Publication No. 88-03-001

STATE OF WASHINGTON

DEPARTMENT OF ECOLOGY

7272 Cleanwater Lane, LU-11 ● *Olympia, Washington 98504-6811* ● *(206) 753-2353*

TO: Maria Peeler

THROUGH: Bill Yake

FROM: Jim Cubbage, Water Quality Investigations Section

SUBJECT: Cascade Pole site in Budd Inlet:
          o Potential source of PAH
          o Review of AGI report

DATE: April 18, 1988

INTRODUCTION

To determine the source of high levels of PAH in sediment near the
McFarland/Cascade wood-treating facility in Olympia, WA, you requested
a review of available literature and the recent report entitled
"Intertidal Sediment Study . . . AGI # 14,825.107" conducted by Applied
Geotechnology Inc for McFarland/Cascade. Their report summarizes
results from Art Johnson's Department of Ecology's sediment investiga-
tion of the area reported in an Ecology Memo to Tom Eaton on July 22,
1985.

My comments are divided into two sections. The first summarizes the
results of the literature search and some data analysis conducted to
determine the source of the PAH in sediments near McFarland/Cascade.
The second is a review of the AGI report. The history of recent inves-
tigations at the site is reviewed in the Feasibility Study Work Plan
for Cascade Pole Company (Black and Veatch, 1986).

LITERATURE SEARCH AND ANALYSIS

Background

Polynuclear aromatic hydrocarbons (PAH) have been found in sediments
worldwide (Laflamme and Hites 1978) and their source is almost univer-
sally accepted to be primarily combustion and pyrolysis. Most of these
PAH's have anthropogenic origins (Wakeman et al. 1980). Creosote oil,
the major wood preservative used at the facility, is a complex mixture
of chemicals derived from distillation of coal tar (Krone et al. 1986)
itself a product of pyrolysis of coal. Substantial amounts of PAH are
found in coal tar (up to 30 percent) and creosote (90 percent) (McNeil
1981 in Krone et al. 1986; McNeil 1959 in Merrill and Wade 1985).

The characteristic ratios of the constituents of the PAH suite have led
researchers to define sources of local PAH contamination in sediments
in estuaries through several methods. In Narraganset Bay RI, Lake et

al. used parent compound distribution (PCD) and alkyl homolog distribu-
tions to determine coal tar treated pilings accounted for some local
sediment contamination. Sporstol et al. (1983) use both the alkyl
homolog distribution (AHD) and the relative amount of each aromatic
series (RAA) (same as PCD above) to determine potential origins of PAH
contamination in Scandinavian sediments. I used a conservative appli-
cation of the RAA method to determine the probable source of PAH in
sediments in East Bay, Olympia adjacent to the McFarland/Cascade site.

Methods

To determine potential sources of PAH, I compared results of PAH analyses
from several other studies using the parent compound distribution
method. The analysis compared ratios of PAH and were focussed on the
heavy molecular weight PAH (HPAH). These 4- and 5-ring HPAH were
fluoranthene, pyrene, benz(a)anthracene, chrysene, benzofluoranthenes,
and benzo(a)pyrene. Because of relatively high limits of detection,
6-ring HPAH were excluded. The lighter PAHs (napthalene, phenanthrene,
anthracene, fluorene) were not considered because differential degrada-
tion and weathering will confound comparison of these constituents to
HPAH. Sporstol et al. (1983) caution that weathering problems complicate
an interpretation of data based on napthalene (an LPAH). From studies
in controlled ecosystem enclosures Lee et al. (1978) concluded that the
degradation processes of LPAH (microbial degradation and evaporation)
are different than HPAH (sorption and photochemical oxidation). These
different mechanisms can be expected to act at different rates and thus
create a large variability in LPAH/HPAH ratios in any environment.

Levels of HPAH reported in the literature were compared as ratios from
several sites near creosote sources and areas that are distant from
direct sources of creosote. Literature sources of HPAH data follow
showing location, matrix, and citation:

o   East Bay, Olympia adjacent to Cascade Pole wood preserving facility;
     Sediment and product from tank #2 (creosote); Johnson (1985); AGI
     (1987)
o   Eagle Harbor, WA adjacent to Wyckoff Company wood preserving
     facility; Sediment; Yake and Norton (1986)
o   South shore Elliott Bay, WA on Wyckoff Company wood preserving
     facility property; Soil samples taken from well drilling; Woodward
     and Clyde through EPA (1985)
o   West Duwamish waterway from Spokane Street to Elliott Bay; Sediment;
     Tetra Tech (in Press)
o   Continental shelf off Washington State; Benthic sediments; Prahl
     and Carpenter (1984)

These last two sites were considered control sites and could be expected
to reflect HPAH concentrations averaged from many different sources in
many different places.

Results and Discussion

Table 1 shows the concentrations of HPAH at the sites. Of these samples, the highest levels were found in soils recovered during a test well drilling a wood preserving plant in Seattle (Wyckoff on Elliott Bay). The next highest concentrations were found in sediments adjacent to the McFarland/Cascade Pole treating plant in East Bay, Olympia.

Also shown in Table 1 are ratios of specific HPAH compared with total HPAH in the samples. An overall pattern becomes clear. The ratios vary little between creosote and the sites where creosote would be expected to be a major constituent (East Bay, Budd Inlet, Eagle Harbor, and Wyckoff in Elliott Bay). However, if the Duwamish and offshore Washington sediment are compared with these sites, the ratios of fluoranthene, benzofluoranthene, and benzo(a)pyrene vary significantly by site (percentages arcsine transformed, ANOVA $p < 0.001$, Zar 1974). In other words, there is a greater than 999 to 1 chance that the samples from these sites reflect an actual difference between sites. These differences between ratios were caused by differences between the creosote sites and the control sites, not by differences within the creosote sites.

To visually compare the differences in HPAH composition by site, concentrations were normalized to fluoranthene = 1, averaged by site and plotted. These plots form a profile of HPAH constituents in various samples. Figure 1 shows plots of creosote HPAH ratios as well as the three potentially contaminated sites. The Budd Inlet-East Bay sediments appear similar in contour to creosote as well as other potentially contaminated sites (sediment beneath an operating wood-treating plant and seeps from another wood treating plant). A little variation is apparent in the chrysenes and benzofluoranthenes, but the East Bay site ratios are bounded by creosote and probable creosote-contaminated sediments. The overall profiles are similar and reflect the profile of creosote.

Figure 2 shows profiles of creosote and sediments from East Bay, Olympia from Figure 1 as well as profiles from the control sites of the Duwamish waterway in Seattle, a river draining a highly industrialized and urban area, and sediments from offshore Washington. Recall that these are ratios. Thus it is interesting that though the HPAH concentrations in the Duwamish are 100 times higher than the offshore concentrations, they still are quite similar in profiles. These control sites provide a background profile by which to compare to contaminated sites. Clearly, the profiles from East Bay, Olympia do not reflect typical urban runoff profiles or profiles from offshore areas distant from sources of creosote contamination. Their obvious similarity to creosote profile suggests a nearby source of creosote contamination.

REVIEW OF AGI REPORT

My comments follow the organization of the report.

Section 3.3 paragraph 3:
 The references to behavior of PAHs adsorbing differentially onto
 the lower organic layer depending on weight is speculation and not
 substantiated in the report. All PAH are fairly insoluble in
 water.

Section 4.0 overall:
 The premise that LPAH/HPAH ratios will yield useful information
 about source is flawed in that LPAH and HPAH degrade at different
 rates in the environment (see Background above). Indeed, the
 report makes much of the differential behavior of LPAH in section
 3 where differential adsorbing of HPAH and LPAH to sediment is
 mentioned as well as in section 4.2 para. 2 where the report
 states that the more water soluble LPAHs should be decreasing
 faster than HPAH due to leaching and biodegradation (no specific
 references are given). The report then tries to make a case that
 the ratios somehow point to a source (section 4.3 paragraph 2)
 implying that the LPAH/HPAH ratios are static in the environment.

 The literature does report using alkyl homolog analysis of LPAH to
 discern source, (Sporstol et al. 1983). However, the alkyl homologs
 reported by Johnson (1986) and analyzed by AGI are not suitable in
 providing an analysis of source. I talked with the chemist in
 charge of the organics analysis in Johnson (1986) (Dick Huntamer
 [Chemist WaDOE/EPA Manchester Lab]) and he reported that all the
 alkyl homologs in Johnson's report are only tentatively identified
 (with the exception of the 2-methylnapthalenes) and not confirmed.
 For the unsubstituted (non-alkylated) PAH, standards are run on
 the analytical equipment (GC-MS) to calibrate identifications and
 measurements of compounds analyzed and thus high levels of confi-
 dence in both the identification and quantification are realized.
 For the alkyl homologs, however, because of unquantified variables
 including mass spectrometer response factor, and lack of calibration
 standards for comparison, the chemists report no confidence of the
 concentrations of these chemicals within at least an order of 10
 in comparison with the non-substituted (non-alkyl) homologs. In
 other words, the levels of alkyl homologs used by AGI to connote
 source of PAH could easily have at least an order of magnitude (10
 times) error. This large analytical variance is consistent with
 the large variability in alkyl homologs between adjacent sampling
 sites. Thus, due to wide variance, the ratios reported in AGI
 Table 4 indicate nothing about potential source.

Section 4.2 paragraph 1:
 The phrase statistically identical implies a statistical test. Was
 one performed? Which one? What were the results?

Section 4.3 paragraph 2:
>   What is the citation for relative smooth changes in parameters as
>   one moves away from a source? The data I have reviewed have not
>   substantiated this observation (Tetra Tech 1986, Johnson 1985)

Section 5.0 paragraph 3:
>   The major conclusions presented here are based on faulty premises.
>   For alkyl homologs of napthalenes, identification is tentative and
>   quantification is potentially inaccurate and certainly variable
>   and thus conclusions based on these data are virtually meaningless
>   (see discussion for #4 above). On the basis of distribution of
>   individual PAH the contention that sample E2 does not resemble
>   creosote in the distribution of individual PAH is simply not true
>   (see Table 1 this report). Finally, as several factors conspire
>   to change the ratios of LPAH/HPAH (mentioned by AGI authors),
>   these ratios provide a poor method to identify source.

Overall the report is poorly substantiated. Repeated assertions of
fact are made without a citation or with only a reminder to "see refer-
ences." The lack of specific citations frustrate efforts to verify
information ascribed to the literature and it renders peer review very
difficult.

CONCLUSION

The data at hand suggest that most of the PAH in the East Bay, Olympia
sampling sites originated from creosote. Through comparison of HPAH
ratios at the East Bay sites with other sites near sources of creosote
and control areas where the influence of creosote is presumably minor,
the HPAH at the East Bay, Olympia sites appear similar to creosote
rather than to urban runoff or background contamination. The conclusion
that the high PAH levels in sediments in East Bay originated from
creosote is consistent with the close proximity of the East Bay sites
to a creosote source at the Cascade Pole Company.

In a report prepared by AGI (1987) for the owners of Cascade Pole
Company, the source for high PAH levels in East Bay the area is conjec-
tured to be urban runoff or oil spills, not the nearby creosote-based
operation. To reach this conclusion, the report relies on two analyses.
The first is alkyl homolog analysis based on unreliable data and thus
the results are invalid. The second method relies on a potentially
specious method of comparing ratios of LPAH/HPAH to identify source
while simultaneously acknowledging in other parts of the report the
variable behaviors and degradation rates between these classes of
compounds. These inconsistencies are not addressed. Comparisons of
ratios to other areas and sources are made without substantiating data
or references. In contradiction to AGI's conclusions, an analysis of
the data in the literature suggests clearly that the HPAH in sediments
near the Cascade Pole site are more similar to creosote than to urban
runoff or background contamination.

REFERENCES

AGI. 1987. Intertidal sediment study: Polycyclic aromatic hydrocarbons
and phenols, Cascade Pole Company, Olympia WA. Report for Cascade
Pole Company from Applied Geotechnology Inc., Bellevue, WA 98009.

Black and Veatch. 1986. Feasibility study work plan for Cascade Pole
Company, Olympia, WA. Engineering report to Washington Dept. of
Ecology, Olympia, WA. 45 pp.

Johnson, A. 1985. Receiving environment survey in Budd Inlet at McFarland
/Cascade, February 13, 1985. Memo to Tom Eaton, Department of
Ecology, Olympia, Washington. 14pp.

Krone, C.A., D.G. Burrows, D.W. Brown, P.A. Robisch, A.J. Friedman, and
D.C. Malins. 1986. Nitrogen containing compounds in sediments from
a polluted harbor in Puget Sound. Environ. Sci. Technol. 22:1144-1150.

Laflamme, R.E. and R.A. Hites. 1978. The global distribution of
polycyclic hydrocarbons in recent sediments. Geochim. Cosmochim.
Acta 42:289-303.

Lake, J.L., C. Norwood, C. Dimock and R. Bowen. 1979. Origins of
polycyclic aromatic hydrocarbons in estuarine sediments. Geochim.
Cosmochim. Acta 43:1847-1854.

Lee, R.F., W.S. Gardner, J.W. Anderson, J.W. Blaylock, and J. Barwell-Clarke.
1978. Environ. Sci. Technol. 12:832-838.

Merrill, E.G. and T.L. Wade. 1985. Carbonized coal products as a source
of aromatic hydrocarbons to sediments from a highly industrialized
estuary. Environ. Sci. Technol. 19:597-603.

Prahl, F.G. and R. Carpenter. 1984. Hydrocarbons in Washington coastal
sediment. Estuarine, Coastal and Shelf Science 18:703-720

Sporstol, S., N. Gjos, R.G. Lichtenthaler, K.O. Gustavsen, K. Urdal, F.
Oreld, and J. Skel. 1983. Source identification of aromatic hydro-
carbons in sediments using GC/MS. Environ. Sci. Technol. 17:282-286.

Tetra Tech. 1988. Elliott Bay revised action program data set 2 February
1988. TC3338-23. Prepared for EPA. DRAFT.

Wakeman, S.G., C. Schaffner and W. Giger. 1980. Polycyclic aromatic
hydrocarbons in recent lake sediments - I. Compounds having anthro-
pogenic origins. Geochim. Cosmochim. Acta 44:403-413.

Woodward and Clyde. 1985. Contaminant data from monitor well sampling
on Wyckoff Property on Elliott Bay. Analyzed by Analytical Resources
Inc. available through Environmental Protection Agency, Seattle.

Yake, B. and D. Norton. 1986. Chemical contamination of ground water,
intertidal seepage and sediments on and near Wyckoff Company
Property; Eagle Harbor, Bainbridge Island. Memo to Glynis Stumpf

and Dave Bradley, Department of Ecology, Olympia, Washington.
31pp. less attachments.

Zar, J.H. 1974. Biostatistical analysis. Prentice Hall, Englewood
Cliffs, N.J.

JC:jms
Attachments

cc: Dale Norton
      Art Johnson
      Dave Bradley

Table 1. PAH concentrations and ratios from six sources.

Sample	ug/kg PAH dry weight						PAH/Total PAH					
	FL	PY	B(a)A	CH	BF	B(a)P	FL	PY	B(a)A	CH	BF	B(a)P
Creosote (1)	4E+07	3E+07	7E+06	6E+06	4E+06	1E+06	0.46	0.32	0.09	0.07	0.05	0.01
Budd Inlet - East Bay (2)												
Sta-1	32000	20000	8000	8300	6600	0	0.43	0.27	0.11	0.11	0.09	0.00
Sta-2	530000	400000	95000	120000	73000	40000	0.42	0.32	0.08	0.10	0.06	0.03
Sta-3	42000	27000	7500	9700	6900	2700	0.44	0.28	0.08	0.10	0.07	0.03
Sta-4	3100	4300	670	740	880	360	0.31	0.43	0.07	0.07	0.09	0.04
Sta-5	1300	1500	330	410	510	190	0.31	0.35	0.08	0.10	0.12	0.04
Sta-6	7300	450	3500	1900	1600	750	0.47	0.03	0.23	0.12	0.10	0.05
Sta-7	4900	3800	1300	1800	1600	680	0.35	0.27	0.09	0.13	0.11	0.05
AG3S	10400	3600	2500	2000	4100	790	0.44	0.15	0.11	0.09	0.18	0.03
Mean							0.44	0.26	0.10	0.10	0.10	0.03
Eagle Harbor Seeps (3)												
IS-1	5411	4200	1300	1300	990	440	0.40	0.31	0.10	0.10	0.07	0.03
IS-3	3600	3000	1300	1700	1550	600	0.31	0.26	0.11	0.14	0.13	0.05
IS-4	110000	75000	20000	29000	42000	14000	0.38	0.26	0.07	0.10	0.14	0.05
Mean							0.36	0.28	0.09	0.11	0.15	0.04
Wyckoff Elliott (4)												
W7-8	2200000	1300000	690000	690000	660000	270000	0.38	0.22	0.12	0.12	0.11	0.05
WC3-8	200000	120000	36000	35000	20000	9000	0.48	0.29	0.09	0.08	0.05	0.02
Mean							0.40	0.25	0.10	0.10	0.08	0.04
Duwamish Sediments (5)												
WW-01	380	330	140	200	320	110	0.26	0.22	0.09	0.14	0.22	0.07
WW-02	450	360	180	550	83	37	0.27	0.22	0.11	0.33	0.05	0.02
WW-03	820	680	200	250	310	150	0.34	0.28	0.08	0.10	0.13	0.06
WW-04	30000	10000	2400	4100	2690	1400	0.59	0.20	0.05	0.08	0.05	0.03
WW-05	450	540	160	260	380	140	0.23	0.28	0.08	0.13	0.20	0.07
WW-06	2900	2300	650	1300	1650	610	0.31	0.24	0.07	0.14	0.18	0.06
WW-08	1500	1200	680	890	1400	480	0.24	0.20	0.11	0.14	0.23	0.08
WW-09	10000	8200	3100	6200	6500	3700	0.27	0.22	0.08	0.16	0.17	0.10
WW-10	2500	2300	1000	2300	2370	1000	0.22	0.20	0.09	0.20	0.21	0.09
WW-11	5000	3400	1900	4300	4900	1200	0.24	0.16	0.09	0.21	0.24	0.06
WW-12	11000	7100	2900	7900	4700	2000	0.31	0.20	0.08	0.22	0.13	0.06
WW-13	2700	2800	1100	2300	2100	730	0.23	0.24	0.09	0.20	0.18	0.06
WW-14	4000	7600	1800	4700	7900	3500	0.14	0.26	0.06	0.16	0.27	0.12
WW-16	1800	2100	700	1600	1580	1500	0.19	0.23	0.08	0.17	0.17	0.16
WW-17	2700	3100	1600	2300	4000	1500	0.18	0.20	0.11	0.15	0.26	0.10
WW-18	1800	2500	890	1300	2200	790	0.19	0.26	0.09	0.14	0.23	0.08
WW-19	2400	2300	870	2600	2700	910	0.20	0.20	0.07	0.22	0.23	0.08
WW-20	930	1300	520	730	1280	490	0.18	0.25	0.10	0.14	0.24	0.09
Mean							0.25	0.23	0.09	0.17	0.19	0.08

(FL=Fluoranthene, PY=Pyrene, B(a)A=Benzo(a)anthracene, CH=Chrysene,
BF=Benzofluoranthenes, B(a)P = Benzo(a)pyrene).

Table 1. PAH concentrations and ratios from six sources (continued).

Sample	ug/kg PAH dry weight						PAH/Total PAH					
	FL	PY	B(a)A	CH	BF	B(a)P	FL	PY	B(a)A	CH	BF	B(a)P
Creosote (1)	4E+07	3E+07	7E+06	6E+06	4E+06	1E+06	0.46	0.32	0.09	0.07	0.05	0.01
Offshore Washington Sediments (6)												
PCW1	4.0	5.9	2.0	4.0	2.0	3.1	0.19	0.28	0.09	0.18	0.09	0.14
PCW2	6.0	6.0	4.1	5.0	7.9	2.9	0.19	0.18	0.12	0.15	0.24	0.09
PCW3	17.9	21.3	9.0	17.9	26.9	9.0	0.17	0.20	0.08	0.17	0.26	0.08
PCW4	60.0	64.8	31.2	40.8	58.8	33.6	0.21	0.22	0.10	0.14	0.20	0.11
PCW5	44.2	53.3	24.7	32.5	45.5	24.7	0.20	0.23	0.10	0.14	0.20	0.10
PCW6	68.0	79.9	28.9	45.9	74.8	32.3	0.21	0.24	0.08	0.13	0.22	0.09
PCW7	38.5	45.1	18.7	24.2	48.4	18.7	0.20	0.23	0.09	0.12	0.25	0.09
PCW8	220.4	118.9	49.3	69.6	150.8	75.4	0.32	0.17	0.07	0.10	0.22	0.11
PCW9	30.0	31.5	15.0	21.0	34.5	18.0	0.20	0.21	0.10	0.14	0.23	0.12
PCW10	10.9	9.4	3.9	4.7	9.4	3.9	0.26	0.22	0.09	0.11	0.22	0.09
Mean							0.24	0.22	0.09	0.12	0.23	0.10

(1) From tank 2 McFarland/Cascade, Budd Inlet; Johnson (1985)
(2) From sediments near McFarland/Cascade, Budd Inlet; Johnson (1985) and one
     sediment sample from AGI (1987) that reported recoverable amounts of all 6 HPAH
     in this analysis
(3) Sediments near Wyckoff Wood Treating, Eagle Harbor; Yake and Norton (1986)
(4) Soils from drilling monitoring well on Wyckoff Company, Duwamish waterway; Woodward/Clyde (1985)
(5) Sediments from West Duwamish waterway; Tetra Tech (in prep)
(6) Sediments from continental shelf off Washington; Prahl and Carpenter (1984)

(FL=Fluoranthene, PY=Pyrene, B(a)A=Benzo(a)anthracene, CH=Chrysene,
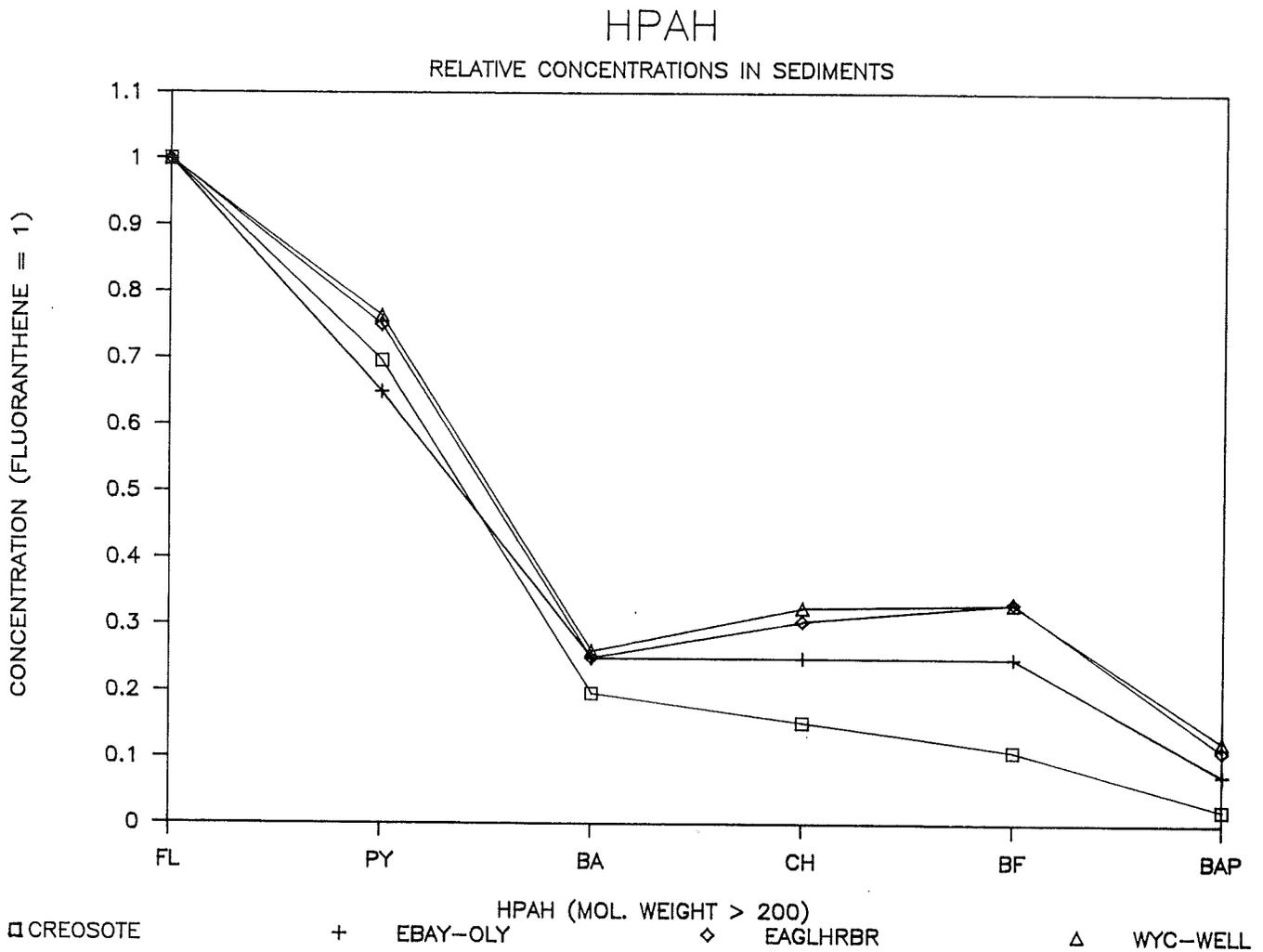BF=Benzofluoranthenes, B(a)P = Benzo(a)pyrene).

Figure 1. Relative concentrations of HPAH (4- and 5-ring PAH) from different sources in Washington State.
CREOSOTE = Creosote from tank 2 at Mcfarland/Cascade wood preserving plant in Olympia (n=1).
EBAY-O1Y = East Bay sediments in Olympia near McFarland/Cascade wood preserving plant (n=8).
EAGLHRBR = Eagle harbor intertidal sediments near Wyckoff wood preserving plant (n=3).
WYC-WELL = Sediment grabs from monitor wells on Wyckoff wood preserving plant on Elliott Bay(n=2).
FL = Fluoranthene, PY = Pyrene, BA = Benzanthracene, CH = Chrysene, BF = Benzofluoranthene
BAP = Benzo(a)pyrene. See report for literature sources of data.

HPAH
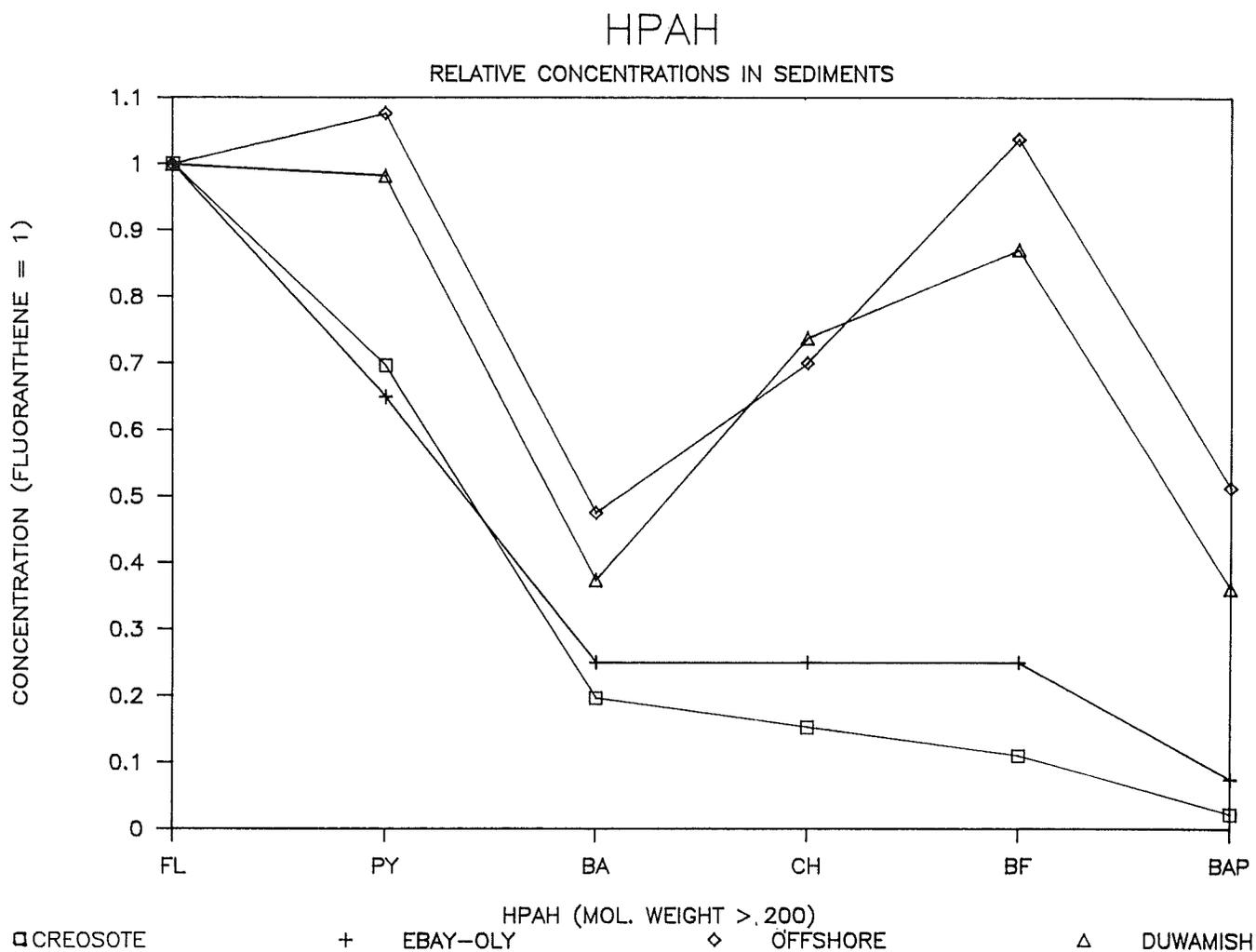## RELATIVE CONCENTRATIONS IN SEDIMENTS

Figure 2. Relative concentrations of HPAH (4- and 5-ring PAH) from different sources in Washington State.
  CREOSOTE = Creosote from tank 2 at Mcfarland/Cascade wood preserving plant in Olympia (n=1).
  EBAY-OlY = East Bay sediments in Olympia near McFarland/Cascade wood preserving plant (n=8).
  OFFSHORE = Sediments from continental shelf and slope off Washington State (n=10).
  DUWAMISH = Sediments from West waterway of Duwamish river (n=18)
  FL = Fluoranthene, PY = Pyrene, BA = Benzanthracene, CH = Chrysene, BF = Benzofluoranthene
  BAP = Benzo(a)pyrene. See report for literature sources of data.