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HYDROCARBON INCORPORATION INTO THE SALT MARSH ECOSYSTEM FROM THE WEST FALMOUTH OIL SPILL

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TECHNICAL REPORT

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Approved for Distribution Richard H. Backus

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Department of Biology

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Abstract

The oil barge "Florida" ran aground just off Little Island, West Falmouth, Massachusetts on September 16, 1969. About 175,000 gallons of Number Two fuel oil leaked into Buzzards Bay and the adjacent Wild Harbor Marsh.

This report presents the results of analyses done on marsh muds and organisms collected nearly a year after the spill. We studied the incorporation of polluting hydrocarbons into, and their movement through the marsh ecosystem.

Analyses of surface muds agreed well with observations on plant growth. The dead areas were the most heavily polluted. A deep mud core in the dead area showed oil has penetrated to at least 70 cm.

Virtually all the marsh organisms living in the contaminated area were affected by the oil at least to the extent that they accumulated oil hydrocarbons in their tissues. Our data suggest that two processes may occur as the oil passes through the marsh ecosystem. There may be a progressive loss in the straight chain hydrocarbons in relation to branched chain, cyclic and aromatic hydrocarbons. There also appears to be a selection for the higher boiling fractions of the contaminants higher up in the food chain.

INTRODUCTION

The oil barge "FLORIDA" ran aground just off Little Island, West Falmouth, Massachusetts on September 16, 1969, and leaked about 175,000 gallons of Number Two fuel oil into Buzzards Bay before it was removed. Heavy winds drove the oil into Wild Harbor and Wild Harbor River Marsh areas.

The most immediate results were massive kills of marine and marsh life. Sanders reported that almost no animals survived in the most heavily polluted areas. Chemical analyses of the surviving shellfish showed their tissues were heavily contaminated with hydrocarbons characteristic of the spilled fuel oil.[1]

Blumer's subsequent analyses showed little reduction in the amount or types of contaminating hydrocarbons in the sediments and shellfish several months after the spill. Weathering and biochemical degradation had the effect of slowly reducing the straight and branched chain hydrocarbons in relation to the cyclic and aromatic compounds; thus, apparently increasing the toxicity of the remaining oil. Periodic sampling indicated the harbor was suffering continued contamination by fresh undegraded oil released from the subsurface sediments. Sediment analysis showed the affected area was spreading along the sea bottom.[2]

We measured the amounts and types of hydrocarbons due to the pollution in species characteristic of the salt marsh rather than the more characteristically estuarine oysters and scallops analyzed by Blumer. For unpolluted control samples we collected in Sippewissett Marsh which opens onto Buzzards Bay 3 Km south of Little Island where the spill occurred and 6 1/2 Km south of the opening of Wild Harbor

River Marsh. Our purpose was to monitor the incorporation of polluting hydrocarbons into, and their movement through, the marsh food chain.

Methods

Marsh organisms were collected in mid-summer 1970, almost a year after the initial kill due to oil. All samples were washed with tap water and frozen at -20°C until analyzed. Further collections were made when necessary.

Hydrocarbons were extracted from samples according to Blumer's methods. After being thawed and weighed tissues were placed in either a Soxhlet Extractor with methanol for 24 to 48 hours or in a Virtis homogenizer with 5 times the tissue weight of anhydrous KA_2SO_4 and extracted with pentane. Hydrocarbons were isolated as follows: Pentane partioning (in the soxhlet technique), column chromatography using an activated copper column (in the case of sediments), and then column chromatography through a partially deactivated silica gel and alumina column with pentane as eluent. Samples, were then evaporated to dryness, taken up in 1/2 ml carbon disulfide and stored in teflon capped vials until chromatographed.

Extracts were analyzed on a Hewlett-Packard model 700 gas chromatograph with a flame ionization detector and linear temperature programmer. Columns were packed with 3% apiezon-L (liquid phase) on chromasorb W AW-DMCS (solid phase). Temperatures were programmed 80° - 280°C at 5°/min. plus, in some cases, an isothermal period at 280°C.

Total hydrocarbon content shown on the chromatogram was determined by planimetry and comparison to a chromatogram of the standard Number

Two fuel oil. Concentrations of individual components of the spectra were obtained by measuring peak heights and comparison to appropriate standards. Blumer has noted that biochemical degradation first reduces straight chain and then branched chain hydrocarbons. Cyclic and aromatic compounds are destroyed only very slowly. The ratio of a straight to a branched chain compound (heptadecane/pristane) provided a measure of relative degradation among samples.

Results and Discussion

The results of our analyses are shown in the table and figures. Sample numbers in the table correspond to figure numbers. The amounts of obvious biogenic hydrocarbons are not included in the table. Boiling points of the major components of the spectra are listed usually as a range. Heptadecane (C_{17}) to pristane ratios are given as an indication of relative degradation among samples.

For example, sample number two was surface mud taken from Wild Harbor Marsh in January, 1971. It contained 3,080 µg hydrocarbons per gram of mud (net weight). The major fraction of these hydrocarbons boiled between 140° and 280°C and appear from their finger print (Fig. 2) to be composed mostly of Number Two fuel oil. The C_{17}/pristane ratio is 1.25 indicating only slight biochemical degradation when compared with the fuel oil standard of 1.67. This mud was taken from a heavily oiled area containing Spartina patens killed in the initial spill.

Sediments

Surface mud samples were taken in January, 1971, from four locations

in the Wild Harbor Marsh area. Chemical analyses agreed well with our observations of the plant growth. In Area Two, which had been a Spartina patens area, there were over 3 mg. oil per gram mud, all the original grass was dead and no other plants were growing. Sample Three was taken from a spot where S. patens had been killed but Salicornia sp. seeds germinated and grew. The oil level was less than 6% of that in the dead area. Two apparently unoiled adjacent areas, one in S. patens marsh (Sample Four), and one in S. alterniflora marsh (Sample Five) had less that 50 µg hydrocarbons per gram mud but clearly showed a small trace of the fuel oil finger print on the chromatograms.

A deep mud core was taken in May, 1971, from the completely dead S. patens area. There were 6.5 mg oil per gram mud at the surface. Oil had penetrated to at least 70 cm. At 70 cm the series of peaks from high boiling plant waxes equaled those of the fuel oil in intensity. Below this depth the plant waxes dominated the spectra. The concentration of oil in the sediment decreased exponentially with depth from the surface to 70 cm indicating diffusion was the mechanism of transport. Since biochemical oxidation of oil proceeds only under aerobic conditions, degradation should cease as soon as it diffuses below the surface in the highly reduced marsh soil. This is evidenced by the decrease in C_{17}/pristane ratio with depth. The small amount of highly degraded fuel oil present at 115 to 120 cm may be attributed to some other process such as flow through channels or pores in the sediment or some sort of biological transport.

Plants

The green alga, Enteromorpha clathrata, was one of the most highly contaminated organisms we analyzed. The spectrum consisted of relatively undegraded oil with boiling point range identical to the standard. The red alga, Polysiphonia fibrillosa, contained much less. Green algae like Enteromorpha is reported to have a very large surface to volume ratio which enables it to absorb nutrients [and oil] faster than its competitors.[3] From cursory observation, the green algae appeared far more abundant and widespread in the marsh than the red. Thus, it may constitute a very significant source for entry of oil into the marsh food chain.

Spartina alterniflora and Salicornia sp. took up about the same amount of fuel oil per gram of tissue. These two higher plants, especially Spartina, provide the bulk of food for detritus feeders.[4] This is another possible path for entrance of oil into the food chain if the oil remains in the plant detritus or associated bacteria as the plants decay.

Animals

Ribbed mussels, Modiolus demissus, took a large amount of oil into their tissues. These animals are filter feeders and may have absorbed oil directly from the water or absorbed to or in their particulate food. A large amount of biochemical breakdown of the straight and branched chains was evident which might indicate the latter pathway. The oil remaining in these shellfish consisted mainly of cyclic and aromatic hydrocarbons. Blumer has reported the persistence of oil contamination in shellfish even when kept in clean running sea water for

months [2] We found 22 ug of oil hydrocarbons per gram in tissue of specimens of the blue mussel, Mytilus edulis, from Wild Harbor. These animals had been kept in fresh running sea water by George Hampson from June, 1970 to April, 1971.

The fish Fundulus sp. contained highly degraded oil in their tissues. (Each animal was gutted before extraction.) The boiling point range is slightly higher than the shellfish.

Eels, Anguilla rostrata were the only marsh animals to show contamination in the control. The Sippewissett eel muscle contained oil slightly less degraded than the Wild Harbor animals, indicating a fresher source of contamination. Eels are highly mobile and spend much of their time outside the marshes in Buzzards Bay. Blumer has reported the oil moving south through the sediments of the Bay, toward the Sippewissett area. The control eels were probably contaminated by fresh oil released from the sediments in the Bay. The boiling range of hydrocarbons in the eels tended to be higher than that in Fundulus.

Herring gulls, Larus argentatus, represent the highest level of the food chain we analyzed. It seemed quite likely becauseof the mobility of the gulls and their habit of feeding in places likely to be contaminated by oil, eg. behind ships, and in garbage dumps, that an uncontaminated gull would be impossible to find. On the other hand, individual gulls do have definite feeding areas and we thought it likely that those feeding in the Wild Harbor area would show a different pattern of pollution, reflecting the Number Two fuel oil, than gulls feeding in other areas. The idea was supported by the observation that the gulls feeding on the animals killed just after the spill were all

immatures. These would be the individuals more likely to be in an unfavorable social position in the regular feeding grounds and to be less selective in their food (supposing that heavily oiled animals are not a preferred gull food). We found no dead gulls in the Wild Harbor area so we killed one immature that fed in the contaminated area and one adult from the Weepecket nesting colony, about 15 Km southwest, but still in Buzzards Bay.

The muscle from the Wild Harbor gull showed the whole spectrum of fuel oil hydrocarbons but contained mostly straight and slightly branched chains as shown by an infra-red spectrum of the sample. The brain of this animal showed a large high boiling envelope identified as aromatics by ultraviolet spectroscopy. The muscle of the Weepecket gull contained very few hydrocarbons boiling below C19 except for C17. There were three groups of peaks resolved between C19 and C25 and an unresolved envelope in this same boiling range that accounted for 67% of the total. Such broad unresolved envelopes are not normally found in uncontaminated animals. We assume this is evidence of oil pollution from some unknown source. The brain of the Weepecket gull contained hydrocarbons very similar to those in its muscle, bearing little resemblance to those in the brain of the Wild Harbor gull. The resolved peaks in the C19 - C25 boiling range are also found in the Wild Harbor gull and are presumably of biogenic origin. The contrast between the chromatograph patterns from the two gulls clearly implicates the Wild Harbor spill as the main source of contamination in the gull from that area.

Conclusion

This survey of marsh animals shows that virtually all the marsh organisms living in the contaminated area were affected by the oil at least to the extent that they accumulated the oil hydrocarbons in their tissues. The oil has also penetrated deeply into the marsh muds where, because of the anoxic conditions, it will presumably be very long-lasting. Whether or not the effects on the organisms will be long-lasting in the same time scale remains to be seen.

The amounts of oil we found are comparable to the amounts found by Blumer et. al.[1], to those found in aquatic animals exposed to oil by Zitko and Carson,[5] and in molluscs from Wild Harbor estuary. What the effects of these hydrocarbons are is not known except for the obvious kill of many sorts of organisms from the most highly contaminated parts of the marsh. Our data suggest that two processes might occur as the oil passes through the food chain of the marsh. However, we cannot separate the effects of food chains from those due to differential uptake from the environment by different species, without experimental data. There may be a progressive loss of the straight chain hydrocarbons that appear in our chromatograms as an unresolved envelope. There may also be a selection for the higher boiling fraction of the contaminants higher up in the food chain.

Sample	Collection and Location	Total Oil Hydrocarbons Wet Weight Basis		Boiling Point Range °C	$\frac{C_{17}}{\text{Pristane}}$	Comments
No. 2 Fuel Oil						
1. STANDARD		54.57	µg	125°-280°	1.67	
A. Sediments						
2. SURFACE MUD	W. H. 1/71	3,080	µg/gm	140°-280°	1.25	Heavily oiled area containing dead Spartina patens.
3. SURFACE MUD	W. H. 1/71	190	"	135°-280°	1.06	Mediumly oiled area containing dead Spartina patens.
4. SURFACE MUD	W. H. 1/71	28.3	"	165°-280°	0.88	Little oil on mud containing live S. patens.
5. SURFACE MUD	W. H. 1/71	20.6	"	150°-280°	0.85	Little oil on mud containing live S. alterniflora.
5a. SURFACE MUD	Sipp. 10/71		"	190°-280°	Biogenic H.C.'s	
6. DEEP MUD CORE	W. H. 5/71	6,510	"	125°-280°	0.99	Heavily oiled area 1 meter from creek edge
7. CORE 25-30cm	W. H. 5/71	71.7	"	140°-280°	1.22	Exponential decrease in oil concentration with depth to 70cm
8. CORE 45-50cm	W. H. 5/71	30.4	"	170°-280°	1.29	
9. CORE 67-72cm	W. H. 5/71	12.7	"	190°-280°	1.39	Decrease in Biochemical degradation with depth to 70cm

	Sample	Date of Collection and Location	Total Oil Hydrocarbons Wet Weight Basis	Boiling Point Range °C	C_{17} Pristane	Comments
10.	CORE 85-90cm	W. H. 5/71	12.7 ug/gm	190°-280°	Biogenic H. C.'s	High boiling plant waxes predominant
11.	CORE 115-200cm	W. H. 5/71	10.5 "	160°-280°	0.96	Influx of relatively degraded oil
B.	Plants					
12.	Enteromorpha clathrata	W. H. 8/70	429 "	125°-280°	1.06	
13.	Enteromorpha clathrata (green algae)	Sipp. 8/70		199°C	Biogenic H. C.	
14	Polysiphonia fibrillosa	W. H. 8/70	6.28 "	123°-280°	8.25	Large biogenic C_{17} peak distorts C_{17}/pristane ratio
15.	Polysiphonia fibrillosa (red algae)	Sipp. 8/70		204° (C_{17})	Biogenic H. C.	
16.	Salicornia sp.	W. H. 8/70	13.2 "	160°-280°+	1.44	Oil incorporated to concentrations equal to natural plant waxes
17.	Salicornia sp.	Sipp. 8/70		160°-280°+ C_{21}, 22, 23, 24, 25 etc.	Biogenic H. C.'s	
18.	Spartina alterniflora	W. H. 7/70	15.2 "	150°-280° + high boilers	Oil and Biogenic H. C.'s	Oil incorp. to conc. less than natural plant waxes

	Sample	Date of Collection and Location	Total Oil Hydrocarbons Wet Weight Basis		Boiling Point Range °C	C_{17} Pristane	Comments
19.	Spartina alterniflora	W. H. 7/70	15.2	ug/gm	150°-280°+ C_{21}, 23, 25 etc.	Biogenic H. C.'s	Odd Carbon number series of plant waxes
C.	Animals						
20.	Modiolus demissus	W. H. 8/70	218	"	140°-280°	0.58	Highly degraded oil with few straight or branched chain H. C.'s
21.	Modiolus demissus (ribbed mussels)	Sipp. 8/70			239°-246°	Biogenic H. C.'s	
22.	Fundulus sp.	W. H. 8/70	74.8	"	155°-280°	0.65	Highly degraded oil with few straight or branched chains
23.	Fundulus sp.	Sipp. 8/70				Biogenic H. C.'s	
24.	Anguilla rostrata Liver	W. H. 8/70	84.9	"	165°-280°+	0.87	Highly degraded oil with few straight or branched chain H. C.'s Sipp. muscle sample more degraded than W. H. sample
25.	Anguilla rostrata Liver (eel)	Sipp. 8/70	50.9	"	165°-280°+	0.75	
26.	Anguilla rostrata (muscle)	W. H. 8/70	23.5	"	165°-280°	0.54	
27.	Anguilla rostrata (muscle)	Sipp. 8/70	80.4	"	150°-280°	0.82	
28.	Larus argentatus Brain (Herring Gull)	W. H. 10/69	384	"	180°-280°+	0.97	High boiling envelope of aromatics. Confirmed by U. V. analysis

	Sample	Date of Collection and Location	Total Oil Hydrocarbons Wet Weight Basis	Boiling Point Range °C	$\frac{C_{17}}{\text{Pristane}}$	Comments
29.	Larus argentatus (fatty muscle)	W. H. 10/69	535 µg/gm	125°-280°+	0.83	I. R. analysis shows mostly straight or slightly branched chain H. C.'s
30.	Larus argentatus (fatty muscle)	Weepecket Island 6/71	10.0 "	200°-280°+	33% Biogenic H. C.'s	High boiling biogenic spectra as in 29. Low boiling contaminants absent
31.	Larus argentatus (Brain)	Weepecket Island 6/71	15.3 "	200°-280°+	Biogenic H. C.'s	High boiling biogenic spectra as in 29 and 30. High boiling aromatics absent

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4. Teal, John, and Mildred Teal. 1969. Life and Death of the Salt Marsh. Audubon/Ballantine, New York. 274p.

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1. Blumer, M., G. Souza, and J. Sass. January, 1970. "Hydrocarbon Pollution of Edible Shellfish by an Oil Spill" Unpublished Manuscript. Reference No. 70-1 W.H.O.I.

2. Blumer, M., J. Sass, G. Souza, H. Sanders, F. Grassle, and G. Hampson. September, 1970. "The West Falmouth Oil Spill" Unpublished Manuscript. Reference No. 70-44 W.H.O.I.

3. Odum, E. et. al. 1958. "Uptake of P^{32} and Primary Productivity in Marine and Benthic Algae" Limnol. Oceanogr. 3, 340-348.

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Figure Legends

The vertical lines in the chromatograms are places where the records were attenuated by a factor of two.

Fig. 1. Number Two fuel oil standard.

Fig. 2. Wild Harbor surface mud. Dead *S. patens* area.

Fig. 3. Wild Harbor surface mud. New *Salicornia* growing where original *S. patens* was killed.

Fig. 4. Wild Harbor surface mud. *S. patens* growing.

Fig. 5. Wild Harbor surface mud. *S. alterniflora* growing.

Fig. 5a. Sippewissett surface mud.

Fig. 6. Wild Harbor mud core from dead *S. patens* area 0-5 cm.

Fig. 7. " " " " 25-30 cm.

Fig. 8. " " " " 45-50 cm.

Fig. 9. " " " " 67-72 cm.

Fig. 10. " " " " 85-90 cm.

Fig. 11. " " " " 115-120 cm.

Fig. 12. Wild Harbor Green Algae, *Enteromorpha*.

Fig. 13. Sippewisset Green Algae, *Enteromorpha*.

Fig. 14. Wild Harbor Red Algae, *Polysiphonia*.

Fig. 15. Sippewissett Red Algae, *Polysiphonia*.

Fig. 16. Wild Harbor *Salicornia*.

Fig. 17. Sippewissett *Salicornia*.

Fig. 18. Wild Harbor *Spartina alterniflora*.

Fig. 19. Sippewissett *Spartina alterniflora*.

Fig. 20. Wild Harbor ribbed mussel, *Modiolus*.

Fig. 21. Sippewissett ribbed mussel, Modiolus.

Fig. 22. Wild Harbor Fundulus.

Fig. 23. Sippewissett Fundulus.

Fig. 24. Wild Harbor eel liver, Anguilla.

Fig. 25. Sippewissett eel liver, Anguilla.

Fig. 26. Wild Harbor eel muscle, Anguilla.

Fig. 27. Sippewissett eel muscle, Anguilla.

Fig. 28. Wild Harbor sea gull brain, Larus.

Fig. 29. Wild Harbor sea gull fatty-muscle, Larus.

Fig. 30. Weepecket sea gull fatty-muscle, Larus.

Fig. 31. Weepecket sea gull brain, Larus.

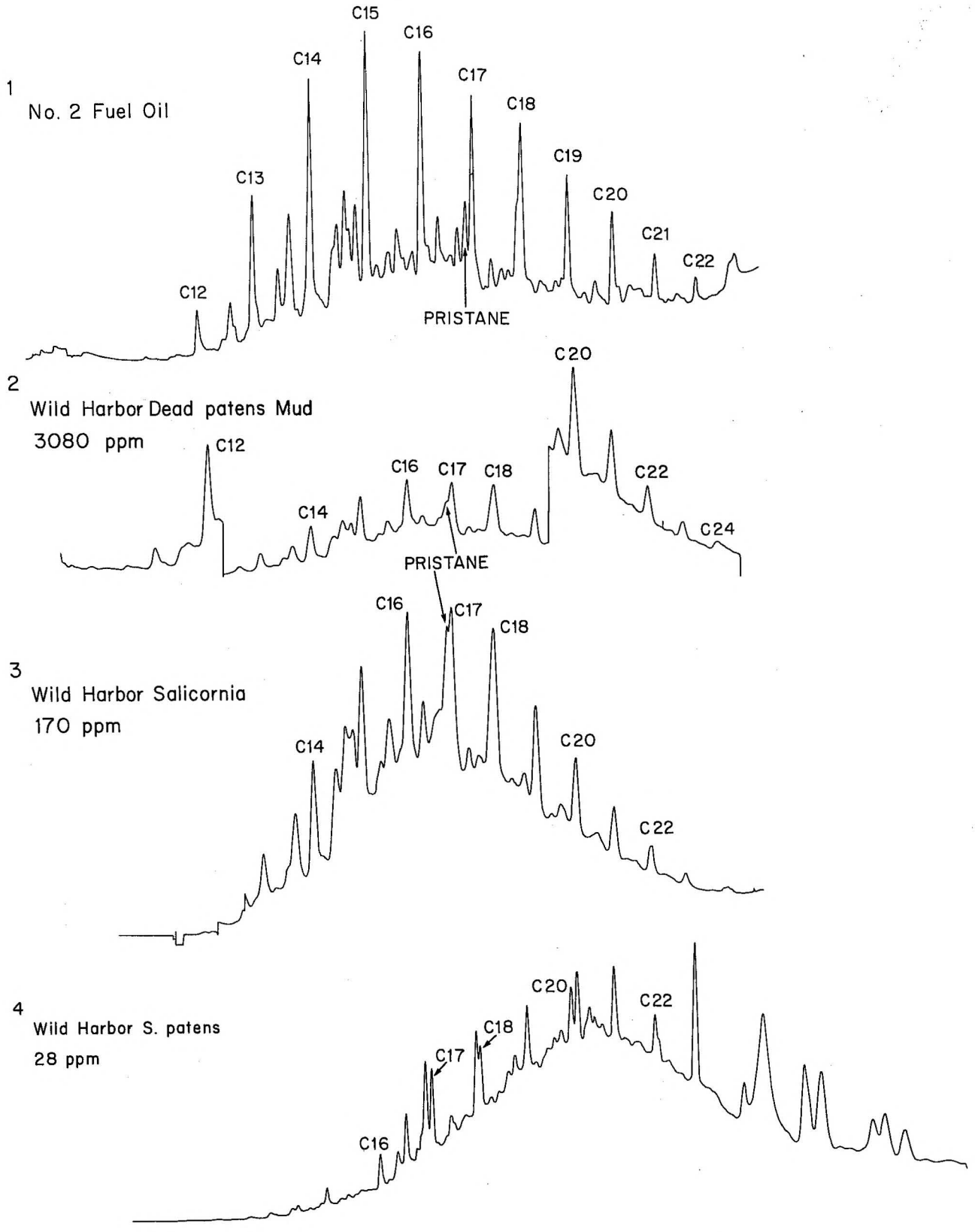


Figure 1. No. 2 Fuel Oil. Figure 2. Wild Harbor Dead Patens Mud 3080 ppm.
Figure 3. Wild Harbor Salicornia 170 ppm. Figure 4. Wild Harbor S. patens 28 ppm.

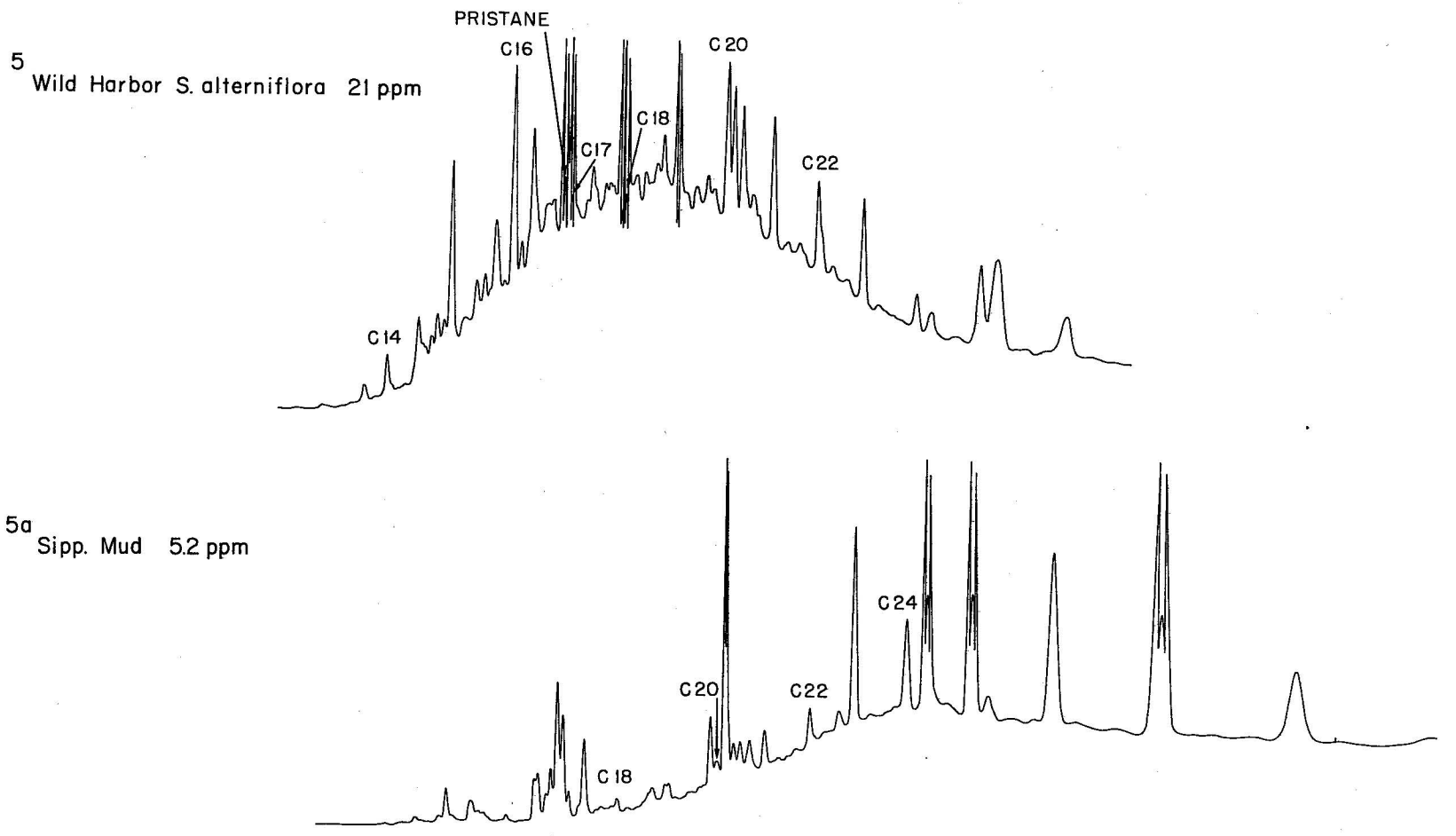


Figure 5. Wild Harbor S. alterniflora 21 ppm. Figure 5a. Sipp. Mud 5.2 ppm.

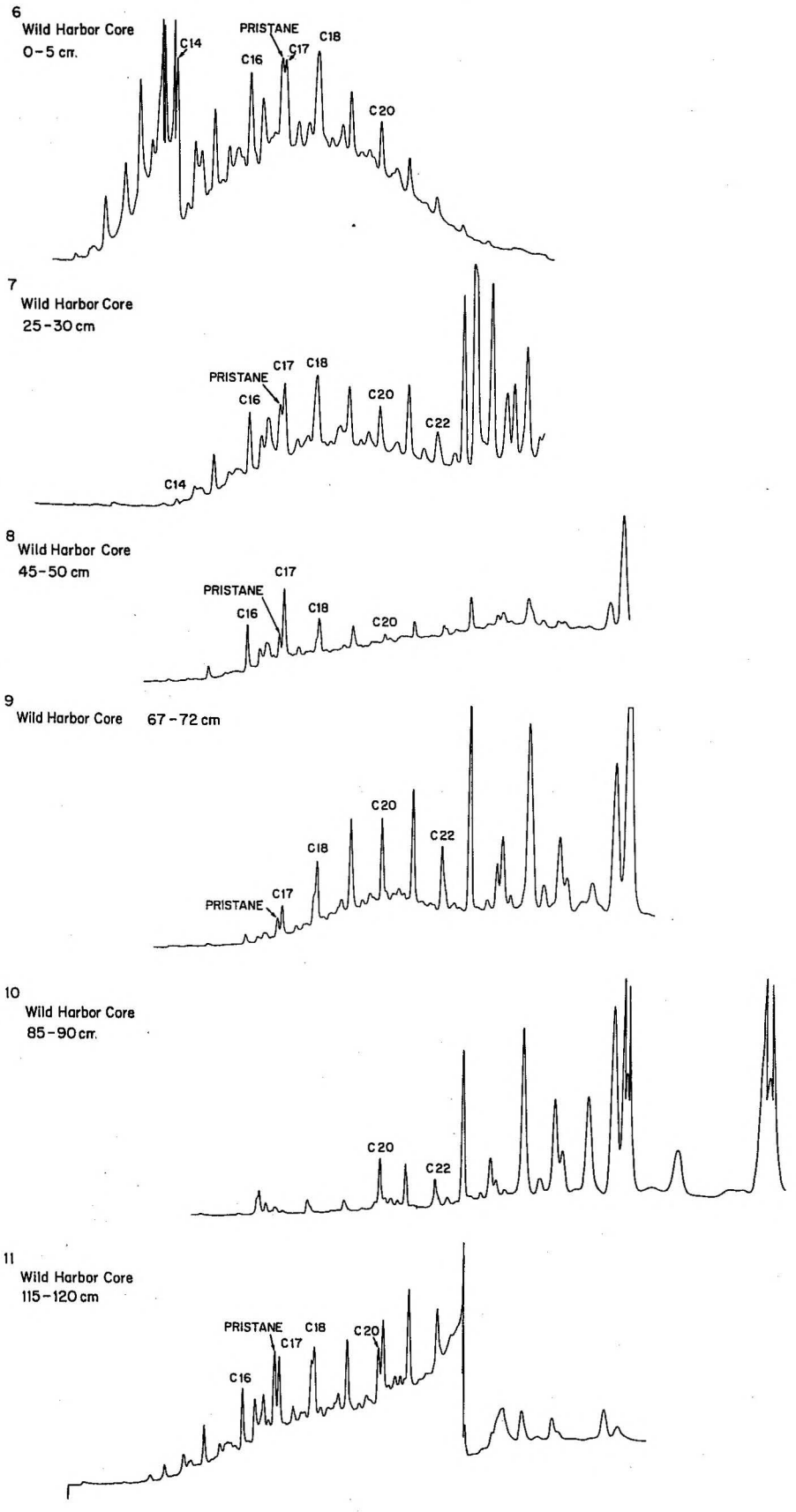


Figure 6. Wild Harbor Core 0-5 cm 6500 ppm. Figure 7. Wild Harbor Core 25-30 cm 72 ppm. Figure 8. Wild Harbor Core 45-50 cm 30 ppm. Figure 9. Wild Harbor Core 67-72 cm 13 ppm. Figure 10. Wild Harbor Core 85-90 cm 13 ppm. Figure 11. Wild Harbor Core 115-120 cm 11 ppm.

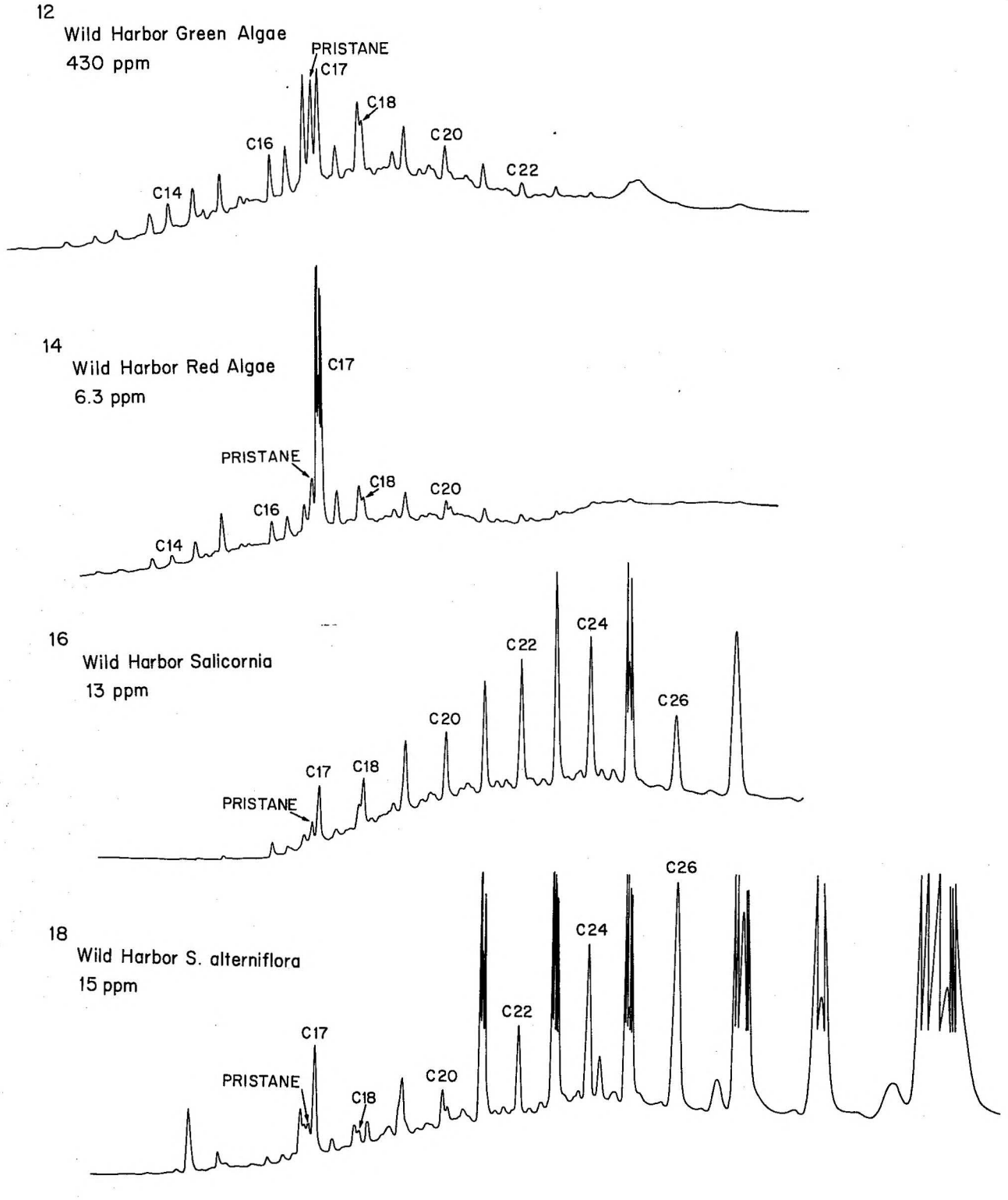


Figure 12. Wild Harbor Green Algae 430 ppm. Figure 14. Wild Harbor Red algae 6.3 ppm. Figure 16. Wild Harbor Salicornia 13 ppm. Figure 18. Wild Harbor S. alterniflora 15 ppm.

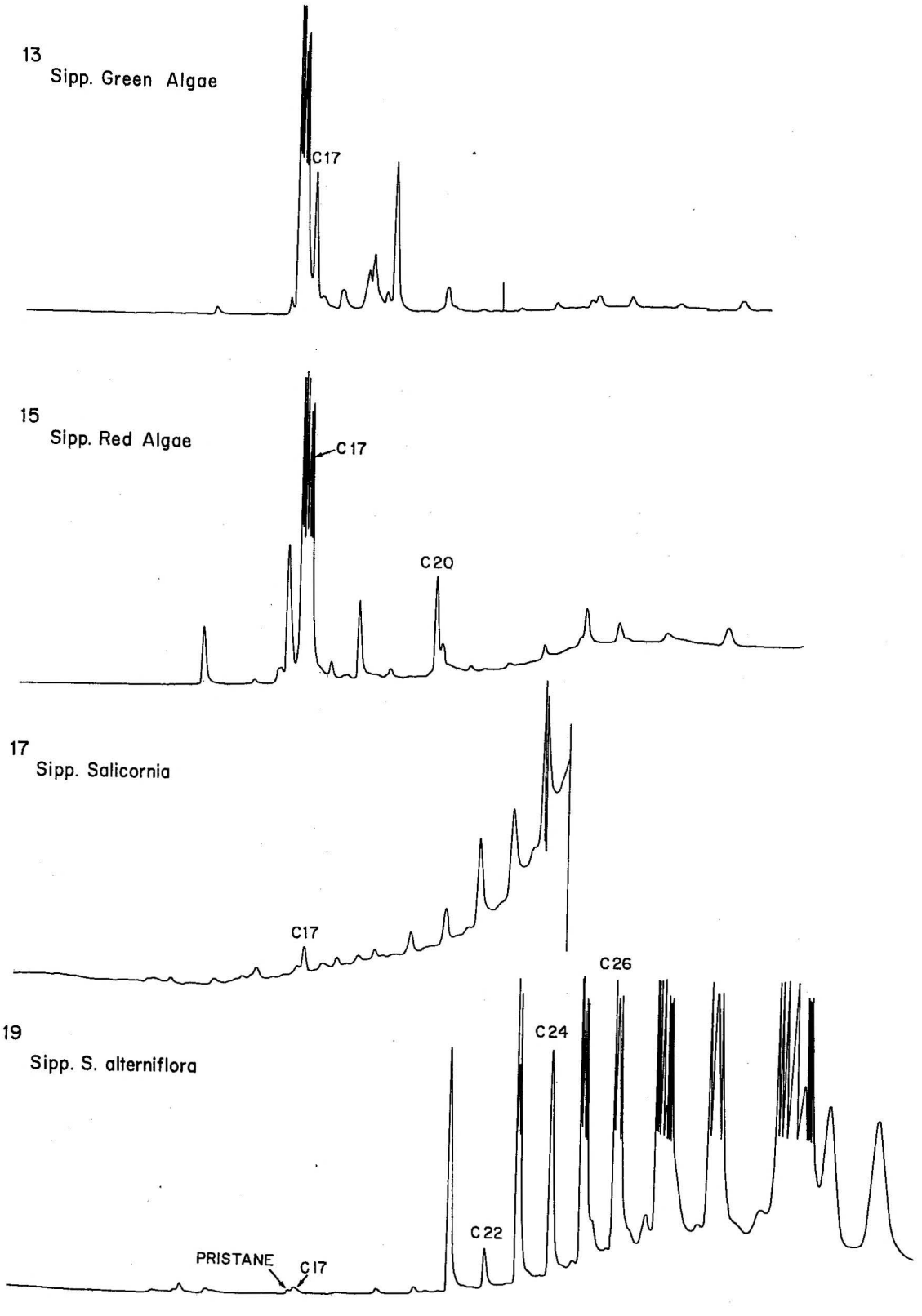


Figure 13. Sipp. Green algae. Figure 15. Sipp. Red Algae. Figure 17. Sipp. Salicornia. Figure 19. Sipp. S. alterniflora.

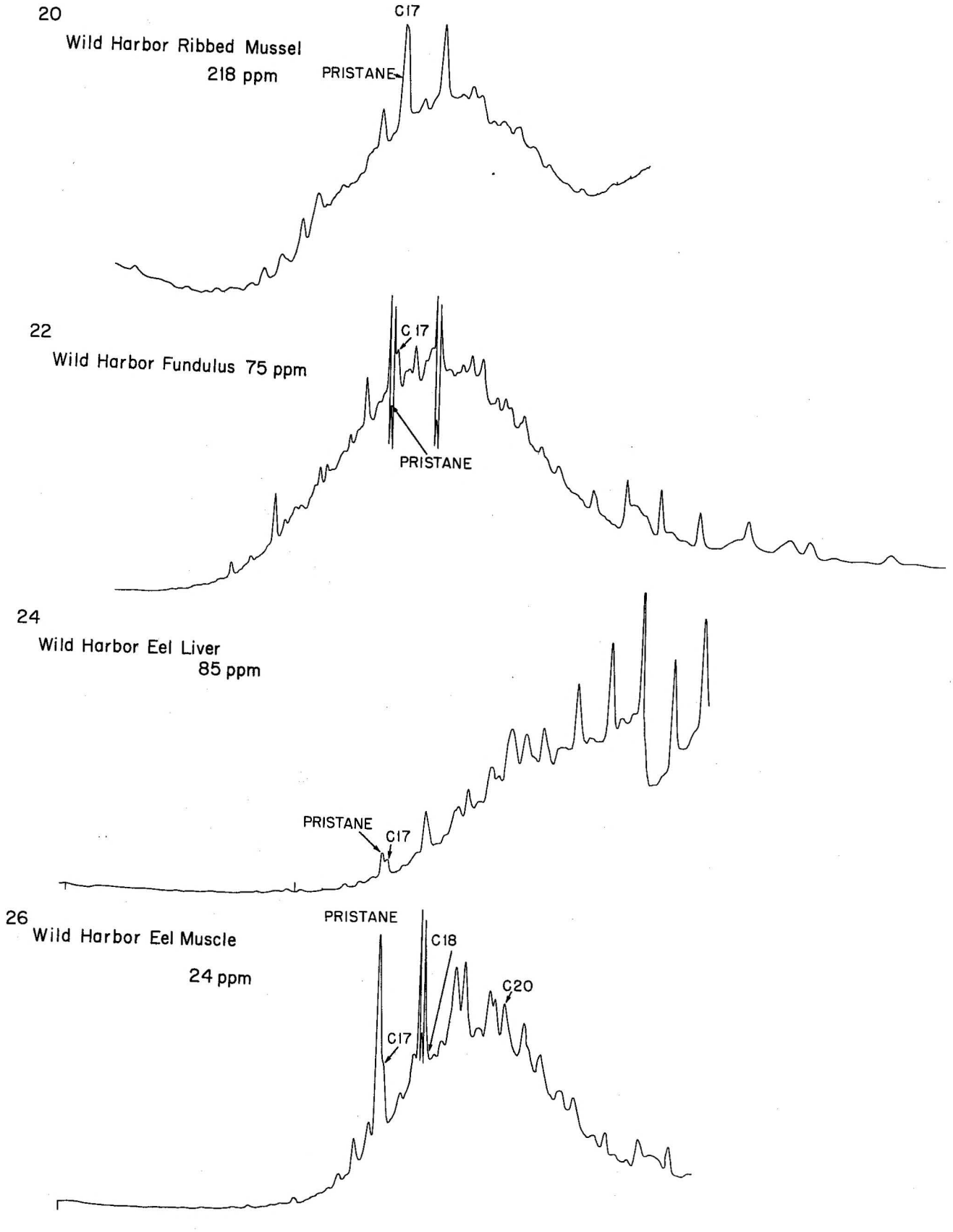
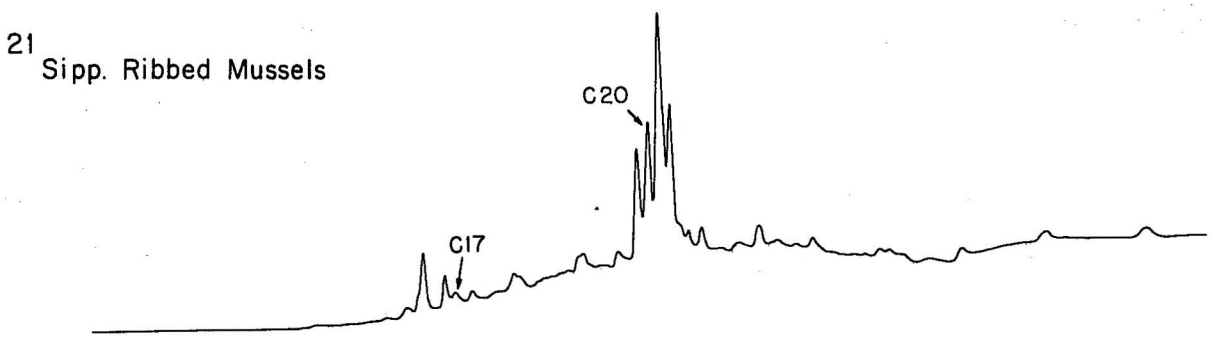
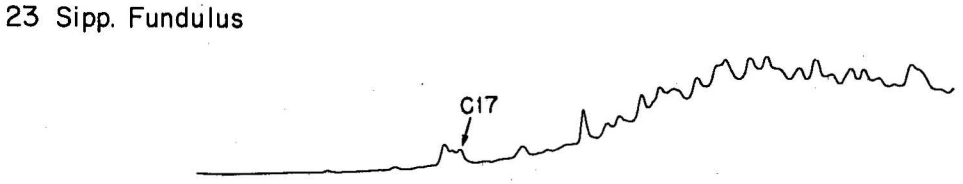
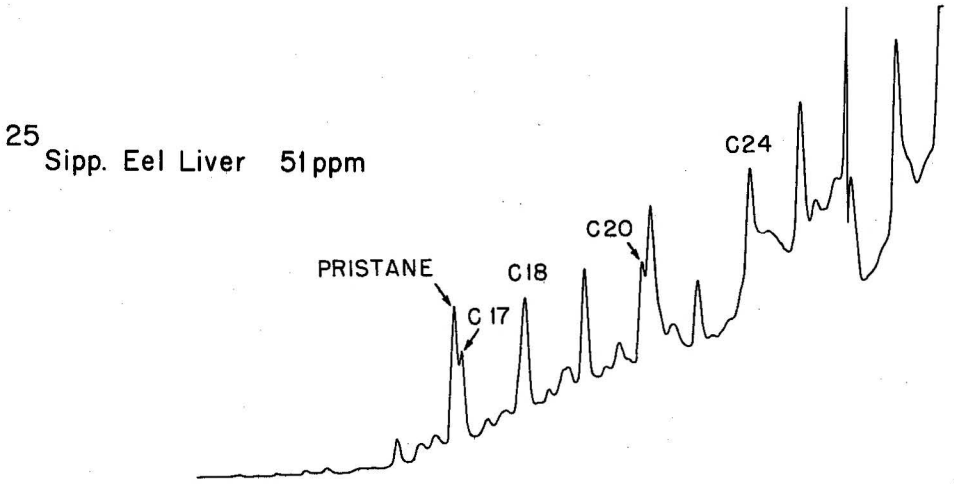


Figure 20. Wild Harbor Ribbed Mussel 218 ppm. Figure 22. Wild Harbor Fundulus 75 ppm. Figure 24. Wild Harbor Eel Liver 85 ppm. Figure 26. Wild Harbor Eel Muscle 24 ppm.







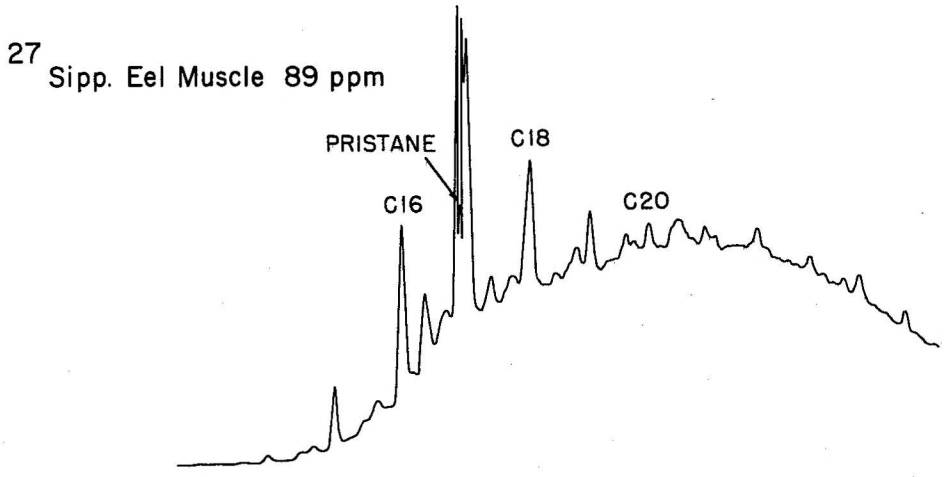


Figure 21. Sipp. Ribbed Mussels. Figure 23. Sipp. Fundulus. Figure 25. Sipp. Eel Liver 51 ppm. Figure 27. Sipp. Eel Muscle 89 ppm.

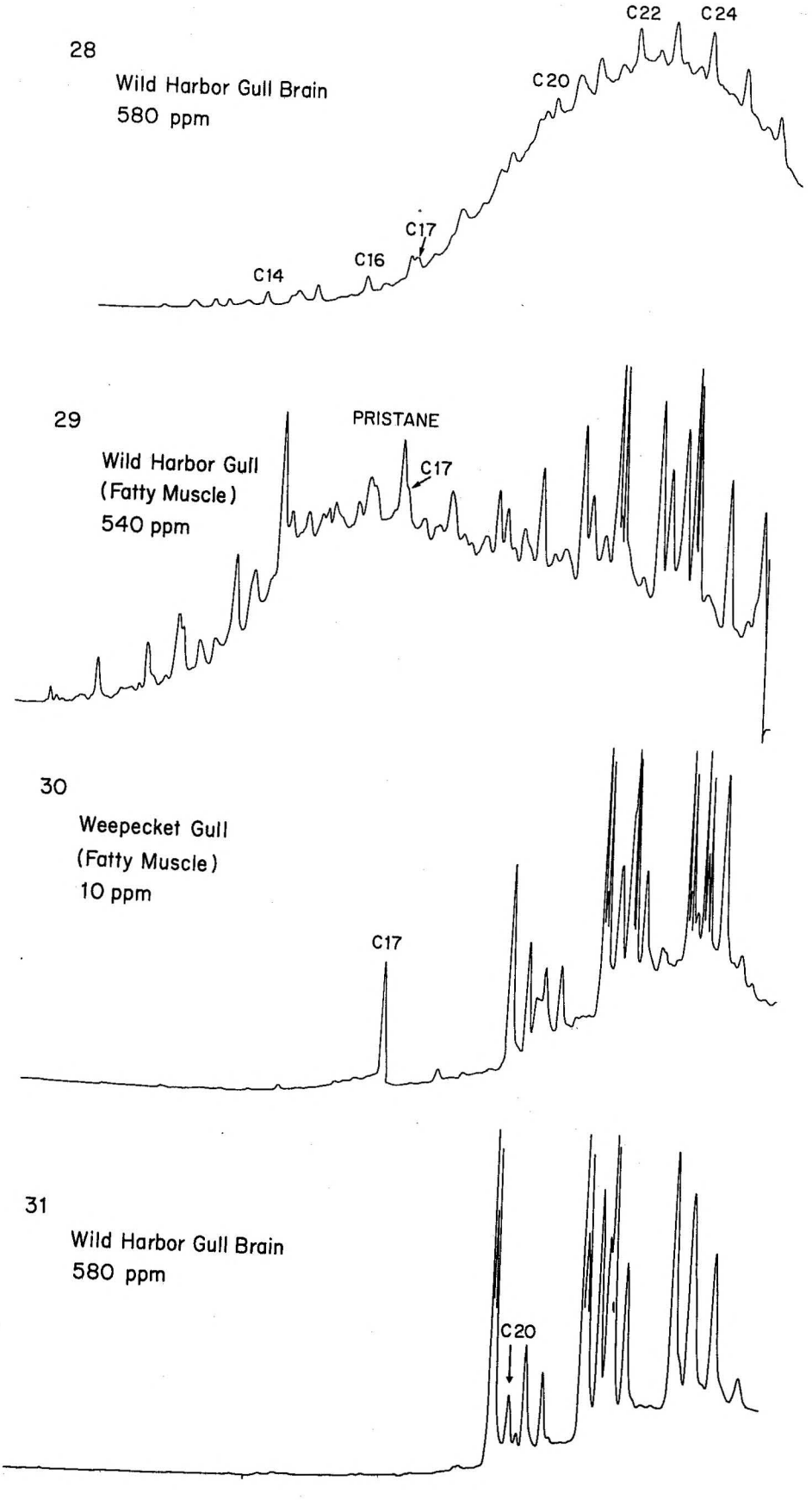


Figure 28. Wild Harbor Gull Brain 580 ppm. Figure 29. Wild Harbor Gull (Fatty Muscle) 540 ppm. Figure 30. Weepecket Gull (Fatty Muscle) 10 ppm. Figure 31. Wild Harbor Gull Brain 580 ppm.