

Appendix 1

Standard Operating Procedures for PEMDs

Introduction

Passive accumulation devices (PADs) are typically hydrophilic membranes with or without hydrophilic reservoirs and they are designed to sample non-polar hydrophobic hydrocarbons, including polynuclear aromatic hydrocarbons (PAH) and persistent organic pollutants (POPs) from air, water, and sediment. A commercially available PAD commonly available in the USA is the semi-permeable membrane device (SPMD); its central reservoir is triolein (e.g., Huckins et al. 1990). Hydrocarbons in SPMDs diffuse through pores in the membranes and are trapped in the central triolein matrix, mimicking uptake by living organisms; additional hydrocarbons are retained by the membrane. Advantages of passive sampling are that they can sample large volumes of water, amplify trace hydrocarbon quantities (part-per-billion or part-per-trillion) to detectable levels, and average the signal over time. In addition, they are cheaper and easier to analyze than biological tissue and can be deployed over a greater range of environmental conditions.

At low ambient hydrocarbon concentrations, low-density polyethylene membrane devices (PEMDs) deployed without inclusion of the central hydrocarbon reservoir are simpler and less expensive sampling devices than SPMDs, yet provide the same benefits (Carls et al. 2004). Loss of accumulated PAH is slow, thus PEMDs reliably capture sporadic or fluctuating events. Composition of PAH accumulated by PEMDs can be used to identify hydrocarbon sources in situations not complicated by multiple sources. At the Auke Bay Laboratory, we also refer to PEMDs as LDPEs (low density polyethylene devices) or PMDs (polyethylene membrane devices). A universal moniker has not yet been established in the literature.

Laboratory preparation

Low-density polyethylene tubing (98 $\mu\text{m} \times 4.9 \text{ cm} \times 50 \text{ cm}$) is sonicated twice in pentane to remove hydrocarbons, placed in aluminum samplers (11.5 diameter \times 6.6 cm with perforated endplates, 3 mm holes spaced 4.8 mm apart, precleaned in dichloromethane), wrapped with two layers of aluminum foil, heat-sealed in two plastic bags, and frozen until shipment (Fig. 1; Carls et al. 2004).



Fig. 1. Example PEMD wrapped in foil and placed in ziplock bags. This example was wrapped with a single layer of foil which has torn, illustrating the need to be careful and double wrap each canister.

Caution

These devices are incredibly sensitive!!! Be careful!!!

PEMDs sample both air and water and tiny unwanted quantities can swamp the target signal! For example, a venting gas tank in a skiff is very bad. (Solution – do not fill the tanks full!) The person who deploys or retrieves the PEMDs should NOT be the same one running the engine, handling the trailer, or fiddling with gas!!! Petroleum products have a way of migrating from hands/clothing to the PEMDs. Open the devices only when ready to deploy without delay; wrap and bag them without delay upon retrieval. Practice your moves and carefully arrange your tools ahead of time to minimize time and the possibility of contamination. Wear disposable gloves and change them between every set or retrieval. If available, an assistant (also with clean gloves) can open or close pails/bags. Do not allow devices to come in contact with clothing, the boat etc; it should go straight from bag to water and vice versa. Design your fastening system to work with minimal effort – rusty shackles that require wrenches add time and increase the odds of unwanted contamination. Any necessary tools should be cleaned ahead of time; this may include the boat. Oil or gas weeping from a boat will ruin samples!

Deployment & Retrieval

The general strategy is to determine where the devices are to be located, place suitable anchors for them, then deploy. All hardware must be very clean; hydrocarbons that leach from anchor cable, for example, will become the sample, compromising the study. “Very clean” typically means solvent-washed in the laboratory and transported appropriately (e.g., in ziplock bags) so that hydrocarbons are not accumulated along the way. Anchors, other hardware, floats, and rope can be reused repeatedly without further cleaning assuming that it is not contaminated during exchanges. New rope (nylon, polypropylene) does not cause contamination. Do not use old rope that has an unknown history or rope that has been exposed to bilge water, etc. Rope should be placed in suitable bags (e.g., garbage or ziplock bags) when transported to avoid contamination! The same is true for transportation of every other item and tool.

Clean bags are acceptable storage for PEMDs, tools, & gear. Start with new clean ziplock and garbage bags and keep them clean in other bags & in pails.

Five gallon pails are an excellent for transportation and collection. Buy new ones and keep the insides clean! Stacking pails with hydrocarbons stuck to the outside will contaminate pail insides! (Buckets can be stacked if lined with clean garbage bags.) Screw-top lids are very useful in this context and a variety of colors is recommended so buckets are easily distinguished (see Table 1.1 for example bucket contents). Two or three half-gallon plastic drinking containers placed inside can provide structure for pails used for tools and small gear (Fig. 2). Place bagged PEMDs inside garbage bags inside pails. When open, place lids upside down (inside showing) on the ground or other



Fig. 2. Example equipment bucket with internal structure.

surfaces to avoid transferring potential external contamination into buckets. Keep buckets closed as much as possible.

Deployment. Do not open a PEMD until you are ready to place it. Put on clean disposable gloves. Tear through the two heat-sealed ziplock bags and remove the aluminum foil. A second person to manage the waste can be helpful, particularly under windy conditions. Fasten the PEMD onto its anchoring device and back/drift away. (Do not contaminate newly installed devices by standing upstream of them, running boat exhaust by them etc.)

Retrieval. Retrieval is essentially the reverse of deployment and should occur first when swapping. ‘Collection kits’ are needed; these are simply pre-cut aluminum foil sheets placed in ziplock bags. Arrange collection gear to optimize efficiency and minimize time; put on clean disposable gloves. Retrieve the PEMD; this may require tools, such as wire cutters, wrenches, etc. Be sure to swirl sediment out of the canister with the water it has been in. Fold the shackle to the canister and place the PEMD at the center of an aluminum sheet; fold to cover completely. Repeat with a second sheet; starting at the opposite side. (A helper make this process easier, particularly in wind. Avoid contact with clothing!) Then place the PEMD in a ziplock bag; close (with as little air as practical). Place this in a second ziplock bag. Add a label and seal. Put this package in a garbage bag inside a bucket. Depending on time and sampling circumstances, you might wish to bundle groups of PEMDs in separate garbage bags, tied shut at intervals to minimize any possibility of contamination. Freeze as soon as possible.

Blanks. Site blanks are a necessary quality assurance technique. Open one container per site / trip, depending upon agreed-upon design. Expose to air about 1 minute, then re-bag, label, and freeze as above.

Labels & record keeping. Make labels out of paper; “Rite in the rain” all weather paper is nice. Pre-printed labels with a minimum of necessary identification information are nice; keep them clean in a small ziplock bag. Each label should have a sample number; use a pencil to write the information. Place labels outside of the inner PEMD bag and inside the second bag. A complete record of collection, including location and time should be kept in a separate notebook. In addition, complete chain of custody forms; these are required by the Auke Bay Laboratory for record keeping and processing (Table 1.2).

Stream deployment

Subdivide streams into oiled/polluted (typically downstream) and non-oiled/non-polluted (upstream) sections. Non-oiled sites are intended to be stream-specific references. Identify and similarly sample matched reference streams. Where feasible, consider determining stream gradients and place samplers at the same elevation in multiple streams. Be aware, however, that stream gradients can vary considerably, thus site elevations and spacing between sites cannot always be uniform from stream-to-stream. To sample the hyporheic zone, bury the PEMDs below the stream bed (e.g., 10 to 20 cm deep; Fig. 3; Carls et al. 2004). Sometimes stream activity will excavate buried devices. PEMDS can be anchored with duckbill anchors (attach shackle to cable with zip ties) or weighted polypropylene mesh bags. Partially fill anchor bags with stream rock. Mark positions with GPS. Floats located downstream of the PEMD, stakes or cairns on the bank, or other identifying marks can be helpful. Photographs are also helpful for locating PEMDs. Place upstream PEMDs first and work downstream; retrieve downstream PEMDs first and work upstream. The procedure avoids potential contamination introduced by boots, waders, etc. and is highly advisable in small systems (e.g., PMS16 & MKS5) but can be relaxed in big systems with large distances (kilometers) between samplers (e.g., SKN14).

Intertidal deployment

We have successfully used several techniques for anchoring PEMDs in intertidal areas. These include weighted bags, duckbill anchors, and expansion bolts drilled into rock. Zip ties or nylon rope are used as connectors. PEMDs can be buried or placed on the surface, depending on objectives. Objectives should also be considered when deciding sampler elevation.

Marine water deployment

Place anchors on polypropylene rope in desired depth of water. Consider using chain on Danforth anchors, then rope (Fig. 3). Alternatively, fasten the rope to the anchor and place a lead cannonball weight about 10' up the rope: this should force the anchor to dig. When tying rope to anchors, be sure to smooth sharp edges on the anchor if present – or use a shackle. Make eye splices with protective sleeves if possible, or reweave rope ends back into the rope several times after knotting (e.g., bowlin or re woven figure eight). Use 3/8" line or larger. Keep float sizes small to reduce lift on the anchors – but large enough to float the hardware and big enough that you can find them. Bullet or seine floats are ok. Assuming the anchors (& other bottom hardware) are reasonably clean (consider a detergent wash) and that there are several meters between the anchor and buoy, solvent cleaning isn't needed. Allow enough line for tidal fluctuation, extra slack, etc. Consider weighting partway down so it sinks to prevent navigation hazard.

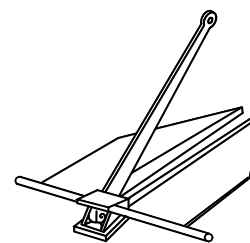


Fig. 3. Danforth anchor.

Gear has a better chance of surviving if placed outside the surf zone and on a broad flat shelf. Lines will eventually part if there is too much wave energy, so inspect them periodically for wear. Anchors have a habit of moving around even if they initially appear to be well set; if they slide too far down a slope the buoys will be pulled under and the gear will be lost.

Deploy/retrieve sequence: set anchor, mark position with GPS. Shut engine off!!! Swing on the anchor until fumes clear from the air. No smoking; it will contaminate the sampler. Only then, deploy (or retrieve) the PEMD.

Subsurface deployment. PEMDs deployed below the surface are designed to assess average hydrocarbon concentrations in various water layers. We typically deploy 1 m below the surface to characterize this layer. The most efficient method is to pass a loop of anchor rope through the shackle on the PEMD and around the PEMD, then cinch it tight (Fig. 4). In our experience, the PEMD will stay put (not sink) on 3/8" polypropylene rope and 3/8" may be the largest rope diameter possible for this method with the standard shackles. To preclude sinking, consider hanging the PEMD from a loop attached directly to the buoy; the disadvantage is that this can snarl. Another way to stop potential sinking is to place a knot in the anchor rope below the device loop. For line larger than 3/8" a second, larger shackle will be necessary (precleaned, of course). Obviously, a knot (e.g., butterfly) can be placed in the anchor line at the appropriate depth (e.g., 1 m below the buoy) and the PEMD can be shackled to it. Shackles can add time at retrieval and are difficult when rusty. One solution is to place a rope loop between both

shackles, again passed around the PEMD. (An effective knot for making loops is the double fisherman's bend; Fig. 5). Shackles could be potentially linked together with zip ties, but this has not yet been tried with this type of deployment and is not recommended.



Fig. 4. Anchor line looped around PEMD shackle



Fig. 5. Fisherman's bend. This knot is likely more secure in a nylon rope than polypropylene.

Surface deployment. PEMDs deployed at the surface are designed to sample the surface microlayer. Well known is the propensity for hydrophobic compounds to accumulate in this layer, increasing the probability of detecting very low hydrocarbon levels. A technique we previously used was to pass a threaded shaft through the center of the PEMD canister; floats were placed at each end of the shaft and the PEMD shackle was tied to the anchor rope. A major disadvantage with this system was that field assembly was necessary and slow. A suggested modification is to revise the sequence; place the two floats near the center of the shaft with a gap for a shackle; this will connect to the anchor rope (Fig 6). Place a dummy (or replicate) PEMD at one end of the shaft; place another PEMD at the other end. These will be held in place with nylon-bushed nuts to prevent unthreading. Two nuts at each end are advisable and an ancillary rope or cable from the PEMD shackle to the anchor line is possible.

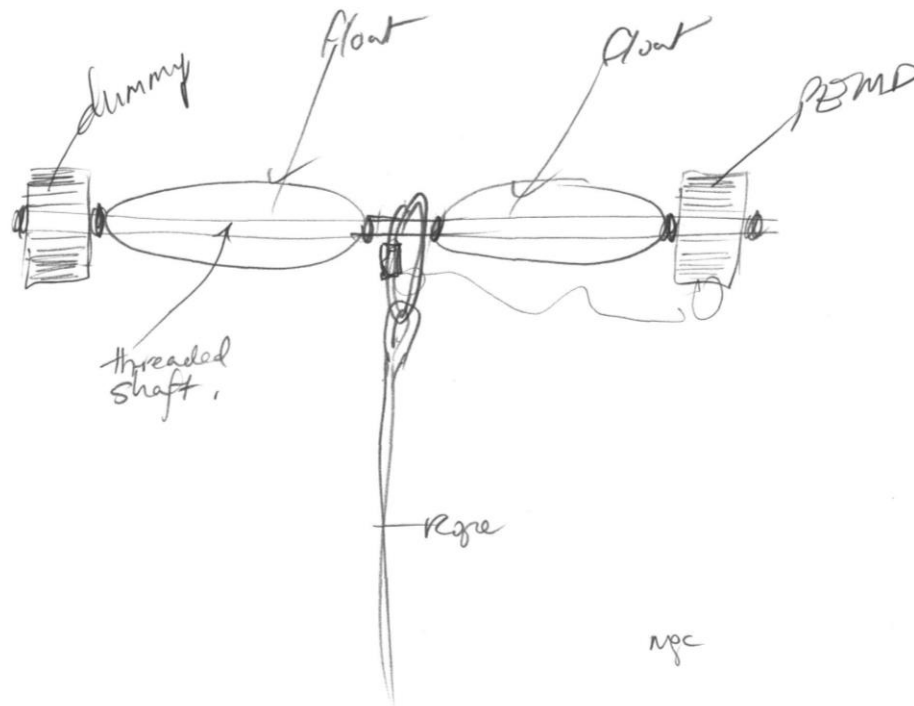


Fig. 6. Configuration for surface sampling. PEMDs are fastened on the ends of the shaft with nylon nuts.

Shipping

PEMDs in buckets and bagged as outlined above can be shipped via Alaska Air Freight. Indicate that the buckets are to be kept frozen. General delivery is ok under these conditions. If freezers aren't working or are not available, then ship priority (or Gold Streak).

References

- Carls, M.G., L.G. Holland, J.W. Short, R. A. Heintz, and S. D. Rice. 2004. Monitoring polynuclear aromatic hydrocarbons in aqueous environments with passive low-density polyethylene membrane devices. *Environ Toxicol Chem* 23:1416-1424.
- Huckins JN, Tubergen MW, Manuweera GK. 1990. Semipermeable membrane devices containing model lipid: a new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* 20:533-552.

Appendix 1, Table 1.1. Example equipment and supply lists, arranged by bucket. Buckets with colored screw-top lids are one convenient way to transport gear and retrieve PEMDs. A four-bucket system is used in this example, each dedicated to a specific purpose. On a first trip, an installation bucket with appropriate gear might be substituted for the pickup kit.

Yellow

Pickup kit

field notebook
labels
Aluminum foil
Disposable gloves
ziplock bags
garbage bags, large, black
garbage bags, small, white

Blue

PEMD deployment kit

New PEMDs

White

PEMD retrieval kit

garbage bags
retrieved PEMDs

Red

Equipment kit

YSI salinity, temperature meter
Sonar (handheld)
GPS
VHF radio
pens, pencils, markers
knife
wrench(es)
nut driver
cutters
wire cutters
screw drivers
spare batteries
marlinspike or fid or plastic stake

Appendix 1, Table 1.2. Example chain of custody form required by the Auke Bay Laboratory as a data record and for analytical processing.

Auke Bay Laboratory Hydrocarbon Assessment Chain of Custody Form

2003 _____ Page _____ of _____

Project _____

Numbering scheme is as follows: assigned serial number of the sheet (14, ...) then individual sample number eg. 01; these last two digits are typed on the sheet already in the 1st column, the serial number is directly above this box **Serial # 14**

Assigned Sample #	Collector's Sample code	Date Collected	Matrix & Species, organ, etc.	Location Collected	Latitude	Longitude	Collection Method	Comments
01								
02								
03								
04								
05								
06								
07								
08								
09								
10								
11								
12								
13								
14								
15								

Continue list on back of page -->

Chain of Custody

Collected by: _____ print name(s) / agency _____ signature _____ date _____
comments, sample quality

Relinquished by: _____ signature _____ date / time _____ place _____
BY: _____

Received by: _____ signature _____ date / time _____ place _____
BY: name / agency _____ comments # _____

* Envelop include center name & art# #, and attach copy of label to form. Revised July 2000 * Exclude condition of shipped samples: all trace? peak list? 1/25/2005

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Appendix 2. Sample streams, dates sampled, and peak numbers of pink salmon observed in the streams. Segment is the beach segment name. Peak numbers (ADF&G) are summarized by mean, median, and maximum; n is the number of observation years; ND = no data. Oil observed refers to oil visible along stream channels only; beaches are not included; the same is true for oil chemically detected by PEMD in stream water.

Segment	Stream name	Sample date(s)	oil observed	oil detected	Latitude	Longitude	mean	median	maximum	n
MKS5	Glacier Valley Creek	3/20/05, 4/13/05 5/16/05, 6/26/05 8/06/05, 9/07/05	light to moderate	yes ≤976 ng/g	53.771967	166.950967	22,038	12,365	70,000	14
PMN20	Outer Pumicestone	3/17/05, 4/11/05	no	yes, mouth only ≤589 ng/g	53.571300	167.130183	9,132	300	46,000	19
PMS16	Pumicestone	3/18/05, 4/11/05	no	no ≤16 ng/g	53.529483	166.978700	31,341	3,300	259,000	27
SKN14	Skan 2	3/19/05, 4/12/05 5/16/05, 6/26/05 8/05/05, 9/07/05	heavy & extensive	yes ≤463000 ng/g	53.646150	167.013867	11,967	^b 16,200	^a 16,200	3
SKN14*	Tributary	3/21/05, 4/12/05 5/16/05, 6/26/05 8/06/05, 9/07/05	moderate to heavy near mouth	yes ≤426 ng/g	53.646267	167.010167	ND	ND	ND	0
SKN4	Skan 3	3/16/05, 4/11/05	light along lower stream	no ≤111 ng/g	53.621400	166.998983	6,008	375	34,000	18
MKS9	Makushin Village Cr	3/20/05	no	ND	53.771389	166.984167	548	75	2,200	24
PTN3 (or 2)	Portage 3	3/20/05	no	ND	53.726844	166.711378	1,302	13	7,200	14
PTN6 (or 7)	Portage 2	3/20/05	no	ND	53.734167	166.761111	1,813	1,200	7,000	24
PTS10	Portage 4	3/20/05	no	ND	53.715975	166.689531	1,333	2,000	2,000	3
CNB8	Cannery Bay	3/20/05	no	ND	53.694914	166.752161	2,082	825	12,400	22
HMP11	Humpback 1	3/21/05	moderate to heavy lower 80 m	ND	53.754794	166.873447	16,489	9,000	^b 71,000	28
HMP9	Humpback 2	3/21/05	no	ND	53.751672	166.862342	48,067	40,000	173,000	35
SKS14	Skan Bay West Arm	3/21/05	no	ND	53.594594	167.038078	ND	ND	ND	0
SKN8	No name	3/21/05	no	ND	53.637492	167.008014	ND	ND	ND	0

*SKN14 and SKN14 tributary are counted as 1 stream system in this document.

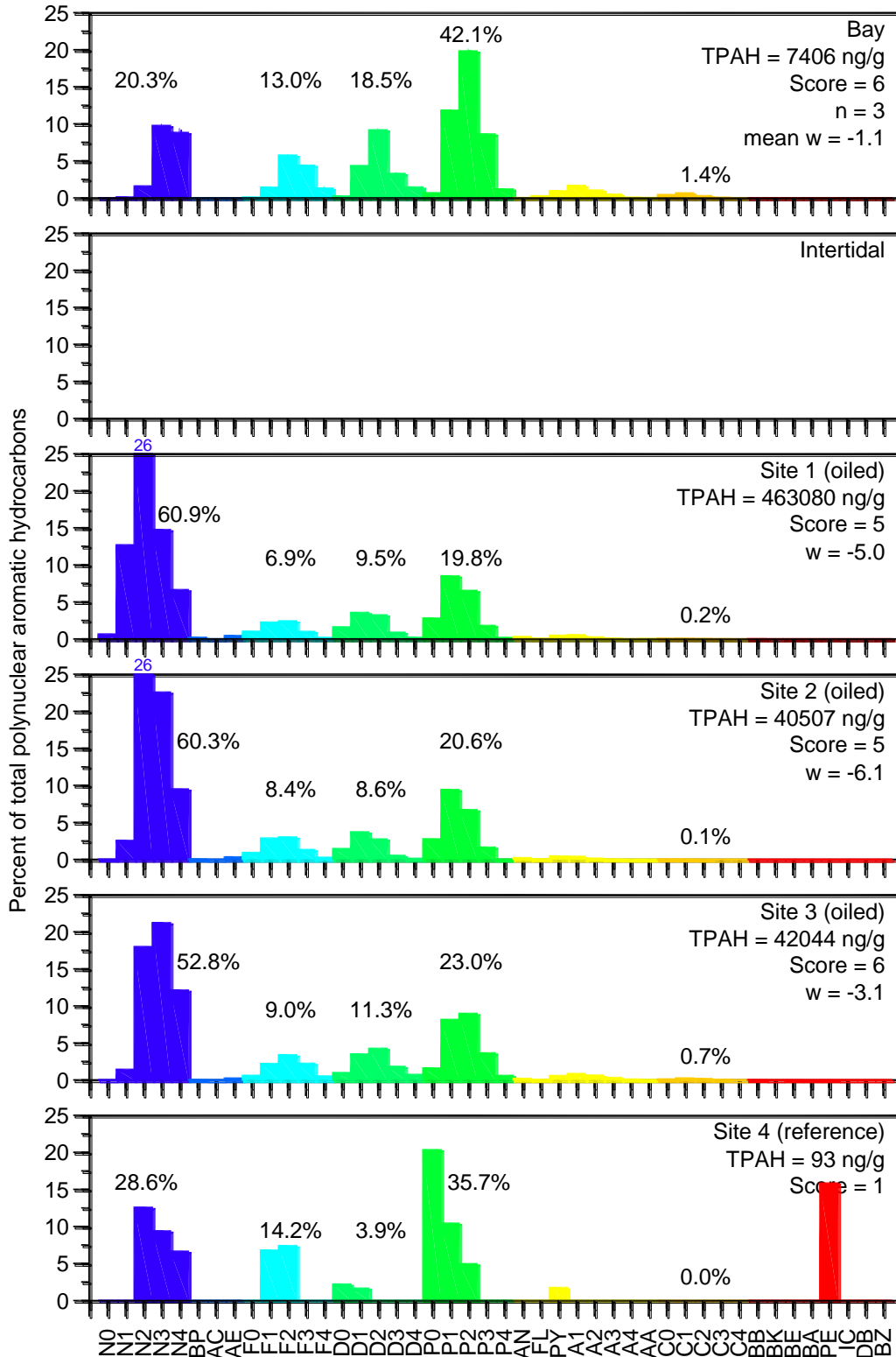
^aMinimum was 3500; ^bminimum was 50; all other minima were 0.

^bADF&G has been asked to verify the data record for SKN14

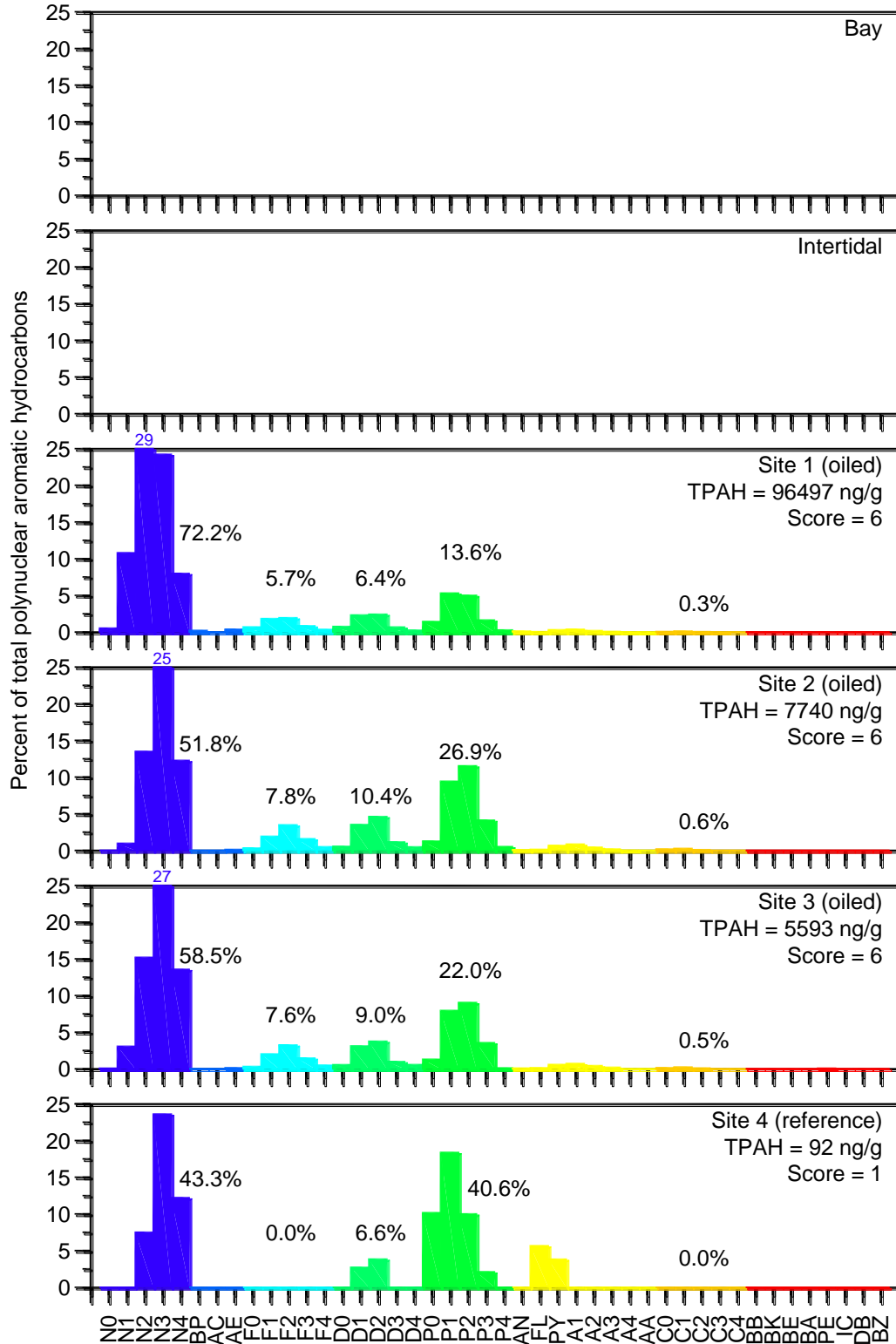
Appendix 3. Passive membrane device (PEMD) deployment and retrieval times, total days in water, and approximate total precipitation during the deployment interval. Climate records from Dutch Harbor were used as the nearest recorded precipitation data. Snowfall in early to mid April (71 cm) is not included in these data. *Some PEMDs in SKN14 were retrieved and deployed on 8/6/2005.

deployment	retrieval	total days	precipitation
SKN14			
03/19/2005	04/12/2005	24	2.16
04/12/2005	05/16/2005	34	8.68
05/16/2005	06/26/2005	41	6.34
06/26/2005	08/05/2005 *	40	2.44
08/05/2005 *	09/07/2005	33	4.16
Tributary (SKN14)			
03/21/2005	04/12/2005	22	
04/12/2005	05/16/2005	34	
05/16/2005	06/26/2005	41	
06/26/2005	08/06/2005	41	
08/06/2005	09/07/2005	32	
MKS5			
03/20/2005	04/13/2005	24	
04/13/2005	05/16/2005	33	
05/16/2005	06/26/2005	41	
06/26/2005	08/06/2005	41	
08/06/2005	09/07/2005	32	

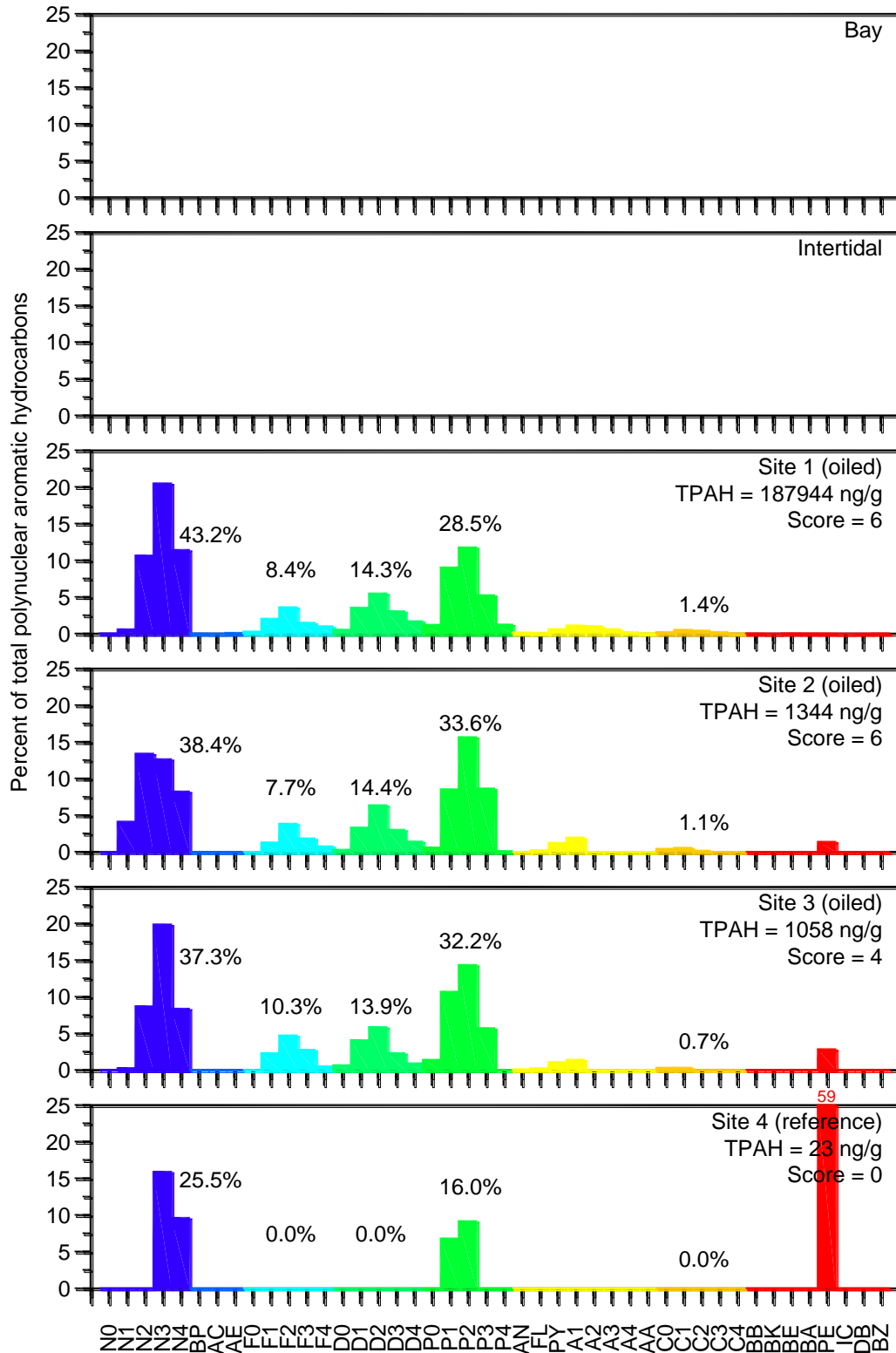
Appendix 4.3a. North Skan Bay and stream SKN14 (March-April 2005); n = 1 per site except observations were replicated in the bay. The latter are means \pm standard error. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



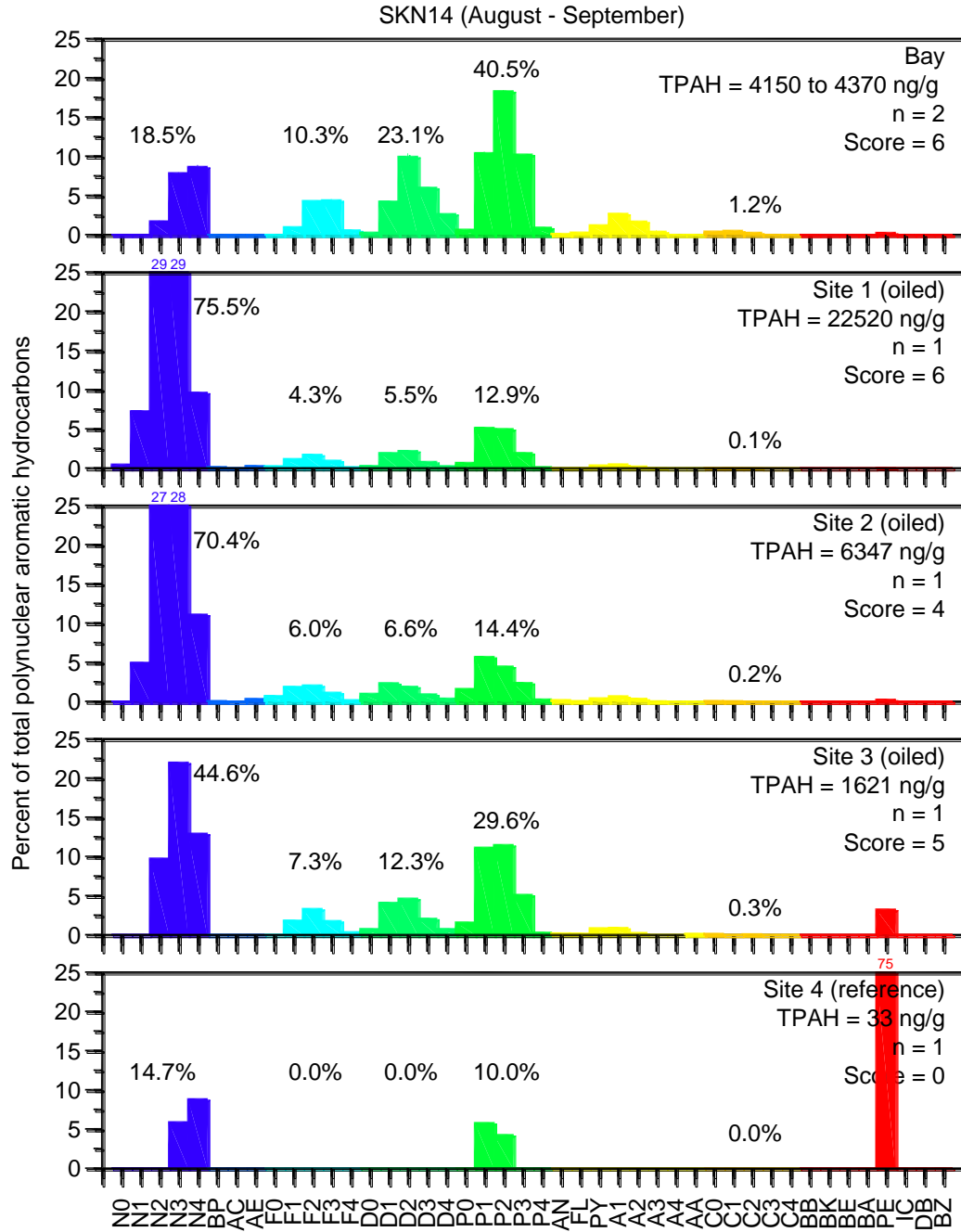
Appendix 4.3b. SKN14 (April-May 2005); n = 1 per site. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



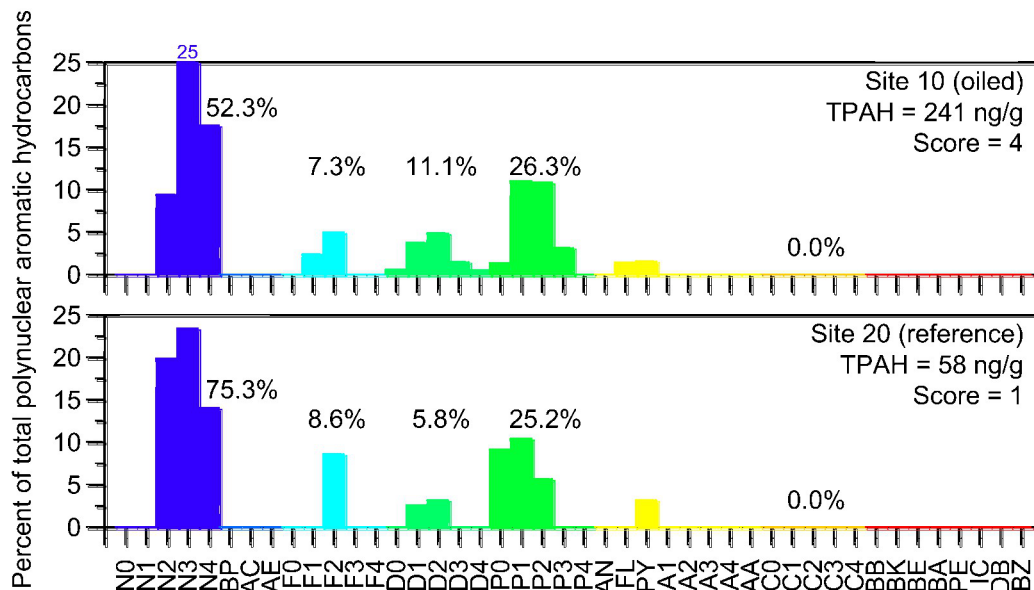
Appendix 4.3c. SKN14 (May-June 2005); n = 1 per site. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



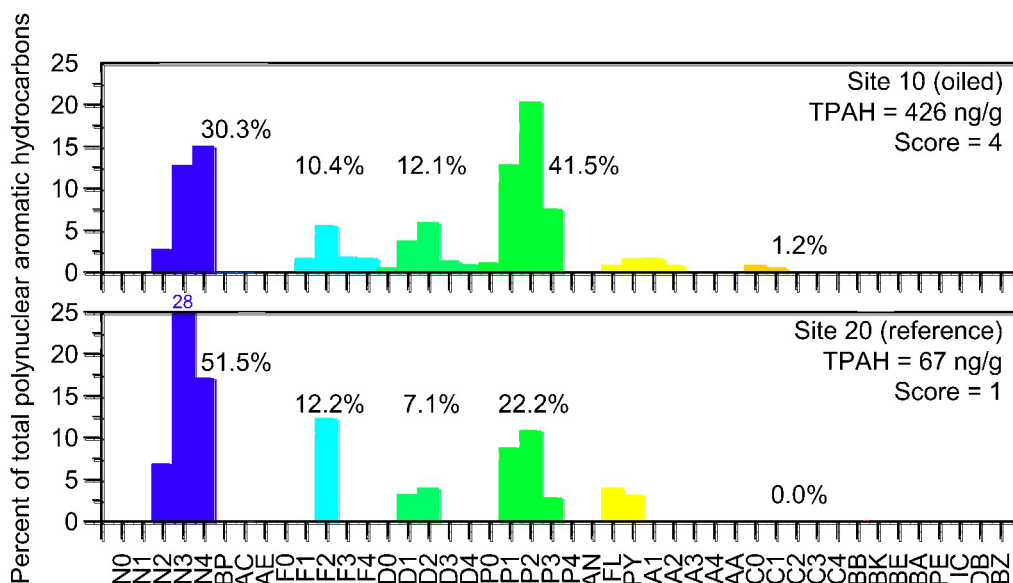
Appendix 4.3e. North Skan Bay and stream SKN14 (August – September 2005) ; n = 1 per site except observations were replicated in the bay. The latter are means ± standard error. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



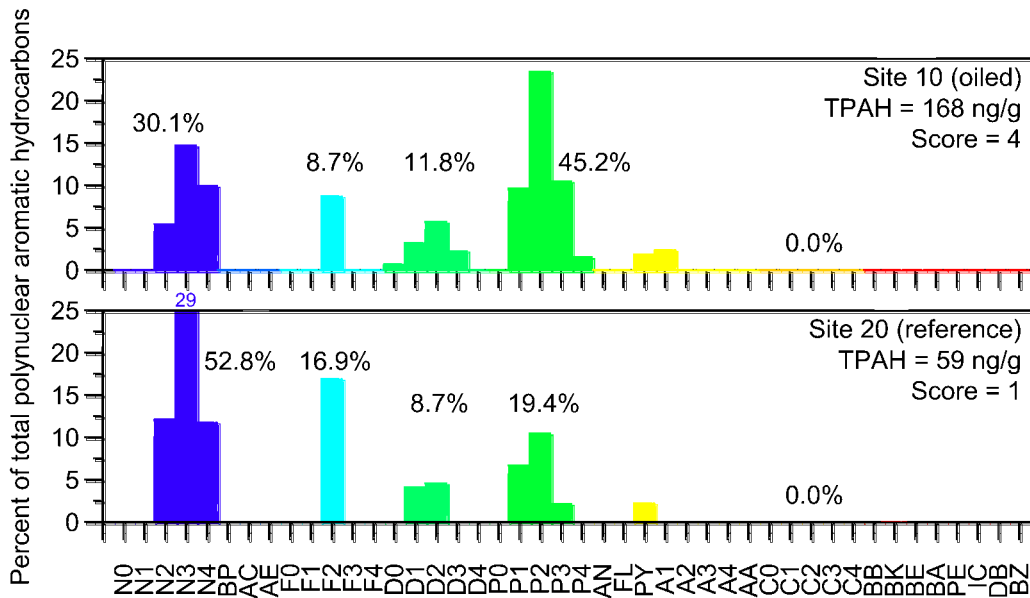
Appendix 4.4a. SKN14 tributary (March-April 2005); n = 1 per site. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



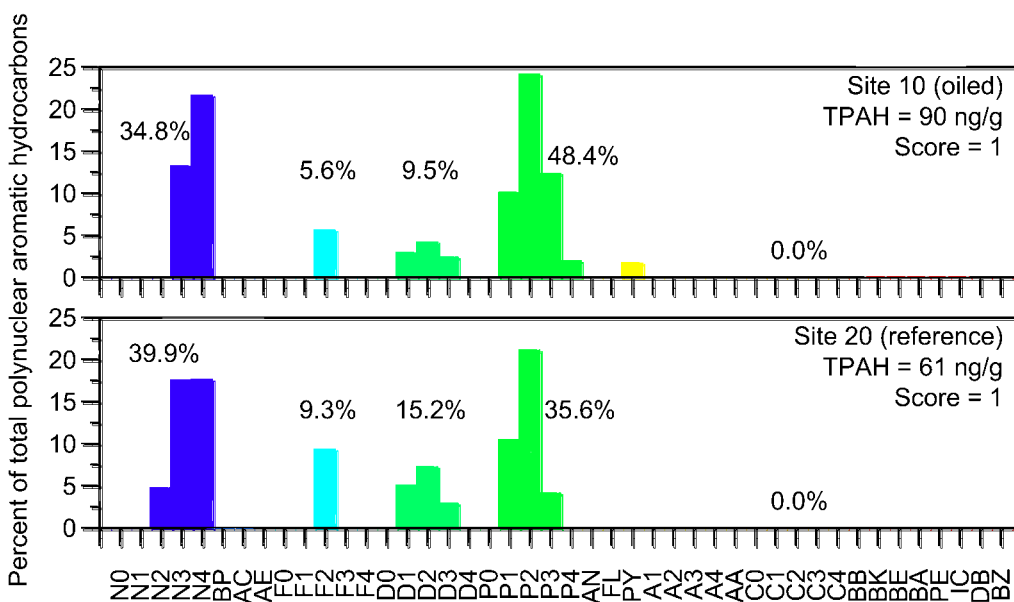
Appendix 4.4b. SKN14 tributary (April-May 2005); n = 1 per site.



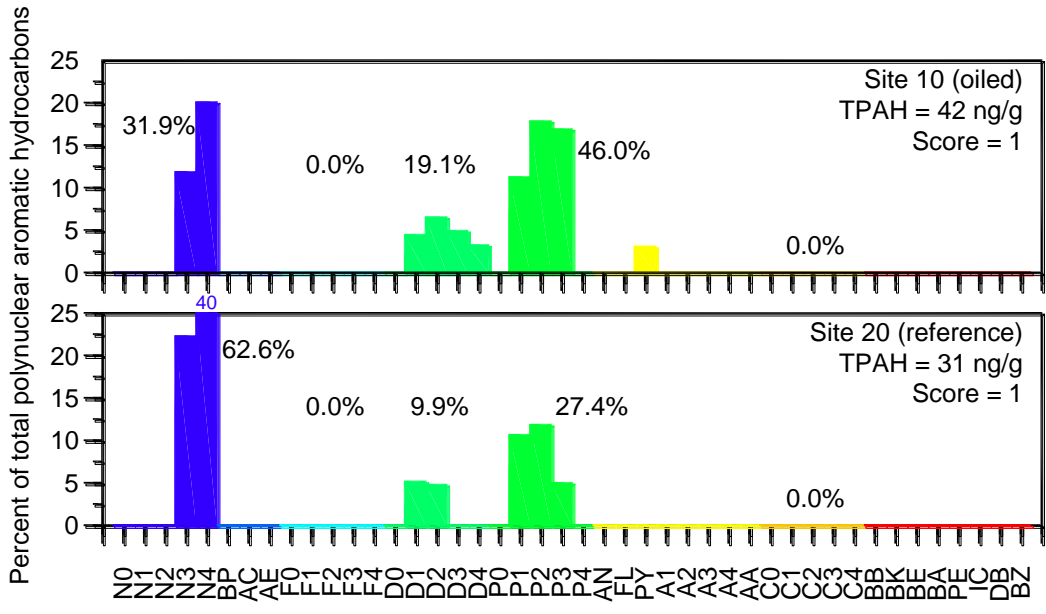
Appendix 4.4c. SKN14 tributary (May-June 2005); n = 1 per site. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



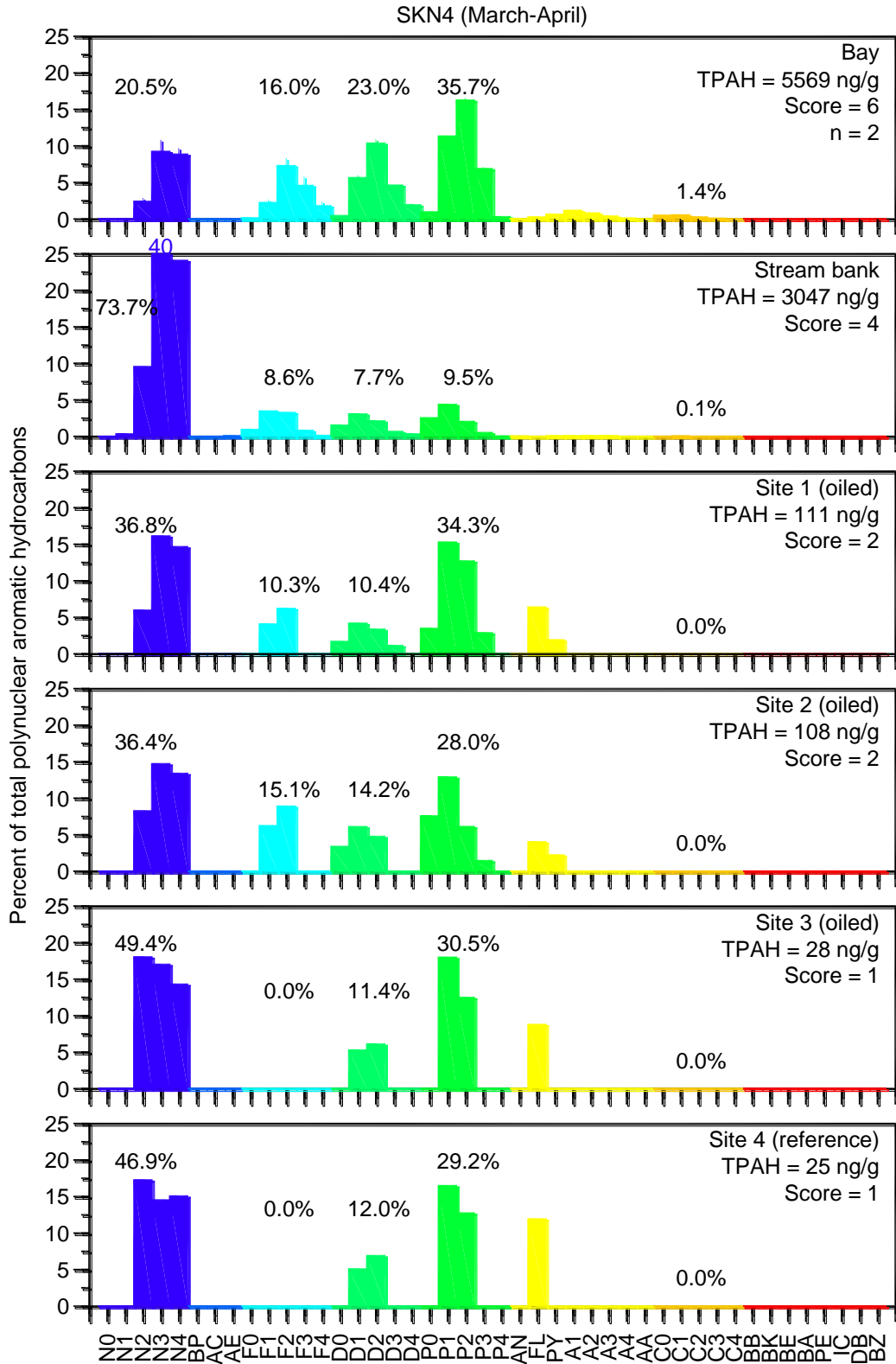
Appendix 5.4d. SKN14 tributary (June-August 2005); n = 1 per site.



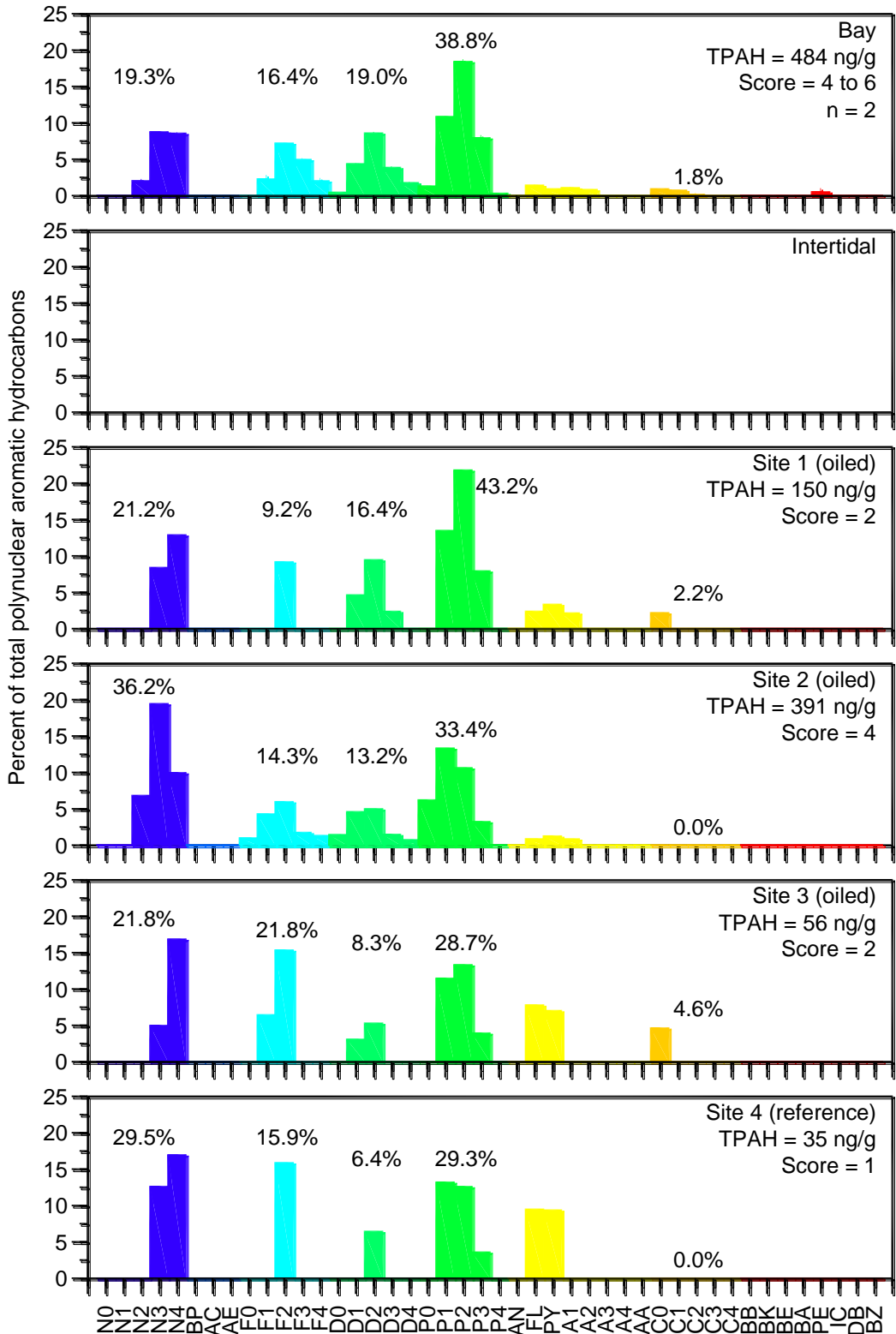
Appendix 4.4e. SKN14 tributary (August – September 2005); n = 1 per site. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



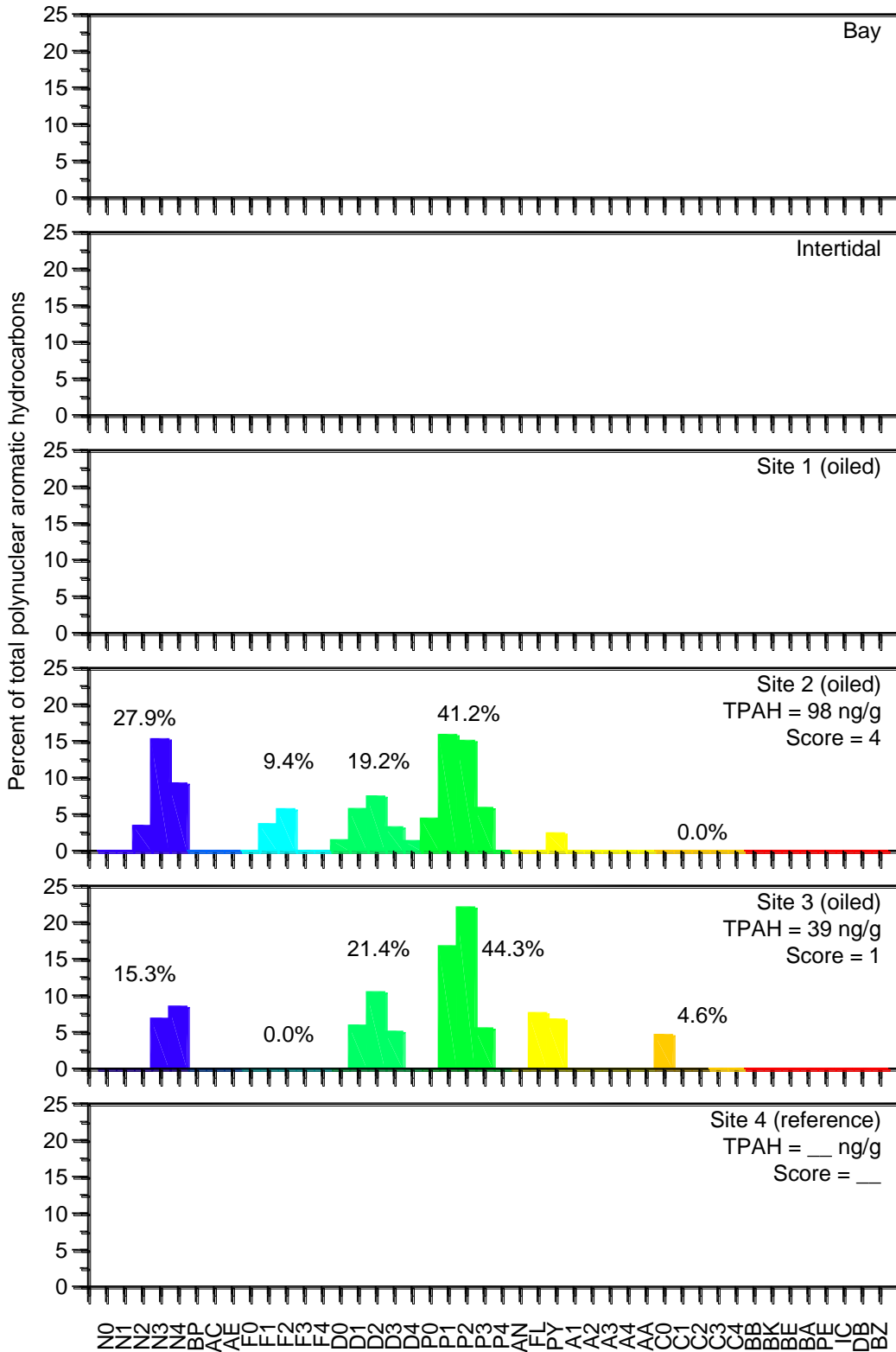
Appendix 4.5. Skan Bay and stream SKN4 (March-April 2005) ; n = 1 per site except observations were replicated in the bay. The latter are means ± standard error. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



Appendix 4.6b. Makushin Bay and stream MKS5 (April-May 2005) ; n = 1 per site except observations were replicated in the bay. The latter are means ± standard error. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



Appendix 4.6d. MKS5 (June-August 2005); n = 1 per site. Percentages (of TPAH) in each panel indicate relative quantities of naphthalenes (N0—N4), fluorenes (F0—F3), dibenzothiophenes (D0—D3), phenanthrenes (P0—P4), and chrysenes (C0—C4).



Appendix 5. Salmon streams and streams sampled in 2005.

