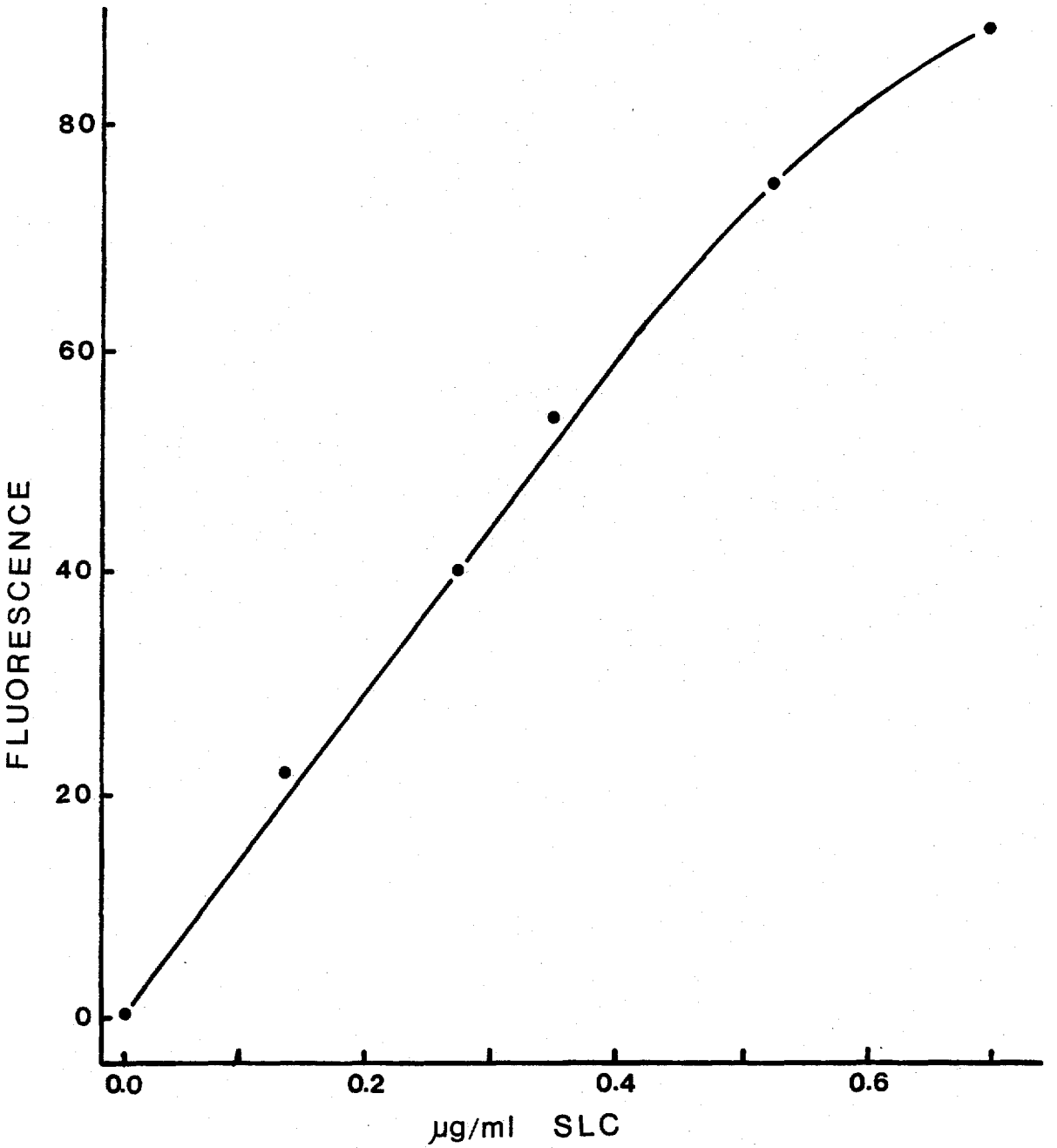
Gas Chromatographic Analysis

GC work was done using a 180-cm x 0.3cm i.d. glass column packed with 3% Dexsil-300 on 100/120-mesh Supelcoport mounted in a Packard 7300 series chromatograph. Analyses were run using the following temperature program: 80°C (hold 5 minutes), program at 8°/min to 250°C, hold for 20 minutes. Injector and detector temperatures were 220° and 260°C. Samples were blown down with nitrogen to 100 µL or less, and an internal standard (n-C_{14} or n-C_{22}) was added to allow the total sample volume to be determined. Quantification was based on flame ionization response factors derived from a series of external standards containing n-alkanes in the n-C_{14} to n-C_{24} range. The total area of chromatograms between the retention times of n-C_{12} and n-C_{30} was determined using an electronic integrator. The ability of the integrator to correctly evaluate the area of a complex chromatogram was checked by injecting known quantities of no. 2 fuel oil. Ten injections of 4-10 µg of fuel oil gave 117 ± 12 percent recovery, as calculated form individual n-alkane response factors.

Figure 3

Standard curve for analysis of SLC by

fluorescence, EX/EM = 320/380 nm, 5 nm bandpasses.


FLUORESCENCE
80
60
40
20
0
0.0
0.2
0.4
0.6
µg/ml SLC

RESULTS AND DISCUSSION

Recovery of Oil From Spiked Samples

The efficiency of the extraction-cleanup procedure for fluorescence analysis was checked by adding known quantities of SLC to Winyah Bay water. Recoveries of 28-693 μg SLC from 3-4 L of water, corrected for the fluorescence of unspiked Winyah Bay water extracts, ranged from 58-84% (mean = 76%, Table 1). When 19 L was extracted with 1200 mL solvent, recoveries were lower (46-52%). The difference in SLC recovery for the large and small water volume sets was probably related to the solvent: water ratio. Dichloromethane (density = 1.34 g/mL) is 2% (w/w) soluble in water, so one would expect to lose 15 mL solvent for each liter of water extracted. For the small volume samples, about 3.5 L of water was extracted with 350 mL dichloromethane and the final solvent:water ratio was 0.07-0.09. For the two 19-L samples extracted with 1200 mL solvent, the final ratio was only 0.048. Two other experiments were carried out in which 347 μg SLC was extracted from 18-19 L water using 1800 mL dichloromethane, and recoveries rose to 71 - 83% (Table 1).

The Effect of Sample Cleanup on Fluorescence-Determined Hydrocarbons

Extracts of Winyah Bay or Sampit River water were pale yellow and fluoresced intensely (EX/EM = 320/380 nm). Several investigators who have reported oil levels in seawater by FS have carried out their measurements using uncleaned up extracts (Keizer et al., 1977; Gordon et al., 1974, 1978; Levy et al., 1981; Law, 1981; Fogelqvist et al., 1982). We found that a

Table 1. Recovery of SLC from Winyah Bay Water[a]

µg Oil Added	Water Volume, L	Solvent:Water	% Recovery
693	3.6	0.077	78
693	4.0	0.068	78
139	3.1	0.093	82
139	3.7	0.075	84
69	3.3	0.086	70
69	3.6	0.077	58
69	3.2	0.089	80
69	3.3	0.086	72
56	3.5	0.094[b]	76
28	3.5	0.094[b]	82
			$\bar{x}$ = 76±8
347	19	0.043	44
347	19	0.043	50
347	19	0.075	83
347	18	0.080	71

[a]Measured by fluorescence after alumina cleanup.

[b]400 mL solvent used instead of 350.

considerable amount of fluorescing material was removed by passing the sample through an alumina column under conditions which gave good recoveries of oil. Thus for Winyah Bay, FS measurements on uncleaned up water extracts greatly overestimate petroleum residues. The magnitude of the difference can be appreciated by comparing fluorescence intensities before and after alumina column chromatography, for samples collected 1/17/82.

Table 2. Removal of Extraneous Fluorescence by Alumina Chromatography[a]

Station[b]	F (before alumina)	F (after alumina)
1	62	7
2	108	10
3	508	32
5	650	43
7	105	11

a) Water volumes were 2.9 - 3.3 L; final extract volumes were 18-21 mL.
b) See Figure 2.

Following alumina cleanup, quantitative measurements of petroleum residues by fluorescence were made by FS. Samples collected after March, 1982 were concentrated and saponified as described in the EXPERIMENTAL section, and the fluorescence was remeasured. In most cases the fluorescence decreased after saponification, although a few samples showed an increase. FS-determined hydrocarbons before and after alcoholic KOH treatment are plotted in Figure 4. The linear regression line is given by:

$$HC = 0.809\ HC_s + 0.68, \quad r^2 = 0.874 \quad \text{(Equation 1)}$$

where HC and HC_s are FS-determined hydrocarbons (μg/L) before and after saponification. Known quantities of SLC carried through the saponification procedure gave 90% recovery by FS, so the decrease does not appear to be caused by analytical losses. The positive intercept in the above equation (0.68 μg/L) thus represents fluorescing material that is not petroleum-related

and survives the alumina cleanup procedure. We did not examine whether saponification alone would provide sufficient cleanup. From these results, it is apparent that alumina chromatography (being the easiest cleanup step) is essential for accurate FS analysis of hydrocarbons in Winyah Bay, and that further cleanup is needed to measure low hydrocarbon levels. From the regression equation, the average difference between oil concentrations measured before and after saponification is 68% at the 1.0 μg/L level.

Fluorescence Characteristics of Samples and Oil Standards

The aromatic content and ring number distribution varies greatly for different petroleum products, so results obtained by FS are sensitive to the oil standard selected. Many workers interested in oil pollution of the open ocean by tanker traffic have selected various crude oils as fluorescence standards (Gordon et al., 1974; Keizer et al., 1977, 1978; Law, 1981; Fogelqvist et al., 1982). To provide a basis for comparison with others' results, we also used a crude oil standard, with the recognition that present petroleum residues in Winyah Bay probably result from refined petroleum products and not from crude oil. However, should the proposed refinery be built, crude oil will be shipped by the bay and a baseline knowledge of oil residues in terms of crude oil equivalents will be useful. Relative fluorescence values for several crude and refined oils at the wavelengths used for water sample analysis (320/380 nm) are presented in Table 3. These values vary by more than a factor of 10; thus a water sample that appears to contain 1.0 μg/L oil when quantified against SLC would be measured as 0.24 or 15 μg/L against VBC or no. 2 fuel oil.

Figure 4

FS-determined hydrocarbons (SLC equivalents) before and after saponification. All samples received alumina cleanup. The line represents a 1:1 relationship; i.e., no change on saponification. Samples marked ↓ were below the detection limit after saponification; these were not included in the linear regression.

● Winyah Bay and Sampit River

▲ Charleston Harbor

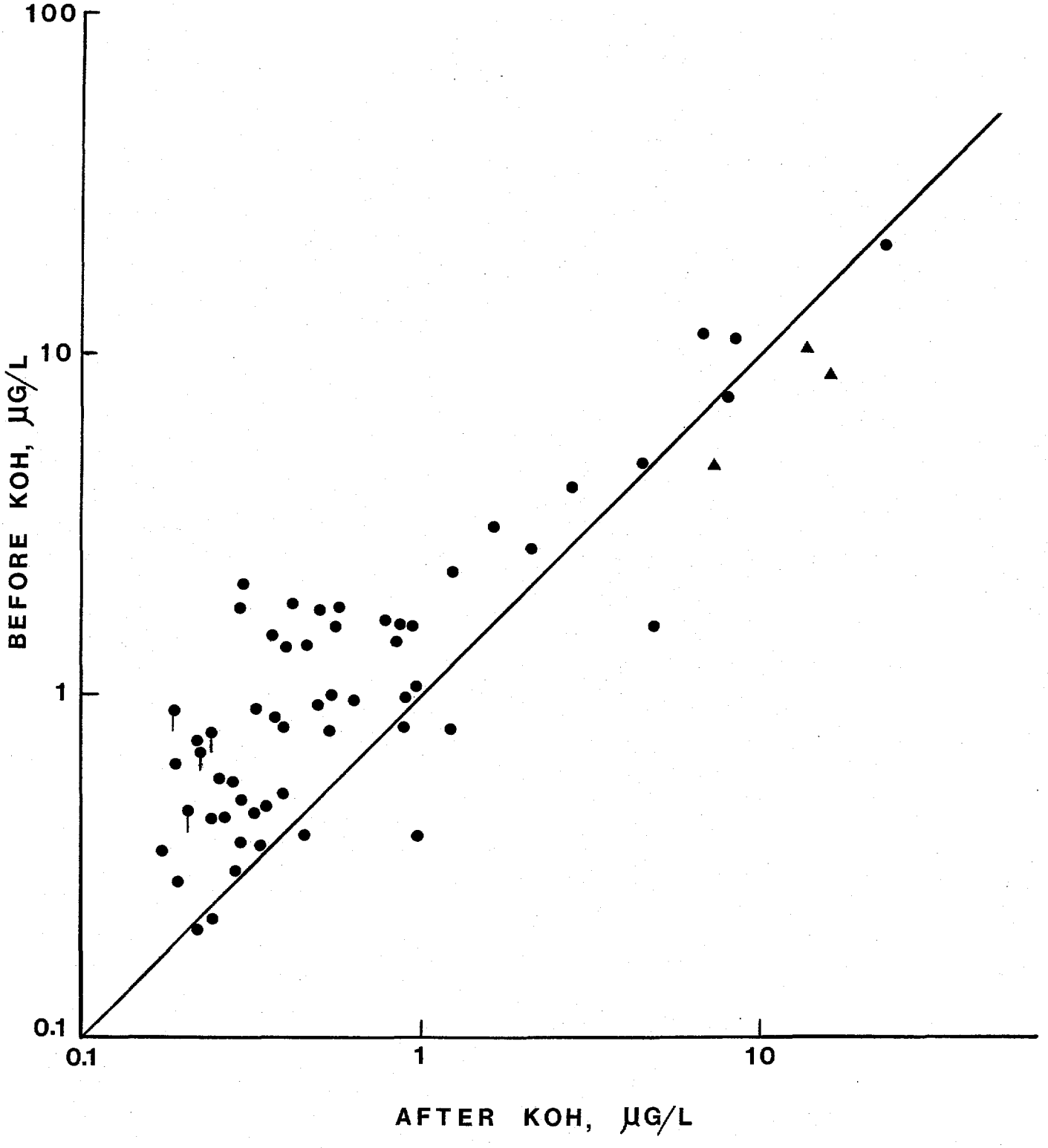

100
10
1
0.1
BEFORE KOH, µG/L
0.1
1
10
AFTER KOH, µG/L

Table 3. Relative Fluorescence Values for Crude and Refined Oils[a]

Oil	F/C[b]	Relative F/C
No. 2 fuel	13	0.068
QS	20	0.10
Used crank-case oil	20	0.10
KC	139	0.73
SLC	191	1.00
VBC	785	4.1

a) See EXPERIMENTAL section for oil identities.

b) Oil concentrations (C) ranged from 0.1 - 2.1 mg/L and were within the F vs. C linear range for the respective oil. F measured at 320 nm EX and 380 nm EM with 5-nm bandpasses.

Emission spectra for the oil standards in Table 3 are shown in Figure 5. Spectra of oils are generally broad band and featureless, with a shift toward longer wavelengths for oils containing aromatics with a greater number of fused rings. Thus no. 2 fuel oil, with contains mainly methylnaphthalenes as its aromatic component, shows a maximum emission at 330 nm, while the crude oils and VBC which contain traces of higher ring aromatics (phenanthrene, benzopyrene, etc.) show strongest emission in the 370 - 380 nm region.

More spectral detail can be obtained from complex mixtures like petroleum by scanning both the excitation and emission monochromators simultaneously, with a constant wavelength offset (usually 10 - 20 nm) between the two. These "synchronous" spectra provide more information about the aromatic content of the sample, since PAH generally show a single sharp peak at wavelengths that increase with higher ring number (John and Soutar, 1976;

Clark and Brown, 1977; Wakeham, 1977; Law, 1981; Vo Dinh et al., 1981). Maximum emission is observed between 310-330 nm for 2-ring aromatics (naphthalenes), 340-380 nm for 3- and 4-ring aromatics (phenanthrene, pyrene, chrysene), and above 400 nm for 5-ring and higher compounds (benzopyrenes, benzoperylenes) (Wakeham, 1977). Synchronous spectra for the oil standards used in this work are shown in Figure 6.

Spectra of water extracts from the Sampit River and Winyah Bay (Figures 7-9) show features of light and heavy aromatics, as might be expected from the diverse nature of hydrocarbon inputs to the bay. The higher emission in the 320-350 nm region for synchronously scanned spectra is indicative of 2- and 3-ring aromatics, and suggests a refined oil source such as no. 2 fuel or lubricating oils (cf. Figures 6, 7, and 9). In many samples traces of heavier aromatics were also present, as indicated by synchronous emission above 360 nm. These heavier aromatics may have their sources in urban runoff and atmospheric dustfall (Wakeham, 1977). A curious feature of several synchronous spectra is a peak at 440-450 nm which is not found in spectra of any of the standard oils (Figures 6, 7, and 9). Wakeham (1977) observed a doublet in this region for extracts of Lake Washington sediments, and identified perylene as the responsible compound. Perylene is a polycyclic aromatic hydrocarbon that is formed by degradation of plant pigments in reducing sediments. Since our water samples were not filtered, suspended sediment was extracted in addition to the water, suggesting a source for perylene. However further work will be required to determine if perylene is present in sample extracts.

Figure 5

Emission spectra of oil standards, 300 nm EX, 5-nm bandpasses. KC = Kuwait crude, VBC = Venezuela bunker C, SLC = South Louisiana crude, QS = Quaker State 10W-40 lubricating oil, No. 2 = no. 2 fuel oil, solvent = 30% dichloromethane-petroleum ether.

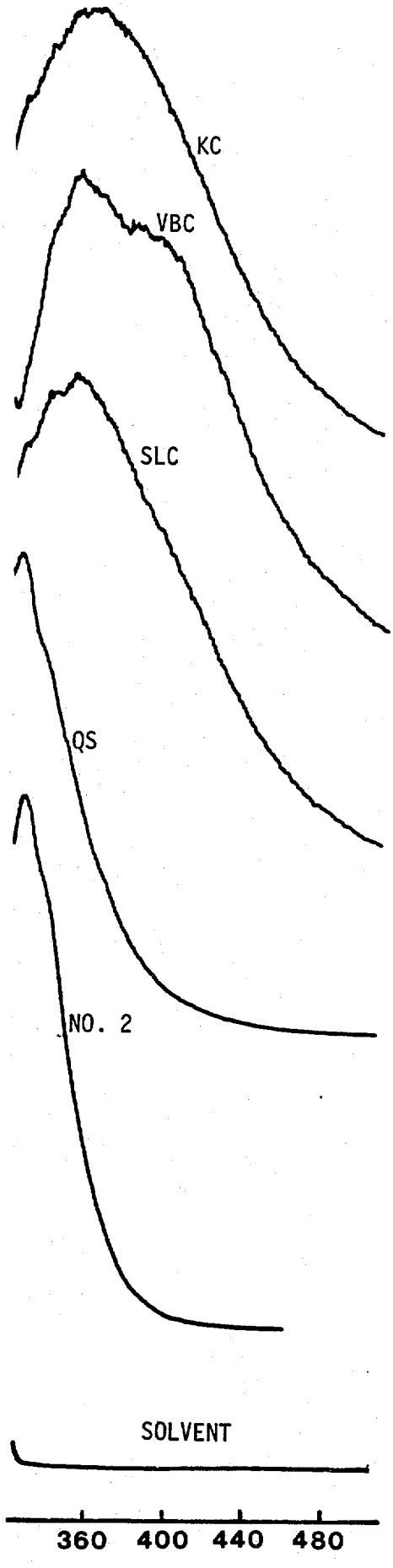

KC
VBC
SLC
QS
NO. 2
SOLVENT
360
400
440
480

Figure 6

Synchronous spectra of oil standards, showing emission regions for aromatics of increasing ring number. $\Delta\lambda$ = 10 nm, 5-nm band-passes. Oil identities as in Figure 5.

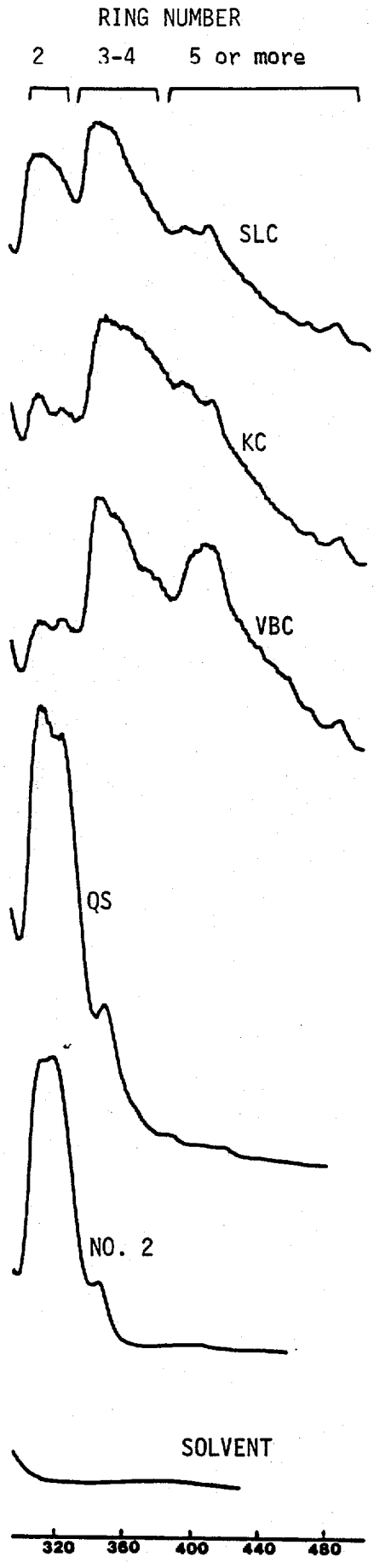

RING NUMBER
2
3-4
5 or more
SLC
KC
VBC
QS
NO. 2
SOLVENT
320
360
400
440
480

Figure 7

Synchronous spectra of SLC and water samples at two Sampit River stations, 6/82, (after alumina and saponification) $\Delta\lambda$ = 10 nm, 3-nm bandpasses.

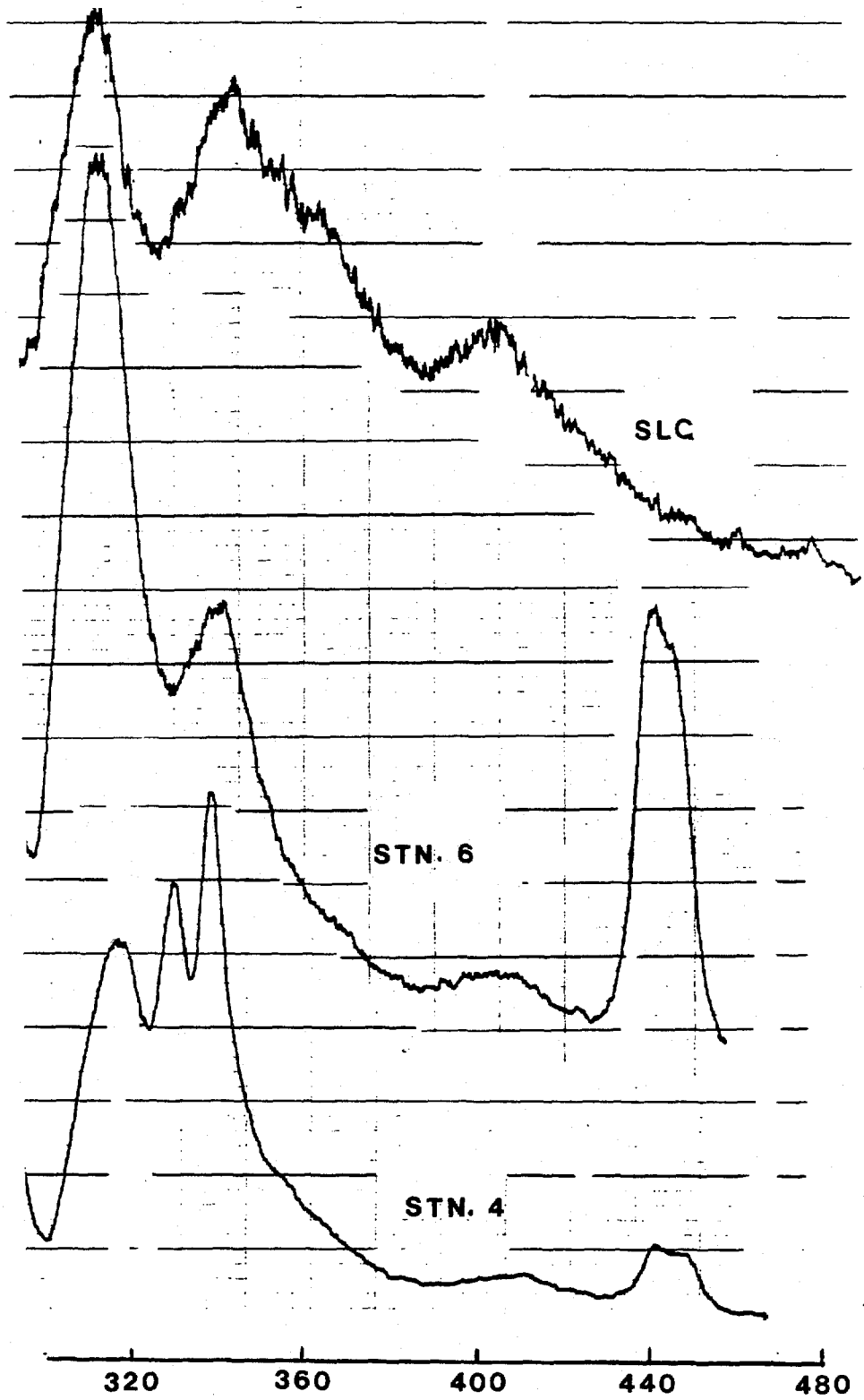

SLC
STN. 6
STN. 4
320
360
400
440
480

Figure 8

Emission spectra (300 EX, 5-nm bandpasses) of a water sample from the Sampit River turning basin, 11/82 (after alumina and saponification) and two oil standards, SLC and no. 2 fuel.

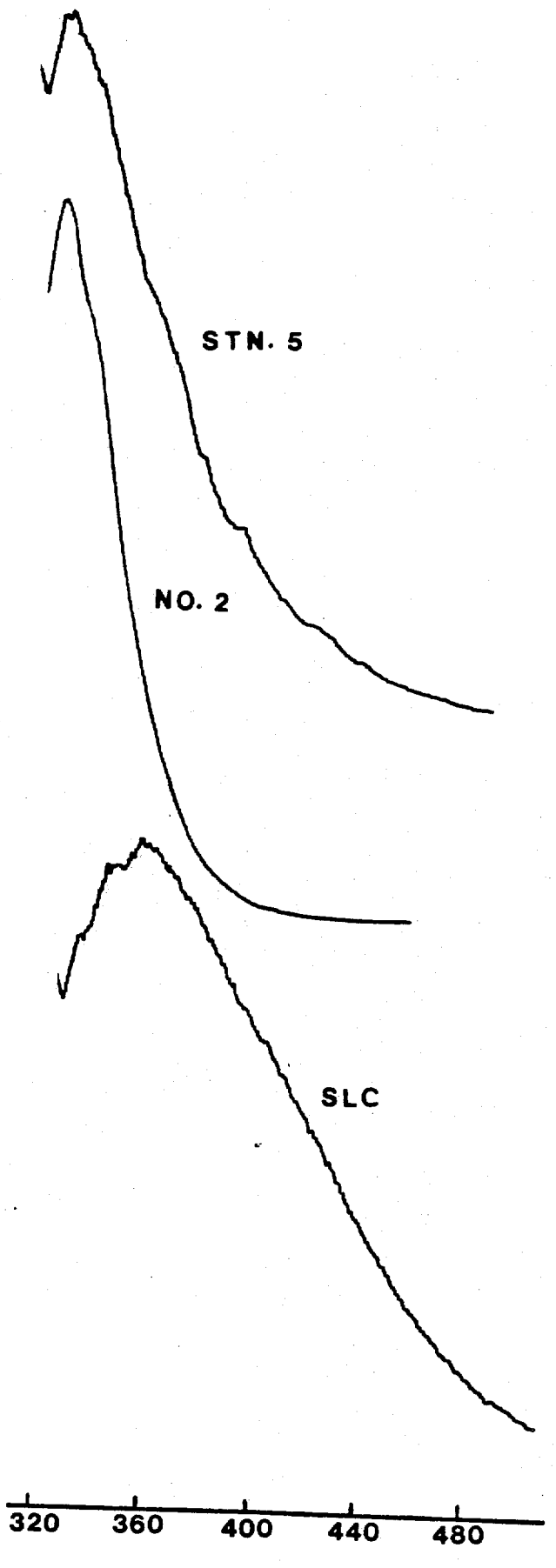
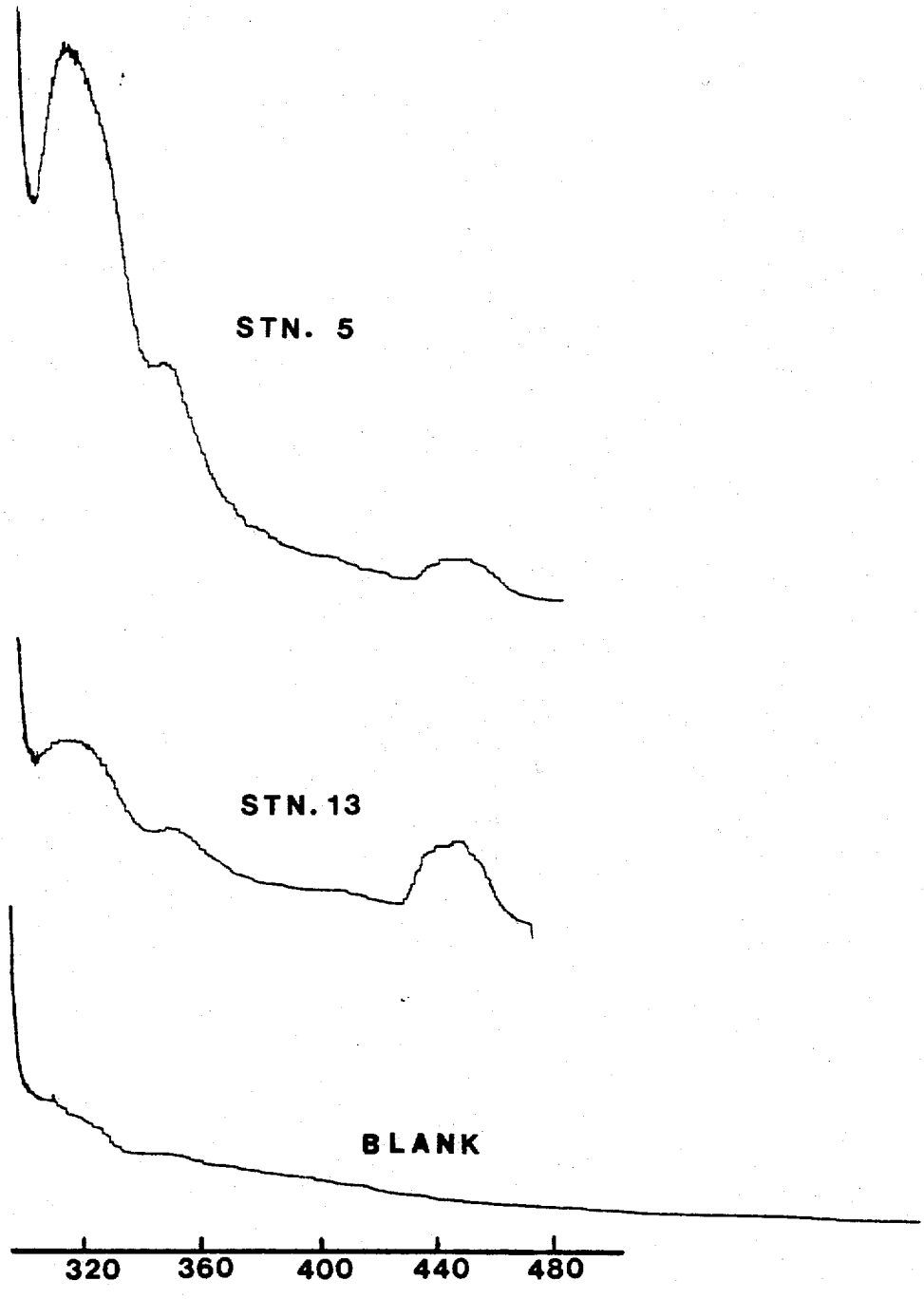

STN. 5
NO. 2
SLC
320
360
400
440
480

Figure 9

Synchronous spectra of the Sampit River sample shown in Figure 8, a station 13 sample, and a blank, all from 11/82. $\Delta\lambda$ = 10 nm, 5-nm bandpasses.


STN. 5
STN. 13
BLANK
320
360
400
440
480

FS-Determined Hydrocarbons in the Sampit River and Winyah Bay

Petroleum concentrations quantified as SLC equivalents are presented in Table 5. Blank values range from 0.3 - 2.1 μg (mean = 0.9 ± 0.5, n = 13), and samples were considered detectable if they measured twice the blank value on that sampling day. The mean blank thus corresponds to a detection limit of 0.26 μg/L for a 3.5-L sample. Samples from October, 1981 - March, 1982 received alumina cleanup only. Since the average saponifiable portion of the fluorescence corresponds to about 0.7 μg/L (Figure 4), SLC equivalents measured at stations 3-6 during this time are probably accurate within about 15-30%. However concentrations found at the other stations should be considered upper limits. Later samples (April - November, 1982) were analyzed after alumina chromatography and alcoholic KOH treatment. As expected, oil concentrations were highest in the turning basin (stations 4-6), and decreased up the river and out in the open bay. For comparison with the upper Sampit River (stations 1 and 2), we analyzed two samples from the Black River, a clean coastal plains river that empties into Winyah Bay above the Highway 17 bridge (Figure 1). The Black River samples were taken at a boat launching ramp (no boats were present at the time of collection) about 25 km northeast of Georgetown. FS-determined hydrocarbons were 0.25-0.32 μg/L.

During the course of this work, several replicate samples were taken at a single station to examine collection and analytical reproducibility (Table 4). On a few occasions the percent relative standard deviation (% RSD) was 15% or less, but in most cases % RSD's were in the 20 - 60% range. Two sample sets at station 5 has % RSD's of 75 - 97%. From the recovery data for Winyah Bay water spiked with SLC, the analytical precision is about 10% RSD (Table 1). Two factors might account for the much greater variability for

the samples: hydrocarbon contamination during collection, and real sample-to-sample differences caused by inhomogeneity in the water column. The first reason does not seem likely. Great care was taken to obtain samples only while the boat was moving foreward in order to avoid any slick from the outboard motor. Oil levels in the upper Sampit River and open bay were lower than those in the industrialized portions of the Sampit River, and were about the same as those measured in the Black River. Black River samples were collected by wading from shore and dipping a jug. The largest RSD's were obtained at station 5, near potential point sources of hydrocarbon contamination. It seems more reasonable that the observed variability was caused by real differences in oil residues sampled with each dip of the jug. These differences may have been due to a non-uniform distribution of dissolved oil in the water column or the collection of different amounts of suspended particulate matter (samples were not filtered).

To put these data into perspective, oil concentrations in the Winyah Bay estuary are compared to measurements in other coastal areas and the open ocean in Table 6. The Winyah Bay averages were obtained from the Table 5 values by considering undetectable values as upper limits, and are thus upper limits to petroleum contamination in the river and bay. Oil levels in the estuary are on the low end of the scale for coastal waters. As a comparison for the Winyah Bay data, we collected three samples from Charleston Harbor in June, 1982. Nearshore samples (no boat was available) were taken at Adger's Wharf near the downtown area and at Fort Johnson. SLC equivalents measured after alumina and saponification ranged from 7.2 - 15.4 μg/L, higher than the Winyah Bay levels.

Table 4. Replicate Collection and FS Analysis of Hydrocarbons

Date	Station[a]	Cleanup[b]	Samples	SLC Equivalents, µg/L Mean	% RSD
12/5/81	9	A	2	1.8	3.8
5/22/82	1	A	2	0.57	14
	2	A	2	0.50	2.8
	5	A	4	3.1	35
	8	A	6	1.4	23
6/19/82	5	A	4	10.2	75
	5	AS	4	9.6	97
	6	A	2	3.2	18
	8	A	6	0.63	44
	8	AS	6	0.33	36
9/5/82	4	A	3	1.0	38
	4	AS	3	0.53	55
	5	A	3	1.6	8.0
	5	AS	3	0.83	7.0
	6	A	4	1.1	60
	6	AS	4	0.81	41
	8	A	3	0.91	57
	8	AS	3	0.40	26
	11	A	4	0.37	44
	11	AS	4	0.20	15
	12	A	2	0.65	59
	12	AS	2	0.39	24
11/21/82	4	A	3	0.77	31
	4	AS	3	0.60	45
	5	A	3	1.3	39

Table 4. Replicate Collection and FS Analysis of Hydrocarbons, continued

Date	Station[a]	Cleanup[b]	Samples	SLC Equivalents, µg/L Mean	% RSD
11/21/82	5	AS	3	0.65	40
	13	A	3	0.48	44
	13	AS	3	$\leq$0.19	77
6/2/82	Charleston Hbr., Adger's Wharf	A	2	4.8	15
	Ft. Johnson	A	3	9.3	20
	Ft. Johnson	AS	2	14.4	9.7

a) Winyah Bay and Sampit River unless otherwise stated. See Figure 2.

b) A = alumina chromatography, AS = alumina and saponification.

Table 5. Average FS-Determined Hydrocarbons, SLC Equivalents, µg/L

	10/11/81	12/5/81	1/17/82	2/20/82	3/20/82	4/18/82	5/22/82	6/19/82	9/5/82	11/21/82
Clean-up[b] / Station[a]	A	A	A	A	A	AS	AS	AS	AS	AS
1			0.42	1.7	<1.5	0.24	0.27	0.56	0.57	
2			0.61			0.33	0.29	0.29		
3	2.5		2.2					0.45		
4			3.7					6.7	0.53	0.60
5	4.9		4.2	4.0	3.4	1.2	2.0	9.6	0.83	0.65
6	3.8							1.6	0.81	7.6[d]
7			0.72					0.29		
8				<1.3	<1.6	0.25	1.4[c]	≤0.33	0.40	<0.23
9		1.8						0.22		
10										0.25
11									0.20	<0.18
12										<0.35
13										≤0.28
14									0.39	0.86
Black River		0.25	0.32							

a) See Figure 2.
b) Cleanup, A = alumina chromatography, AS = alumina and saponification.
c) Alumina cleanup only for this sample.
d) Oil slick present, includes slick material.

Table 6. FS-Determined Hydrocarbons in Coastal and Open-Ocean Waters

Location	µg/L Oil Range	Mean	Fluorescence Oil Standard	Reference
Upper Sampit River Stns. 1-3	0.29-2.5	0.80	S. Louisiana crude	This work
Sampit River turning basin, Stns. 4-6	0.53-9.6	3.3	S. Louisiana crude	This work
Upper Winyah Bay, Stns. 7-10	<0.23-1.8	0.73	S. Louisiana crude	This work
Lower Winyah Bay, Stns. 11-14	<0.18-0.86	≤0.38	S. Louisiana crude	This work
Charleston Harbor, SC	7.2 - 15.4	12.0	S. Louisiana crude	This work
Bedford Basin, Nova Scotia	1.6 - 9.3	2.5	Guanipa crude	Keizer et al., 1977; Gordon et al., 1978
St. Margaret's Bay Nova Scotia		0.6	Guanipa crude	Gordon et al., 1978
Gulf of St. Lawrence	0.6 - 1.1		Guanipa crude	Keizer et al., 1977
Nova Scotia Shelf	0.2 - 0.8		Guanipa crude	Keizer et al., 1977
North Atlantic, Nova Scotia - Bermuda		0.6	Venezuela crude	Gordon et al., 1974
Irish Sea	2.1 - 3.5	2.6	Ekofisk crude	Law, 1981
Western English Channel	1.1 - 1.7	1.5	Ekofisk crude	Law, 1981
Eastern English Channel and Southern North Sea	1.7 - 3.1	2.5	Ekofisk crude	Law, 1981
Northern North Sea	1.1 - 1.7	1.3	Ekofisk crude	Law, 1981
Several British estuaries	24 - 74[a]		Ekofisk crude	Law, 1981
Arctic Ocean	0.05 - 0.20	0.11	Kuwait crude	Fogelqvist et al., 1982

a) Range of maximum concentrations reported for 5 estuaries.

Hydrocarbon Levels Determined by GC

After FS analysis, saponified samples were examined by GC using a Dexsil-300 packed column and flame ionization detection. The GC method was much less sensitive than FS. Sample fluorescence from 3.5 L water was easily measureable in 10-20 mL solvent. By comparison, extracts from 7 L water had to be concentrated to 100 µL or less to obtain good GC patterns. Three Winyah Bay water samples spiked with 2-5 µg quantities of hydrocarbons gave good recoveries for n-C_{16} through n-C_{24}, and phenanthrene (average recovery = 102%), but the recovery of n-C_{14} was only 40%. In quantifying chromatograms, the total resolved and unresolved area beyond the retention time of n-C_{12} was used; however the lower members of this series (n-C_{12} through n-C_{14} and naphthalene) were underestimated due to low recovery. Probably these more volatile hydrocarbons were partially lost during concentration steps. Thus the GC method provided a quantitative estimate for total hydrocarbons heavier than n-C_{14}. Blank values for total hydrocarbons $\geq$ n-C_{12} ranged from 2.3 - 6.0 µg (mean = 4.9 ± 1.3, n = 6). Samples were considered detectable if they measured twice the blank value obtained on that sampling day. Detection limits thus ranged from 0.3 - 0.9 µg/L, based on a 7-L water sample.

Chromatograms from three sampling periods are shown in Figures 10-15. Because sample residues were so low, we did not separate them into aliphatic and aromatic fractions as is common in petroleum analytical work. Several chromatograms showed a regular series of peaks superimposed on an unresolved complex mixture (UCM), suggestive of a petroleum origin. Some samples from the Sampit River turning basin and station 4 also showed a few large peaks (Figures 10 and 11). The identities of these components are unknown. Since the samples were saponified, lipids were not likely to be

present. The peaks may be due to biogenic hydrocarbons or compounds released by some of the Georgetown industries. Even for samples showing these large peaks, most of the total hydrocarbon residues was contributed by the other resolved components and the UCM. For example, the sample from station 4 collected during June, 1982 (Figure 11) contained 30 µg total hydrocarbons. Omitting the three largest peaks in the pattern reduced the estimate to 19 µg.

Matsumoto (1982) and Matsumoto and Hanya (1981) recently compared the GC characteristics of organics from polluted and unpolluted sources. Biogenic sources usually produce odd-numbered n-alkanes, while petroleum products contain about a 1:1 ratio of odd:even alkanes. Unresolved complex mixture hydrocarbons are synthesized by some bacteria, but are also components of petroleum products. Many workers have taken the presence of a UCM as indicative of petroleum pollution.

Chromatograms of two crude and two refined oils are shown in Figures 13 and 15. Sample chromatograms do not resemble those of crude oils nor no. 2 fuel oil. The crude oils lack the hump-shaped UCM, while the UCM for no. 2 fuel is centered between n-C_{14} and n-C_{15}. Sample UCM's are centered near n-C_{22} and n-C_{24}, as is the UCM for the one lubricating oil examined (QS, Figure 13). Hydrocarbons in the bay probably come from a variety of sources, as pointed out earlier. The similarity of lubricating oil and sample UCM's suggests one possibility. Aerial deposition may also contribute high molecular weight hydrocarbons to the bay (Wakeham, 1977). Airborne hydrocarbons have a very pronounced UCM (Keller, 1983). Recently Dr. Eva J. Hoffman at the University of Rhode Island Graduate School of Oceanography (personal communication) found that hydrocarbons in urban runoff from the city of Providence resembled the hydrocarbon distribution in a dustfall sample.

On November 21, 1982 we noticed an oil slick near some trawlers at station 6. A surface sample was collected by immersing a bottle just below the surface, so that some of the slick material was also pulled into the bottle. The sample chromatogram (Figure 15) shows a series of resolved components and a large UCM centered near n-C_{22}. The oil residue may be the heavier components of fuel oil remaining after evaporation of the lighter isomers and/or a lubricating oil. By GC, the sample contained 97 µg/L hydrocarbons. Such oil slicks are probably common around docking areas, and transiently high oil residues can occur in the water column even though petroleum concentrations in the river and bay are comparatively low.

Figure 10

Chromatograms of samples from stations 5 and 8, collected 2/82. Some of the n-alkanes are numbered; n-C_{22} was the internal standard.

Station 5: 7 μL injection, 44 μL total volume.

Station 8: 7 μL injection, 105 μL total volume.

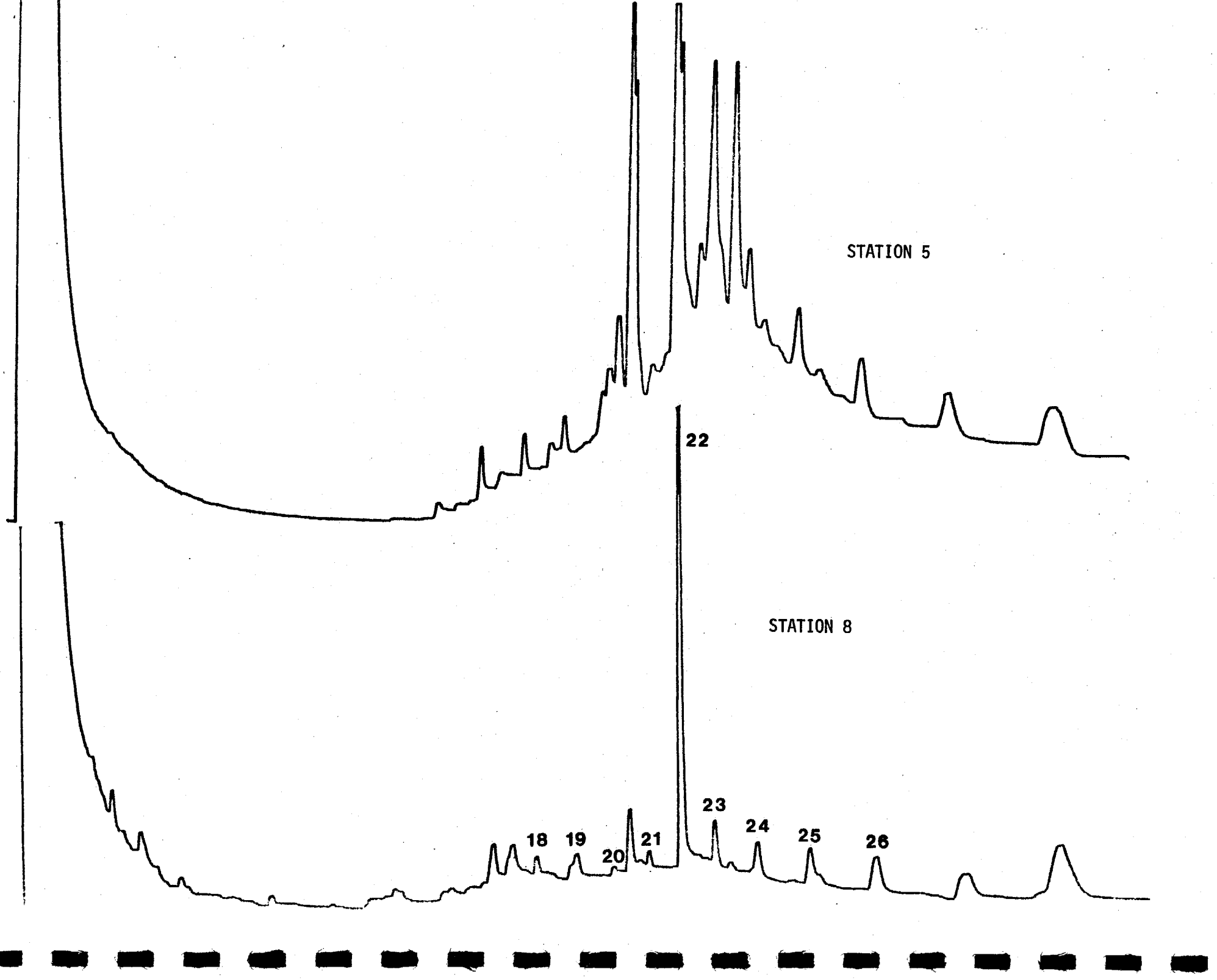

STATION 5
22
STATION 8
18
19
20
21
23
24
25
26

Figure 11

Chromatograms of samples from Stations 4 and 6, and a blank, collected 6/82. Internal standards used were n-C_{14} for station 4 and n-C_{24} for station 6 and the blank.

Station 4: 8 μL injection, 184 μL total volume.

Station 6: 8 μL injection, 46 μL total volume.

Blank: 7 μL injection, 103 μL total volume.

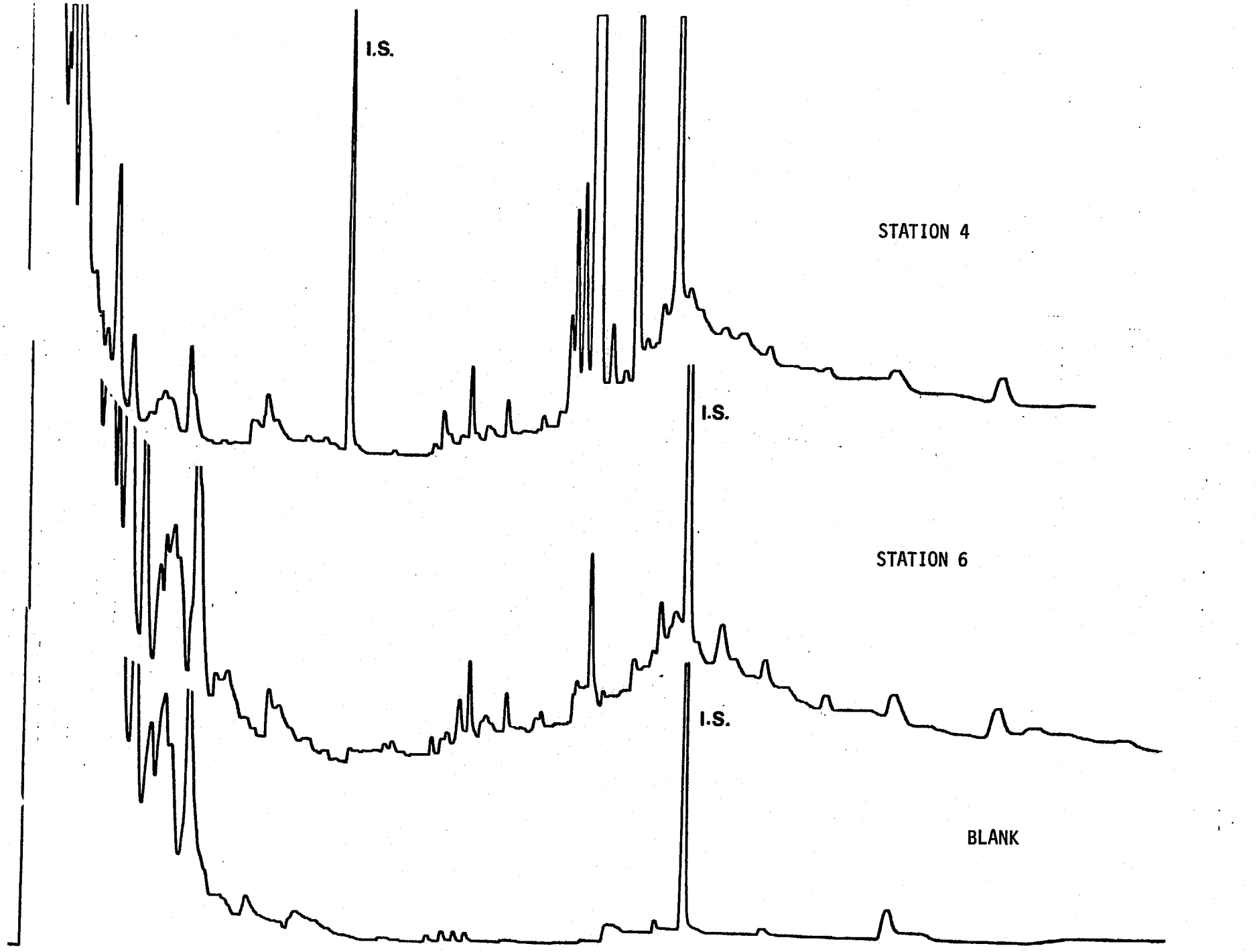

I.S.
STATION 4
I.S.
STATION 6
I.S.
BLANK

Figure 12

Chromatograms of samples from stations 4 and 13, and a blank, collected 11/82. The internal standard is n-C_{14}.

Station 4: 9 μL injection, 80 μL total volume.

Station 13: 8 μL injection, 128 μL total volume.

Blank: 9 μL injection, 124 μL total volume.

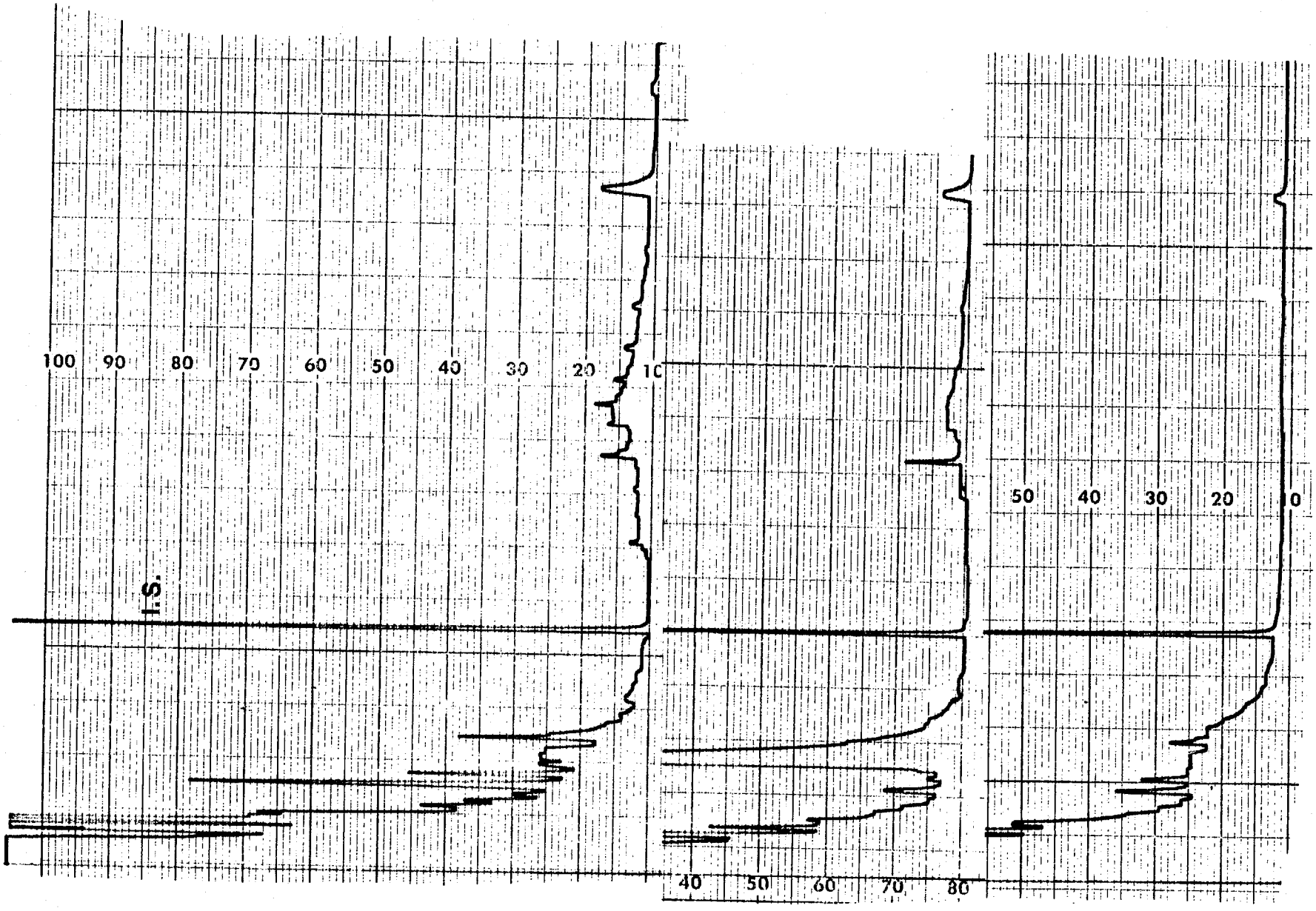

100
90
80
70
60
50
40
30
20
10
I.S.
40
50
60
70
80
50
40
30
20
0

Figure 13

Chromatograms of station 4 sample from 11/82 (also in Figure 12), 10 μL injection, 80 μL total volume; and 6 μg QS lubricating oil.

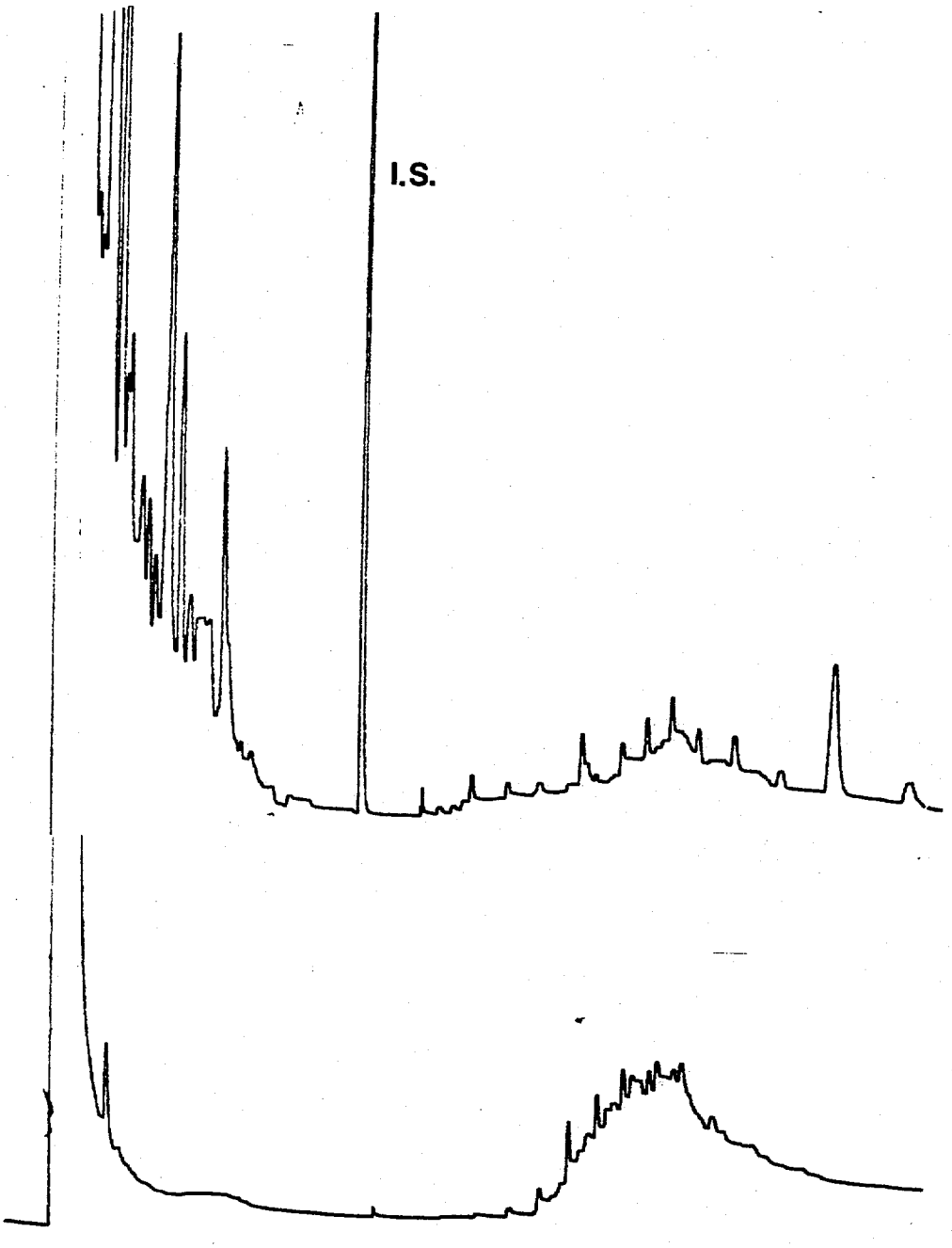

I.S.

Figure 14

Chromatograms of 8 µg, KC, 10 µg SLC, and 10 µg no. 2 fuel oil. Numbers indicate n-alkanes.

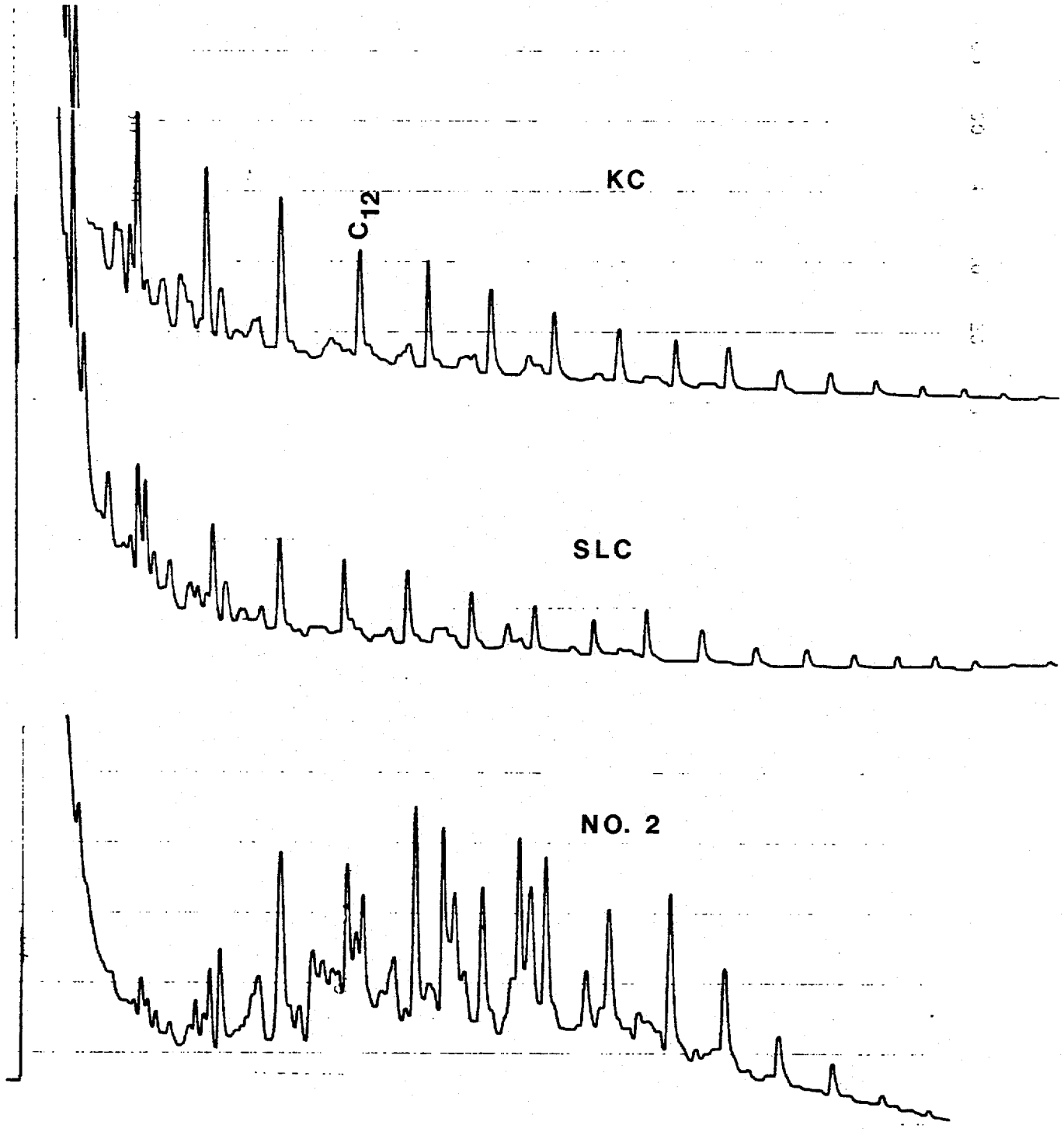
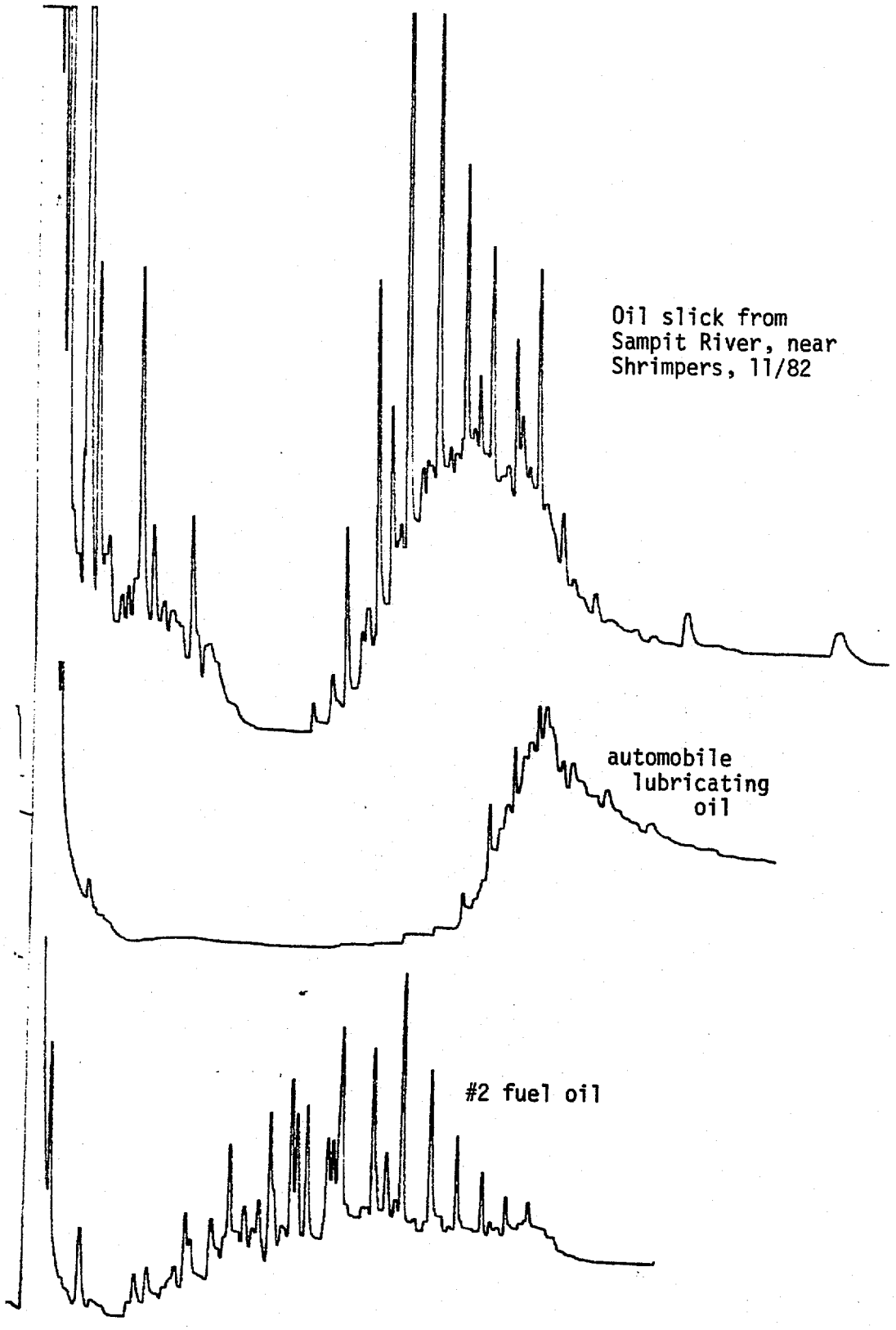

KC
C_{12}
SLC
NO. 2

Figure 15

Chromatogram of an oil slick at station 6, 11/21/82, compared to GC fingerprints of QS and no. 2 fuel oil.


Oil slick from
Sampit River, near
Shrimpers, 11/82
automobile
lubricating
oil
#2 fuel oil

Comparison of FS and GC for Petroleum Analysis

Twenty-six samples were analyzed by FS and GC, and the results obtained by the two methods are shown in Table 7. For 7 samples, petroleum residues were below the detection limit by GC; 18 samples contained hydrocarbons measureable by both methods. FS values in Table 7 are expressed as SLC equivalents. Quantifying the oil residues as lubricating oil (QS) equivalents gave results ten times higher, as indicated by the oil standards relative fluorescence values in Table 3.

Comparison of the two analytical methods is facilitated by Figure 16, where GC results are plotted against FS-determined hydrocarbons expressed as SLC or QS equivalents. For low oil concentrations (0.5-5 μg/L) FS values as SLC equivalents agreed reasonably well with the GC analyses. Although the GC values were usually higher, the difference in most cases was no more than a factor of two or three. The discrepancy was greater when QS was used as a fluorescence standard. For two high concentration samples (30 and 98 μg/L, by GC), GC and FS agreed more closely when the FS values were expressed as lubricating oil equivalents. The latter is not hard to understand, as chromatograms and spectra suggest the presence of lubricating oils as at least part of the petroleum load in the estuary.

For the low-range samples, why is there better correspondence between SLC equivalents and GC results? Near point sources, the aromatic composition of samples appears to be similar to that of a fuel oil or lubricating oil (Figures 8, 9, 13, 14, and 15). Away from point sources we are probably seeing a weathered petroleum residue containing an enrichment of heavy aromatics (the lighter naphthalenes in fuel oils are more volatile). Aerial deposition also may contribute predominently heavy aromatics to the bay (Wakeham, 1977). The distribution of aromatics away from immediate sources

may thus approximate that in a crude oil. If so, measurements by FS against a crude oil standard might provide a reasonably accurate estimate of petroleum in an estuary receiving chronic inputs, even though no source of crude oil is present. Such a conclusion, if supported by data from other estuaries would enhance the reliability of FS for petroleum monitoring.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

The Winyah Bay - Sampit River estuary is relatively clean with respect to petroleum hydrocarbons. FS-determined hydrocarbons, expressed as SLC equivalents, average 3 μg/L in the industrialized portion of the Sampit River, 0.8 μg/L in the upper river, and 0.5 μg/L in Winyah Bay. The concentrations in the bay are more typical of those found in continental shelf water than in industrialized estuaries. Fluorescence spectra and gas chromatograms of water extracts suggest lubricating oils as a source of petroleum in the estuary. Fluorescence spectra also suggest the presence of heavy aromatic compounds, possibly resulting from urban runoff and atmospheric deposition.

This study provides baseline data for petroleum compounds in Winyah Bay. Such a study is the first for the bay, or for any South Carolina estuary. Should petroleum residues increase in the future as a result of higher ship traffic or refinery discharges, state officials will have a basis for quantitatively assessing the increase.

Hydrocarbon concentrations in the water column are transient. Because high molecular weight organic compounds are strongly adsorbed to particulate matter, they are removed from the water column by sedimentation. The sediments of an aquatic system thus serve as a long-term reservoir where pollutants are concentrated and recycled by resuspension, diffusion into overlying water, and uptake by bottom-feeding organisms. A further study of pollutants in the Winyah Bay estuary should include a survey of the sediments for hydrocarbons and other pollutants.

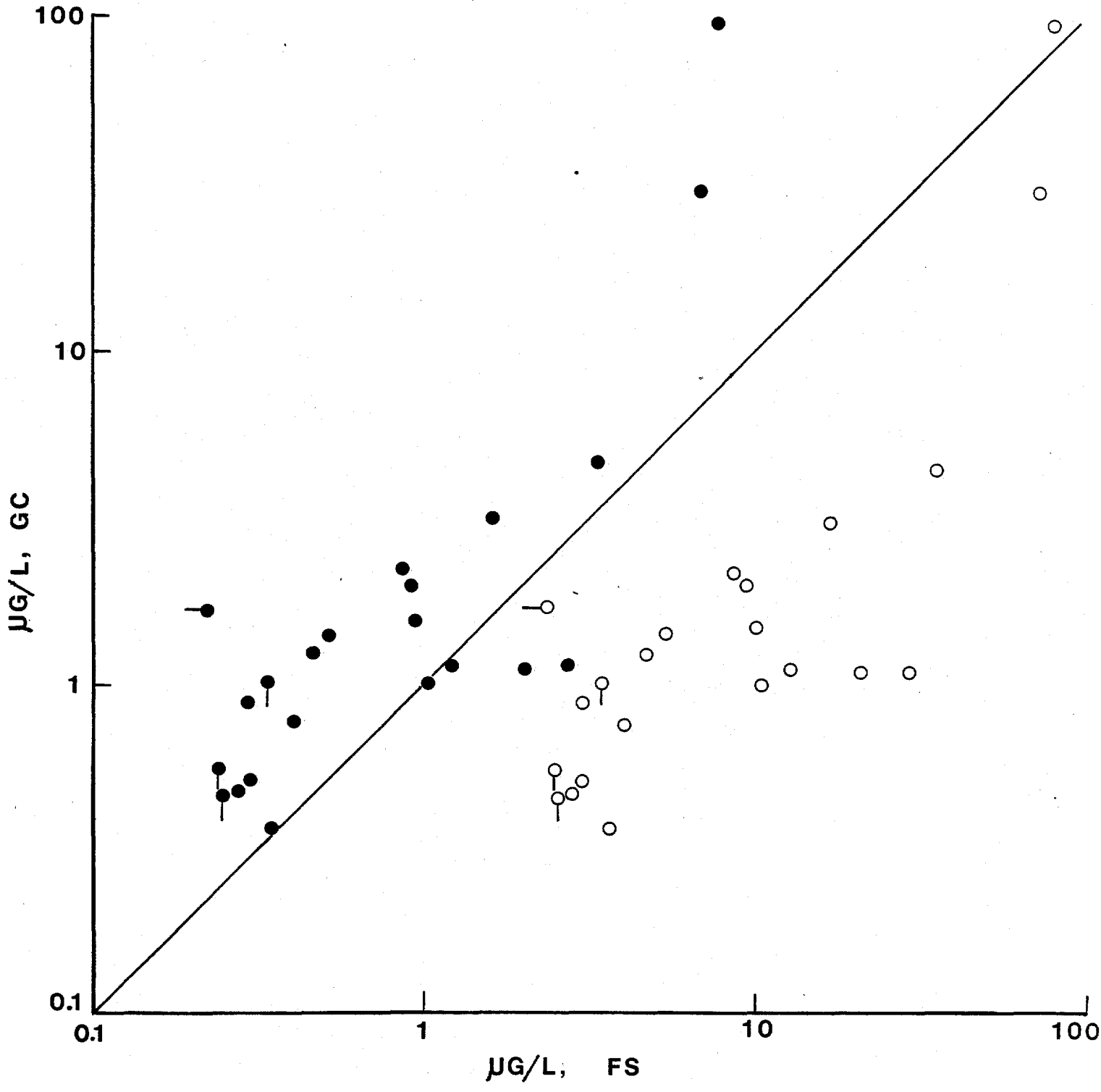
Table 7. Comparison of FS and GC for Petroleum Analysis in the Winyah Bay Estuary

Date	Station	FS SLC Equivalents, µg/L	FS Cleanup[a]	GC, Total Hydrocarbons $>C_{12}$, µg/L[b]	GC/FS
2/20/82	1	1.7(1.0)[c]	A	1.0	1.0
	5	4.0(3.3)[c]	A	4.5	1.4
	8	<1.3	A	<1.1	-
3/20/82	1	<1.5	A	<1.2	-
	5	3.4(2.7)[c]	A	1.1	0.41
	8	<1.6	A	<0.8	-
4/18/82	1	0.24	AS	<0.55	<2.3
	2	0.33	AS	<1.0	<3.0
	5	1.2	AS	1.1	0.92
	8	0.25	AS	<0.45	<1.8
5/22/82	1	0.27	AS	0.46	1.7
	2	0.29	AS	0.51	1.8
	5	2.0	AS	1.1	0.55
6/19/82	4	6.7	AS	29.9	4.5
	6	1.6	AS	3.1	1.9
9/5/82	4	0.39	AS	0.73	1.9
	5	0.84	AS	2.2	2.6
	8	0.29	AS	0.85	2.9
11/21/82	4	0.90	AS	2.0	2.2
	4	0.45	AS	1.2	2.7
	5	0.93	AS	1.5	1.6
	5[d]	0.51	AS	1.4	2.7
	6[d]	7.7	AS	97.5	12.7
	8	<0.22	AS	1.7	<7.7
	13	<0.20	AS	<1.0	
	13	0.34	AS	0.36	1.1

a) A = alumina AS = alumina and saponification.
b) AS cleanup for all samples.
c) Corrected to AS values by subtracting 0.7 µg/L from A values.
d) Oil slick plus underlying water.

Figure 16

Comparison of FS and GC for analysis of petroleum in the Winyah Bay estuary. The line depicts a 1:1 correspondence between the two methods. All FS values are after alumina and saponification (AS) cleanup; three samples receiving alumina (A) cleanup only were corrected to AS values by subtracting 0.7 µg/L (see Table 7). Filled circles represent FS values as SLC equivalents; open circles refer to concentrations expressed as lubricating oil (QS) equivalents. Samples $\leq$ blank values are indicated by ○ ● for GC, and —○— —● for FS.


100
10
1
0.1
µG/L, GC
0.1
1
10
100
µG/L, FS

The close agreement between FS and GC for low hydrocarbon levels in the Winyah Bay estuary suggests that FS measurements using a crude oil standard may provide a reasonably accurate estimate of hydrocarbons in a estuary receiving hydrocarbon inputs from a variety of sources. A comparison between the two techniques in other estuaries would provide a test of this hypothesis. Within South Carolina, we suggest Charleston Harbor as a good location for further comparisons. This estuary is much more heavily industrialized than Winyah Bay and has more ship traffic. Preliminary FS measurements indicate hydrocarbon levels in the harbor about 10-20 times higher than those in Winyah Bay.

Although a measurement of total hydrocarbon levels is useful for monitoring purposes, a knowledge of specific aromatic hydrocarbon concentrations is more useful for assessing the toxicant burden of the estuary. Individual aromatic compounds vary widely in their toxicities; a few are highly carcinogenic (e.g. benzo[a]pyrene, benz[a]anthracene). We recommend that further investigations include the measurement of individual PAH. This would be best carried out using capillary GC or high performance liquid chromatography (HPLC), with mass spectral confirmation for selected samples.

Finally, a study of the sources of hydrocarbons in the bay would be enlightening. As mentioned earlier, urban runoff appears to be an important input mechanism for total hydrocarbons and PAH. The relative importance of urban runoff, atmospheric deposition, and discharges from ships and industries should be investigated to determine the main hydrocarbon contributors to the bay.

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