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M E M O R A N D U M

March 15, 1982

To: Frank Monahan

Through: Dick Cunningham

From: Art Johnson *aj* and Shirley Prescott *SP*

Subject: Receiving Environment Survey in Hylebos Waterway at the Pennwalt Corporation Facility, Tacoma, Washington, June 2, 1981

INTRODUCTION

This is the third in a series of six Commencement Bay surveys* conducted by the Water Quality Investigations Section during the summer of 1981. The focus of this work has been the assessment of impacts to the near-shore marine environment from effluents discharged by Tacoma's major industries.

The primary objectives of each survey have been the determination of priority pollutant concentrations in the immediate vicinity of each discharge and evaluation of the toxicity of this environment to marine life. Conventional water quality parameters were also measured. Class II surveys to determine NPDES permit compliance and pollutant loadings were conducted by WDOE at each facility in conjunction with the receiving environment surveys and are described in separate reports by Bill Yake. EPA Region 10 assisted in the field work, sample handling, and analysis for each project. Their help is gratefully acknowledged.**

*Other surveys included: Reichhold Chemicals, Inc., (4/21/81); U.S. Oil and Refining Company (5/5/81); Sound Refining (6/30/81); St. Regis Paper Company (8/11/81); and the Tacoma Central STP (8/25/81). ASARCO and Hooker Chemical Corp. were surveyed 2/24/81 and 9/25/79, respectively.

**EPA personnel assisting in the field work were Jim Hileman, Dan Tangarone, Anna DeSilva, Joe Cummins, Barry Townes, and Carolyn Gangmark.

SITE DESCRIPTION

The Pennwalt Corporation borders about 1,000 feet of the lower turning basin on Hylebos Waterway's southern shoreline. Chlorine, sodium hydroxide, sodium chlorate, and hydrochloric acid are produced. Sodium arsenite was produced historically. Pennwalt also conducts basic research with agricultural herbicides and pesticides. The facility was established in the 1920s.

Point sources to Hylebos Waterway at Pennwalt include the process effluent, two storm sewers, and two seeps. A drainage ditch lies outside the eastern property line. Figure 1 shows the plant layout, point source discharges, and locations of water and sediment samples collected during the WDOE receiving environment survey on June 2, 1981. Also shown are EPA water sampling sites from their June 1 and September 2 collections in 1980 (1, 2).

SURVEY METHODS

Nearshore surface waters were sampled at opposite ("downstream") ends of the Pennwalt property on ebb and flood tides. Two composite samples were collected, one each prior to higher high and lower low water, and analyzed for priority pollutants, toxicity to embryos of the Pacific oyster (*Crassostrea gigas*) and conventional water quality parameters. Individual grabs were taken for oil and grease, total phenolics, and cyanide. Temperature, pH, salinity, dissolved oxygen, and chlorine residual were measured in the field. Water samples were also collected at Dash Point, 1-1/2 miles north of Commencement Bay, as a control for the bioassay.

Samples of the top 2 cm surface layer of intertidal sediments were collected near each of the Pennwalt point source discharges described above. Each sample was analyzed for priority pollutants and bioassayed using the infaunal amphipod *Rhepoxynius abronius* as a test organism. Bay mussels (*Mytilus edulis*) were collected from pilings supporting the main effluent diffuser and analyzed for priority pollutants.

Table 1 gives the details of sample collection and analysis.

RESULTS AND DISCUSSION

Priority Pollutants in Receiving Waters

Table 2 shows the concentrations of priority pollutants measured in the receiving waters. Included in the table are the data collected at Pennwalt in 1980 by EPA. Contaminant levels are contrasted with presently available criteria for the protection of saltwater aquatic life.

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Eight organic priority pollutants were detected in the receiving waters, all at low levels. None exceeded concentrations considered protective of marine life. Results from the Class II survey (see Appendix I) show that seven of these eight compounds were also present in Pennwalt's point source discharges to the Hylebos. Nineteen other organic priority pollutants were detected in Pennwalt discharges but were not found in Pennwalt nearshore waters. 1-2-trans-dichloroethylene was detected in the waterway only. Since a number of other point sources, not monitored in this study, also enter Hylebos Waterway, simultaneous occurrence of contaminants in the Pennwalt discharges and in the receiving waters only indicates one of the possible contributing sources. The percentage of contaminants contributed by Pennwalt to the amounts observed in the waterway cannot be determined from the results of this survey.

Based on the Class II results, Yake (3) calculated that 98.5 percent of Pennwalt's organic priority pollutant load to the Hylebos consisted of haloforms. Ninety four percent of this load was contributed by bromoform (18.6 pounds/day) and chloroform (1.54 pounds/day). These compounds were also those most abundant in the surface receiving waters. Deeper Hylebos water, represented by the saltwater intake sample, had lower concentrations of chloroform and no detectable bromoform. Two other haloforms, chlorodibromomethane and trichloroflouromethane, accounted for an additional 3.5 percent of the total organic pollutant load from Pennwalt but were not detected in the receiving waters.

The presence of 1,1,1-trichloroethane, chloroform, 1,2-trans-dichloroethylene, bromoform, tetrachloroethylene, and trichloroethylene in the nearshore waters is common to results from both the WDOE and EPA surveys at Pennwalt. With the exception of bromoform, these compounds are routinely detected in Hylebos Waterway, detection frequency having ranged from 40 to 96 percent, depending on the compound in question, in each of the 25 waterway samples collected by EPA in 1980 (1, 2). Their reports showed the highest concentrations occurring at the Pennwalt and Hooker facilities and adjacent waters. The detection of bromoform was limited to these two sites. Due to their volatility, all of the above compounds are thought to be rapidly lost to the atmosphere in well-mixed coastal waters (4, 5) which suggests that these contaminants are continually entering the waterway. The levels of chlorinated ethylenes that have been measured in Hylebos Waterway are higher than reported for other marine environments (6).

Other organic compounds in Table 2 - bis (2-ethylhexyl-) phthalate and the polycyclic aromatic hydrocarbons (PAH) naphthalene, chrysene, anthracene, fluorene, and phenanthrene - have been detected infrequently and at low levels in water samples taken along the Pennwalt shore. PAH have been routinely quantified, however, in suspended matter samples from the Hylebos (7).

Traces of the pesticide aldrin appear to have been present in the receiving waters. Aldrin was also present in water collected from the east storm sewer during the Class II survey.

Results from the present study and each of EPA's 1980 surveys showed copper to be the only priority pollutant consistently in excess of EPA "maximum allowable" criteria (23 $\mu\text{g/L}$ for copper) in these nearshore waters. Class II results showed that the amount of copper in Pennwalt process water was only increased by about 10 $\mu\text{g/L}$, over values at the saltwater intake, by passage through the system. The west seep contained 90 $\mu\text{g/L}$ copper but is a low-volume discharge. The remaining Pennwalt point sources had copper concentrations below receiving water levels. These findings, coupled with EPA data (1, 2) showing uniformly high copper throughout the waterway, indicate the Pennwalt discharges are probably not a major source of contamination.

EPA's survey data shown in Table 2 for September 1980 represents worst-case conditions for trace metals -- along the shoreline immediately below Pennwalt seeps and storm sewers where dilution is at a minimum. In this environment, arsenic, lead, mercury, and zinc (in addition to copper) were at levels considered potentially harmful to marine life.

Conventional Water Quality Parameters

Conventional physical and chemical water quality measurements are shown in Table 3. The principal differences noted are relatively higher turbidity and greater amounts of ammonia, nitrate, and phosphate off Pennwalt relative to the Dash Point bioassay control. Dissolved oxygen, pH, and temperature were within Washington State Class A (Good) standards. Bacterial quality was not determined. Hylebos Waterway is presently designated Class C (Fair).

A DPD colorimetric field kit sensitive to 0.1 mg/L was used to measure residual chlorine in the receiving waters. None was detected. However, using a DPD ferrous titrimetric method during the Class II survey, Yake (3) measured 0.25 mg/L total chlorine residual in a surface sample near the main effluent diffuser. This occurred during an atypical 2-1/2 hour period when Pennwalt exceeded its permit limit for chlorine because the evaporators and plant flow were down. Yake noted that this level is substantially above EPA's protection criterion of 0.002 mg/L. Substantial residual chlorine was also present in the east and west seeps.

Receiving Water Toxicity

Findings of the 48-hour oyster embryo bioassays* on Pennwalt point source and receiving waters are discussed in a separate report (8) by Joe Cummins, EPA Region 10 laboratory at Manchester, Washington. The bioassay results were as follows:

	<u>% Mortality</u>	<u>% Abnormality</u>
Hylebos, ebb composite at Pennwalt	20	10.2
Hylebos, flood composite at Pennwalt	8.6	8.7
Dash Point (control)	0.4	1.8

Adverse effects on survival and development clearly occurred in both Hylebos samples. However, as noted by Cummins, each was within the water quality criteria of less than 20 percent mortality and abnormality established by Woelke (9) who developed the test. Mortality and abnormality in Pennwalt's point-source discharges ranged from 0 to 100 percent. Yake (3) discusses these results in detail.

Cummins suggested that the combined effects of the low salinities (23.1 0/00 flood, 21.3 0/00 ebb) and the dense phytoplankton populations he observed in the receiving water samples may have stressed the larvae. Salinities less than 24 0/00 have been shown to have negative effects on embryo development, although major increases in mortality do not occur until salinities between 19 0/00 and 15 0/00 are reached (10). It was not determined if the dinoflagellates *Ceratium* or *Gymnodinium* thought responsible for oyster larvae mortality in Puget Sound were present, but the observation of relatively greater amounts of algae in the receiving water samples was supported by Cummins' citing TOC values of 3 to 4 mg/L versus 2 mg/L in the Dash Point water.

Conventional parameters such as ammonia, pH, and dissolved oxygen were not at harmful levels in the receiving water samples.

The low levels of the relatively few organic compounds identified in the receiving waters are unlikely causes of the acute effects observed on the larvae. Although copper concentrations were three times as high as both the EPA maximum allowable level of 23 ug/L and the 20 ug/L measured in the Dash Point control, concentrations of 55 ug/L also existed in the "overall" bioassay control water from Clam Bay used for adjusting salinity

*Briefly, the oyster bioassay procedure involves seeding test waters with recently fertilized Pacific oyster embryos at a density of 20,000 to 30,000 per liter, incubating them at 20°C for 48 hours, and enumerating a subsample of 150 to 250 larvae under a microscope. Larvae are counted as abnormal when not fully shelled.

in the Pennwalt effluent samples. Mortality and abnormality in the overall control were less than 2 percent. Copper, therefore, was probably not a factor in increasing adverse effects in the receiving waters. The absence of toxic effects from copper when present at concentrations well above open ocean values (about 0.5 $\mu\text{g/L}$) is usually attributed to its tendency to form non-toxic complexes with organic matter (11).

Priority Pollutants in Sediments

Priority pollutant data from the June 2, 1981 collection of Pennwalt intertidal sediments are shown in Table 4 and compared to other results for Hylebos Waterway from NMFS' (12) and Battelle's (13) recent investigations. Contaminant levels considered to represent background for Puget Sound are also shown.

Considerable amounts of PAH and pesticides were evident relative to concentrations in the overlying waters, reflecting their tendency to adsorb to particulate matter. The PAH content of the Pennwalt sediments was within the range shown for other samples of main channel Hylebos sediment. PAH were at a maximum below the west seep, east seep, and near the diffuser. Class II data indicate that Pennwalt discharges were not active sources of PAH.

Chlorinated butadienes (CBB), significant contaminants in many of the Commencement Bay sediment samples collected during the NMFS and Battelle surveys, were, with the exception of trace amounts of hexachlorobutadiene in the east seep sediment, not detected in the Pennwalt intertidal samples. This may be an artifact of the analytical method employed (14). NMFS' and Battelle's analyses were specific for chlorinated butadienes and a selected group of target compounds as opposed to the broad-range priority pollutant scan used for samples collected in the present study.

The types of volatile, halogenated hydrocarbons described earlier as being common in Hylebos marine waters were not well represented in the intertidal sediments, possibly due to loss through volatilization when the lower beach is exposed during minus tides. The data presently available on Hylebos subtidal sediments do not include analyses for these compounds.

Concentrations of DDT and its metabolites shown for samples below the west seep and east storm sewer are the highest so far reported for Commencement Bay. Class II results show the two Pennwalt storm sewers to be active sources of these compounds. Polychlorinated biphenyls were also detected in-shore of the diffuser and below the west drain, PCB-1254 and -1260, respectively.

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Arsenic concentrations in Pennwalt intertidal sediments are very high relative to the 3 to 15 ppm background range reported by Crecelius (15) for uncontaminated Puget Sound sediments. Crecelius' analysis of 34 deepwater sediments from Commencement Bay (none taken within the waterways) showed that concentrations of several hundred ppm arsenic, as found off Pennwalt, were reached only within a 1-kilometer radius of the ASARCO smelter. The high concentrations of arsenic in Pennwalt storm sewers and seeps and/or the presence of ASARCO slag in these Pennwalt sediments probably account for this. Recent studies commissioned by Pennwalt (16) concluded that the inactive sodium arsenite disposal area was the major source of arsenic to ground and surface waters.

Determination of the degree of arsenic contamination in Pennwalt intertidal sediments relative to other parts of Hylebos Waterway awaits results of analysis of samples collected by WDOE and EPA during June-August 1981.

Other trace metals considerably above background levels in these sediments were copper, lead, mercury, and zinc -- the same metals found at elevated levels in the nearshore waters. The highest levels exceeded the maximums reported by NMFS for Commencement Bay and adjacent waterway sediments and occurred below the west seep, east storm sewer, and by the diffuser. Mercury concentrations below the east storm sewer were an order of magnitude higher than any reported in the NMFS study.

Sediment concentrations of cadmium, chromium, and nickel were not elevated relative to values assigned by Dexter (17) to Puget Sound background sediments.

Sediment Toxicity

The results of amphipod bioassays* conducted by EPA at the Marine Science Center, Newport, Oregon on Pennwalt sediments (and other Commencement Bay sediments) are contained in a separate report (18) by R.C. Swartz. His Pennwalt results are compared below with total concentrations of the major groups of toxic chemicals measured in each sample. Higher (4-7 ring) aromatics were excluded from this comparison as they are primarily carcinogenic rather than acutely toxic (19).

*In the amphipod bioassay a 2-cm layer of test sediment is placed in a 1-liter beaker and covered with 800 ml of saltwater. Twenty amphipods are placed in each beaker. The beakers are maintained at 15°C, under aeration, for 10 days, after which the contents are sieved and the survivors counted.

Sample Location	Amphipod Survival	Total 2-3 Ring PAH (ppb)	HCBD (ppb)	Total Volatiles (ppb)	Total Σ DDT (ppb)	PCBs (ppb)	BHC (ppb)	Total As, Cu, Pb, Zn (ppm)	Hg (ppm)
West Storm Sewer	0/20	200	--	--	--	420	--	680	0.11
East Storm Sewer	3/20	320	--	trace	1180	--	--	2170	15
Diffuser	8/20	1740	--	trace	trace?	trace?	trace?	2650	0.41
West Seep	9/20	860	--	2180	3570	--	trace?	2880	0.97
East Drainage Ditch	12/20	310	--	--	--	--	--	180	0.20
East Seep	19/20	180	trace	3120	--	--	trace?	200	0.31

The sediments fall into three groups based on the mortalities observed: (1) severely toxic conditions below the storm sewers; (2) moderately adverse effects in-shore of the diffuser and below the west seep and east drainage ditch; and (3) high survival below the east seep. Mean survival in Yaquina Bay, Oregon sediments used as a control in these tests was 19.0 in five replicates. Tests on the Pennwalt samples were not replicated which would have improved the reliability of these results.

Neither the biology or toxicology of *Rhepoxynius*, the physical/chemical character of the test sediments, nor potential synergistic or antagonistic effects due to mixtures of toxicants are known well enough to determine the cause(s) of the mortalities observed. PCBs and mercury are the only contaminants which appear to be associated with high mortality, but the above comparison is undoubtedly over-simplified in assuming only additive effects from each toxicant known to be present. The toxic thresholds for these chemicals, in sediment, are unknown. Amphipod mortality may have occurred in response to contaminants (or physical factors) not included in these analyses. In spite of the problems in interpreting these results, it should be noted that had one relied on the chemical data alone to identify potential toxicity problems, the highly toxic conditions below the west storm sewer might have been underestimated and the relative toxicity of each of these samples improperly ranked.

Priority Pollutants in Mussels

The organic priority pollutants detected in the Pennwalt mussel tissue sample are shown in Table 5.

Relatively few compounds were present. All were at low levels except the PAH fluoranthene, benzo(a)anthracene/chrysene, and pyrene which were at concentrations equal to the maximums measured in Hylebos marine biota by NMFS (12).

Mussel tissue trace metals are shown in Table 6 and compared to metals data on *Mytilus* from other parts of Commencement Bay and Puget Sound. Differences in environmental and physiological factors can cause wide variations in trace metal accumulation by mussels as well as in other organisms (20) so the data shown here should be interpreted with caution. Except for mercury, trace metal concentrations in the Pennwalt mussels agreed well with results reported by Price (21) for a mussel sample from this same waterway. Arsenic in both Hylebos samples exceeded that measured by WDOE in mussels near the ASARCO facility on Commencement Bay, the major anthropogenic source of arsenic to Puget Sound (15). Copper, however, was considerably higher at ASARCO versus Pennwalt. Copper has been identified as the principal metal of concern in ASARCO liquid effluents to Commencement Bay (22).

Consistent with the already presented findings for trace metals in near-shore water and intertidal sediment at Pennwalt, arsenic, lead, and zinc were the metals elevated in Pennwalt mussels relative to mussels at WDOE background stations in Puget Sound removed from urban-industrial activity. The remaining metals - cadmium, chromium, copper, and nickel - were within background levels.

Mercury data were not available from the WDOE background stations, but Pennwalt concentrations appear low relative to the 0.016 to 0.130 ppm range for mussels reported by Olsen (22) in a baseline study of trace metals in Puget Sound biota.

Tentatively Identified Organics

An additional 16 organic compounds were tentatively identified in samples from WDOE's June 2-3, 1981 surveys at Pennwalt. These are listed in Table 7.

2-Butenal is commonly referred to as crotonaldehyde. Estimated 96-hour LC₅₀ for the silverside (*Menina beryllina* - a marine fish) is 1.3 ppm (26). Uses include as a warning agent in fuels (strong irritant) and in the manufacture of resins and insecticides.

No information was found on 3-hexen-2-one.

Bicyclo [3.1.1] heptane, 6-6-dimethyl-2-methylene,1(s)- is a terpene also known as beta-pinene, a natural product found in oils from coniferous trees and a constituent of turpentine. No information was found on 4-carene, but 3-carene is also a naturally occurring terpene.

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2,4,5,6-Tetrachlorobenzene-1,3-dicarbonitrile may be the isomer 2,3,4,6-tetrachlorobenzene-1,4-dicarbonitrile (trade name "BRAVO") an insecticide.

The decanoic acids are naturally occurring fatty acids in animal and vegetable fats and oils.

Additional information on those compounds tentatively identified in samples of Pennwalt point source discharges is given in Yake's Class II report (3).

SUMMARY AND CONCLUSIONS

The major findings of the Pennwalt receiving environment survey are as follows:

1. Low concentrations of eight organic priority pollutants were detected in the receiving waters; none were above criteria for the protection of marine life.
2. Although it was not possible to separate Pennwalt's contribution of these compounds from other potential sources to the Hylebos, chloroform and bromoform were identified as the major constituents in both point-source and nearshore waters at Pennwalt.
3. Concentrations of total copper in the receiving waters exceeded aquatic life protection criteria in this survey and in past EPA surveys. Arsenic, lead, mercury, and zinc have also been shown to exceed protection criteria immediately below Pennwalt's discharges to the Hylebos.
4. Oyster embryo bioassays on the receiving waters demonstrated adverse effects on survival and development. These effects were moderate (i.e., not more than 20 percent mortality) and were probably attributable to low salinity and high algal density rather than toxic chemicals.
5. Polycyclic aromatic hydrocarbons (PAH) and pesticides were the principal organic priority pollutants detected in Pennwalt intertidal sediments. PAH concentrations were within the range found in other investigations of Hylebos sediment. Pennwalt operations did not appear responsible for PAH concentrations. Two Pennwalt sediments contained DDT compounds at levels greater than previously reported for Commencement Bay sediments. Pennwalt storm sewers are active sources of this pesticide.

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6. Arsenic, copper, lead, mercury, and zinc were elevated in the intertidal sediments relative to background levels in Puget Sound sediment and to levels previously reported for Commencement Bay subtidal sediments.
7. Based on bioassays with the infaunal amphipod, *Rhepoxynius abronius*, Pennwalt intertidal sediments range from severely toxic to non-toxic. The cause(s) of the mortalities observed is not known.
8. PAH were the only organic priority pollutants detected at relatively high concentrations in mussels collected at Pennwalt. Arsenic, lead, and zinc were elevated in mussel tissue relative to Puget Sound background levels.

Previous investigations by NMFS, Battelle, and EPA have demonstrated that contamination from chlorinated compounds, aromatics, and trace metals is widespread in Hylebos Waterway. This survey showed similar levels of chlorinated compounds and aromatics in the nearshore marine environment at Pennwalt, but with increased amounts of trace metals and DDT compounds. It was an acutely toxic habitat to the one benthic invertebrate studied. The potential problem of long-term effects on marine life, suggested by NMFS' reports of increased incidence of lesions in waterway biota, has not been addressed.

No evidence was found to implicate the Pennwalt area as a major source of contaminants to other parts of Hylebos Waterway. However, adverse impacts to the waterway may have been underestimated by the timing of the survey which maximized flushing (spring tides) and minimized loading (low runoff).

AJ:SP:cp

Attachments

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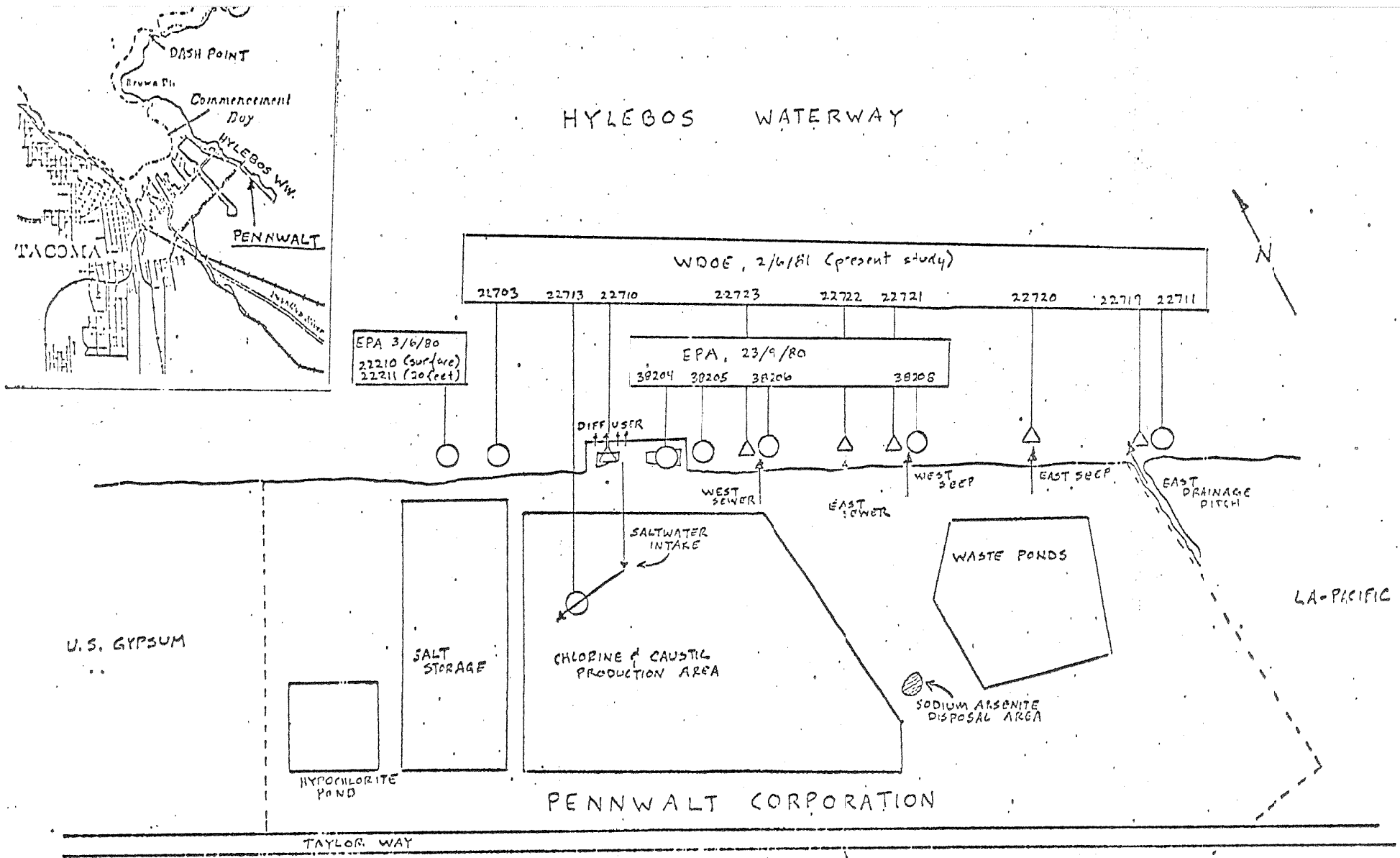


Figure 1. Locations of near-shore water (O) and intertidal sediment (Δ) samples collected at the Pennwalt facility by WDOE on June 2, 1981 and by EPA on June 3 and September 23, 1980 (EPA sample number shown).

Table 1. Sample handling and analysis for WDOE's receiving environment survey at Pennwalt, June 2, 1981.

Sample Type	Parameter(s)	Sampling Method ^a	Sample Container ^b	Analysis	Laboratory
Water	Organic Priority Pollutants	1-hour manual composite of four 1-liter aliquots	1-gallon glass except volatiles in screw-cap 40 ml vial	As per 1979 EPA guidelines ^c	California Analytical Laboratories, Inc., Sacramento, CA. (EPA contractor)
	Trace Metals, Conventional Water Quality Parameters, and Bioassay	1-hour manual composite of four 2-liter aliquots	Metals - 250 ml poly., HNO ₃ pres. Nutrients - 250 ml poly., H ₂ SO ₄ pres. Turbidity, Suspended Solids PBI - 2 liter poly. Bioassay - 1 gal. poly.	Metals, Conventional Parameters - Standard Methods ^e . Bioassay - 48-hr. oyster embryo technique ^d	Mercury - WDOE, Tumwater, WA. Other Metals - EPA, Region 10, Manchester, WA. Conventional - WDOE, Tumwater, WA. Bioassay - EPA, Region 10, Manchester, WA.
	Cyanide	Grab	1-qt. glass., H ₂ SO ₄ pres.	Standard Methods ^e	WDOE, Tumwater, WA.
	Total Phenolics	Grab	1-qt. poly., NaOH pres.	Standard Methods ^e	WDOE, Tumwater, WA.
	Oil and Grease	Grab	1-qt. glass	Standard Methods ^e	WDOE, Tumwater, WA.
	Chlorine Residual	Field Measurement	--	LaMotte DPD field kit	--
	Dissolved Oxygen	Field Measurement	--	Winkler, azide modification	--
	pH	Field Measurement	--	Orion Research pH meter	--
	Salinity	Field Measurement	--	Beckman salinometer	--
	Sediment	Priority Pollutants Bioassay	Composite of 2 x 10 ² cm surface samples along transect below mean low water	Organics - 8 oz. glass. Trace Metals - 4 oz. poly. Bioassay - 1 qt. glass	As above As above Amphipod bioassay ^f
Mussel Tissue	Priority Pollutants	--	Poly. bag	As above	Calif. Analytical Labs, Inc.

^aAll samples placed on ice at time of collection.

^bContainers for organic priority pollutants cleaned with sequential rinses of soap and water, 15% HNC₃, 50% HCl, distilled water, de-ionized water, nannograde acetone, and nannograde methylene chloride. Trace metal procedure omits solvent rinses.

^cEPA. 1979. Guidelines establishing test procedures for the analysis of pollutants; and proposed regulations. *Federal Register* Vol. 44 No. 233.

^dAmerican Society for Testing and Materials. 1980. *Standard Practice for Conducting Static Acute Toxicity Tests with Larvae of Four Species of Bivalve Molluscs*. Ann. Book ASTM Standards. Philadelphia, PA

^eEPA. 1979. *Methods for Chemical Analysis of Water and Wastes*. EPA-600/4-79-020

^fAdaption by R.W. Swartz of technique for dredged material in EPA/COE. 1977. *Ecological Evaluation of Proposed Discharge of Dredged Material into Ocean Waters*. Environ. Effects Lab. Vicksburg, Miss.

Table 2. Priority pollutants detected in Hylebos nearshore waters^a at the Pennwalt facility during WDOE's June 2, 1981 receiving environment survey and in EPA 1980 surveys (concentrations in µg/L).

Sample Description	WDOE, Present Survey			EPA, June and September, 1980 surveys						Water Quality Criteria for Protection of Saltwater Aquatic Life ^b			
	Ebb Composite	Flood Composite	Saltwater Intake, 24-hr Composite	Grab	Grab	Grab	Grab	Grab	Grab	Acute Toxicity	Chronic Toxicity	24-hour Average	Maximum Allowable
EPA Sample Number	22703	22711	22713	38204	38205	38206	38208	22210	22211				
Collection Date	6/2/81	6/2/81	6/2-3/81	9/23/80	9/23/80	9/23/80	9/23/80	6/3/80	6/3/80				
Time	1000-1100	1545-1645	230-1230	1031	1034	1039	1124	1445	1445				
Base/Neutral Compounds													
Naphthalene	--	--	--	0.93	--	1.0	1.0	--	--	2,350			
2-chloronaphthalene	--	--	--	--	--	--	--	--	3.6	7.5			
bis(2-ethyl hexyl)phthalate	--	--	14	--	--	--	--	--	--	2,944			
Chrysene	--	--	--	--	<0.5	--	--	--	--	300 (polycyclic aromatic hydrocarbons)			
Anthracene	--	--	--	--	--	1.4	--	--	--	300 (polycyclic aromatic hydrocarbons)			
Fluorene	--	--	--	--	--	--	--	<0.5	--	300 (polycyclic aromatic hydrocarbons)			
Phenanthrene	--	--	--	--	--	--	--	--	--	300 (polycyclic aromatic hydrocarbons)			
Volatiles													
1,1,1-Trichloroethane	--	--	2.2	--	--	9.7	16	3	--	31,200			
Chloroform	1.7	36	1.2	7.8	8.3	--	380	3.4	1.2	12,000	6,400	(halomethanes)	
1,2-trans-dichloroethylene	--	--	T	--	--	--	--	2	1.1	224,000			
Bromoform	4.2	1.4	--	--	--	--	16	--	--	12,000	6,400	(halomethanes)	
Dichlorobromomethane	--	--	--	--	--	--	2.5	--	--	12,000	6,400	(halomethanes)	
Chlorodibromomethane	--	--	--	--	--	--	3.4	--	--	12,000	6,400	(halomethanes)	
Tetrachloroethylene	--	4.2	--	--	1.4	1.5	140	0.8	--	10,200	450		
Trichloroethylene	T	T	T	1.9	1.9	2.6	4.0	1.4	2.1	2,000			
Pesticides													
Aldrin	T*	--	0.11*										1.3
Trace Metals													
Antimony			26	16	4	17	<2	<2	<2	508 (+3, inorganic)			
Arsenic	26	76	26	970	1990	3815	150	33	17				
Beryllium				0.6	0.8	0.6	0.9	<0.2	0.3				
Cadmium	1.1	1.3	<0.3	0.4	0.4	<0.2	<0.2	1.3	2.8			4.5	59
Chromium	17	19	9	14	<1	5	14	3	4	10,300 (Cr+3)		18 (Cr+5)	1,260 (Cr+5)
Copper	62	62	73	37	22	37	14	80	83			4.0	23
Lead	30	26	35	40	43	10	75	12	16	668	25		
Mercury	<0.2	0.23	0.3	0.14	0.35	0.84	0.63	0.3	0.3			0.025	3.7
Nickel	9	9	9	18	41	66	26	19	31			7.1	140
Selenium				7	10	7	10	23	37			54	410
Silver				<0.4	<0.4	<0.4	<0.4	<0.3	<0.3				2.3
Thallium				<3	<3	<3	<3	1	1	2,130			
Zinc	50	50	30	800	780	50	50	35	30			58	170

^aUnfiltered surface waters except 22713 and 22211 which were collected at depths of about 20 feet.

^bUSEPA, 1980. Water Quality Criteria Documents; Availability. Fed. Reg. vol 45 no. 231, November 28, 1980.

-- = Not detected.

T = Trace, value is greater than limit of detection but less than limit of quantification.

* = Concentration too low to permit confirmation by mass spectrophotometer.

Table 3. Conventional measurements of water quality in Hylebos Waterway at the Pennwalt facility and at Dash Point (bioassay control), June 2, 1981.

Parameter	West End Pennwalt	East End Pennwalt	Dash Point
Sampling Period	1000 - 1100 hours	1545 - 1645 hours	1500 hours
Tide Stage ^a	late ebb	mid-flood	mid-flood
Temperature (°C)	12.8 - 13.1	13.9 - 14.4	15.5
Salinity (o/oo)	21.3	23.1	26.1
pH (Units)	8.0	8.0	8.3
Dissolved Oxygen (mg/L)	9.3	10.2	10.0
Total Residual Chlorine (mg/L)	<0.1	<0.1	<0.1
Turbidity (NTU)	23	12	6
Suspended Solids (mg/L)	16	36	26
Ammonia-nitrogen (mg/L)	.09	.02	<.01
Nitrite-nitrogen (mg/L)	<.01	<.01	<.01
Nitrate-nitrogen (mg/L)	.30	.06	.06
Total Phosphate-phosphorus (mg/L)	.10	.11	.04
Orthophosphate-phosphorus (mg/L)	<.01	.08	<.01
Oil and Grease (mg/L)	<1	<1	<1
Total Phenolics (as phenol) (mg/L)	<.001	.003	.002
Pearl-Benson Index	0	9	9

^aLLW -3.0 feet, 1135 hours; HHW 12.6 feet, 1849 hours.

Table 4. Priority pollutants detected in Hylebos intertidal sediments^a collected at the Pennwalt facility, June 2, 1981.

Sampling Site EPA Sample Number	Inshore of Diffuser 22710	West Storm Sewer 22723	East Storm Sewer 22722	West Seep 22721	East Seep 22720	East Drainage Ditch 22719	Hylebos Waterway Main Channel (refs [12, 13])	Puget Sound Background Sediments (refs [12, 17])
ORGANICS (ppb, dry)								
<u>Base/Neutral Compounds</u>								
Acenaphthene	--	--	320	--	--	--	<0.70-280	<.10
Fluoranthene	1300	250	1800	1100	180	400	60-7100	30
Hexachlorobutadiene	--	--	--	--	T	--	<1-90	0.2
Napthalene	340	--	--	--	--	--	35-2600	8
Diethyl phthalate	--	--	--	T	--	--		
Benzo(a)anthracene and/or chrysene	2300	310	3500	2100	T	470	685-6200	40
Benzo(a)pyrene	1100	--	2800	1100	--	--	74-6700	9
3,4-benzofluoranthene and/or benzo(k)fluoranthene	1300	240	2400	1800	--	--	2900-11000	40 (benzofluoranthenes)
Anthracene and/or phenanthrene ^b	1400	200		860	180	310	388-8000	23
Berzo(g,h,i)perylene	--	--	--	400	--	--	40-596	10 (perylene)
Ideno(1,2,3-cd)pyrene	--	--	--	380	--	--	430-1100	10
Pyrene ^c	1500	220	3600	1100	T	290	74-6700	30
<u>Volatiles</u>								
1,1,1-Trichloroethane	--	--	--	--	T	--		
Chloroform	T	--	T	1500	2200	--		
Bromoform	--	--	--	--	T	--		
Dichlorobromomethane	--	--	--	T	180	--		
Chlorodibromomethane	--	--	--	--	T	--		
Tetrachloroethylene	--	--	T	680	740	--		
Toluene	T	--	--	--	--	--		
Trichloroethylene	--	--	--	--	T	--		
<u>Pesticides and PCBs</u>								
4,4'DDT	T*	--	360	3000	--	--	13-120	<0.7
4,4'DDE	--	--	670	T*	--	--	1-30	<0.06
4,4'DDD	T*	--	150	570	--	--	1-14	<0.1
BHC-B	T*	--	--	T*	T*	--		
PCE-1254	T*	--	--	--	--	--	11-1200	3 (total chlorinated biphenyls)
PCE-1260	--	420	--	--	--	--		
<u>TRACE METALS (ppm, dry)</u>								
Arsenic	240	270	690	560	87	66		18
Calcium	1.5	0.57	3.7	23	0.40	0.20	6.8-9.6	3
Chromium	37	23	13	28	40	9	33-48	101
Copper	1400	72	1000	1400	28	23	85-259	35
Lead	610	84	310	300	22	21	111-154	21
Mercury	0.41	0.11	15	0.97	0.31	0.20	0.43-0.79	0.06
Nickel	25	27	86	28	11	8.7	42-64	42
Zinc	400	250	170	620	60	74	134-324	87
% Dry Weight	53.3	63.6	72.0	47.4	59.8	76.8		

^a2 cm surface layer.

^b690 ppb methyl anthracene measured in east storm sewer sediment, #22722.
920 ppb methyl anthracene measured in west seep sediment, #22721.

^c1900 ppb methyl pyrene measured in diffuser sediment, #22710.

T = Trace, value is greater than limit of detection but less than limit of quantification.

* = Concentration too low to permit confirmation by mass spectrophotometer.

Table 5. Organic priority pollutants in mussels (*Mytilus edulis*, entire soft parts) collected at the Pennwalt diffuser, June 2, 1981 (concentrations in ppb, dry).

Acid Compounds

Pentachlorophenol	T
Phenol	T

Base/Neutral Compounds

Fluoranthene	2,300
Napthalene	T
Benzo(a)pyrene and/or chrysene	2,600
Anthracene and/or phenanthrene	T
Pyrene	1,300

Volatiles

Tetrachloroethylene	T
Toluene	T

PCBs

PCB-1254	T*
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% dry weight = 11.5
 Sample size = 80 individuals,
 33-57mm length range
 EPA sample no. 22725

T = Trace, value is greater than limit of detection but less than limit of quantification.

* = Concentration too low to permit confirmation by mass spectrophotometer.

Table 6. Trace metals in mussels (*Mytilus edulis*, entire soft parts) collected at the Pennwalt diffuser June 2, 1981 compared to data on mussels from other parts of Commencement Bay and Puget Sound (concentrations in ppm, dry^a).

Sampling Site	Hylebos Waterway at Pennwalt ^b	Mouth of Hylebos Waterway	Blair Waterway at Lincoln Ave.	Commencement Bay Near ASARCO		BWMP ^c Background Stations at Dabob Bay, Carr Inlet, Case Inlet
Investigator	WDOE (present survey)	Evergreen St. Col. (Price, 1978)	WDOE (Bernhardt, 1982)	(Cloud, 1979)	WDOE (Heffner, 1981)	WDOE (unpublished data)
Collection Date	6/2/81	Summer, 1977	5/5/81	9/20/78	8/24/81	9/6/79 to 8/25/80
Arsenic	28	44.8	19	4.6	16.2	0.77-2.61
Cadmium	3.3	3.9	2.3	7.9	2.95	3.57-17.0
Chromium	2.2	--	1.6	<6	1.7	0.72-2.1
Copper	15	11.0	13	297.0	135	7-18
Lead	13	26.8	<5.0	35.2	0.89	1.23-1.86
Mercury	0.02	0.19	0.015	--	--	--
Nickel	4.5	--	2.7	<30	1.4	0.78-4.0
Zinc	500	969.7	330	472.7	533	81-261

^a0.165 dry/wet ratio used to convert data reported on wet-weight basis.

^bSample size = 50 individuals, 33-55mm length range.

^cBasic Water Quality Monitoring Program; range of four samples.

Table 7. Tentatively identified compounds.

Compound	West Sewer	East Sewer	West Seep	East Seep	E. Property	Saltwater	Main Eff.	Low Tide	High Tide	Mussel	
	Sedi- Water ment	Sedi- Water ment	Sedi- Water ment	Sedi- Water ment	Line Drain Sedi- Water ment		Sedi- Water ment	Receiving	Receiving		Water
<u>Volatile Organic Acid Fraction</u>											
2-methyl, 2-butenal	--	--	--	--	--	--	--	--	--	--	TI
<u>Base Neutral Fraction</u>											
3-hexen-2-one	--	--	--	--	--	--	--	--	--	--	TI
hexadecanoic acid, methyl ester	--	--	--	--	--	--	--	TI	--	--	TI
1-(2-butoxyethoxy) ethanol	--	--	--	--	--	--	TI	--	--	--	--
4-carene (1S,3S,6R)-(-)-	--	--	TI	--	--	--	--	--	--	--	--
bicyclo[3.1.1]heptane,6-6-dimethyl	--	--	TI	--	--	--	--	--	--	--	--
-2-methylene, 1(S)-	--	--	--	--	--	--	--	--	--	--	--
2,4,5,6 tetrachloro 1,3-benzene di-	--	--	--	TI	--	--	--	--	--	--	--
carbonitrile	--	--	--	--	--	--	--	--	--	--	--
<u>Acid Fraction</u>											
tetradecanoic acid	TI	TI	--	TI	--	--	+	TI	TI	TI	TI
pentadecanoic acid	--	--	--	--	--	--	--	--	--	--	TI
hexadecanoic acid	TI	--	TI	TI	--	TI	+	--	TI	TI	TI
heptadecanoic acid	--	--	--	--	--	--	--	--	--	--	TI
dodecanoic acid	TI	--	--	--	--	--	--	--	--	--	--
benzoic acid	--	--	--	TI	--	TI	--	TI	--	--	--
benzene acetic acid	TI	--	--	--	--	--	--	TI	--	--	--
3,4-dichlorobenzoic acid	--	--	--	TI	--	--	--	--	--	--	--
dichloroacetic acid	--	--	--	TI	--	--	--	--	--	--	--

TI = Tentatively identified.
 + = Present in sample; also present in blank.

Priority pollutants in Pennwalt point source samples collected by WDOE during the June 2-3, 1981 Class II survey (concentrations in ug/L).

Source Name	Process Effluent	West Storm Sewer	East Storm Sewer	West Seep	East Seep	East Drainage Ditch	Total Point Source Loading for 6/2-3/81 in lbs/day
Collection Date	6/2-3/81	6/2/81	6/2/81	6/2/81	6/2/81	6/2/81	
EPA Sample No.	22712	22709	22708	22707	22706	22705	--
<u>Acid Compounds</u>							
2,4,6-Trichlorophenol	--	--	--	--	--	2.3	<.01
Phenol	+	--	--	--	--	4.0	0.050
<u>Base/Neutral Compounds</u>							
Hexachloroethane	--	--	--	478	26	--	<.01
Fluoranthene	--	--	--	--	--	T	<.01
Hexachlorobutadiene	--	--	--	8.7	4.8	--	<.01
Naphthalene	--	--	--	T	--	--	--
bis(2-ethyl hexyl) phthalate	--	4.1	--	--	--	--	**
Dielhyl phthalate	--	--	--	--	--	--	0.045
Benzo(a)anthracene and/or chrysene	T	--	--	--	--	--	0.083
Benzo(a)pyrene	--	--	--	--	--	--	--
Anthracene and/or phenanthrene	--	--	--	--	--	--	--
Benzo(k)fluoranthene and/or 3,4-benzofluoranthene	--	--	--	--	--	--	--
Pyrene	--	--	--	--	--	--	--
<u>Volatiles</u>							
Carbon tetrachloride	--	--	--	--	16	--	<.01
1,1,1-trichloroethane	--	210	--	--	4.8	--	**
1,1-dichloroethane	--	3.1	--	--	3.8	--	<.01
Chloroethane	--	--	--	5.0	15	160	<.01
Chloroform	7.9	14	2700	2300	13,000	--	1.54
1,1-dichloroethylene	--	6.3	--	--	--	--	<.01
1,2-trans-dichloroethylene	--	--	--	--	--	--	**
Bromoform	180	--	--	44	9.4	--	18.6
Dichlorobromomethane	--	--	T	28	130	--	<.01
Trichlorofluoromethane	1.2	--	--	--	--	--	0.124
Chlorodibromomethane	6.0	--	--	43	36	--	0.62
Tetrachloroethylene	--	--	--	180	94	17	<.01
Toluene	2.2	1.3	--	--	--	--	0.29
Trichloroethylene	--	T	--	4.7	--	--	**
<u>Pesticides</u>							
Aldrin	--	--	0.26*	--	--	--	**
4,4'-DDT	--	0.15*	4.1*	--	--	--	<.01
4,4'-DDE	--	--	0.62*	--	--	--	<.01
4,4'-DDD	--	--	0.27*	--	--	--	<.01
BHC-G	--	--	0.58*	--	--	--	<.01
<u>Metals</u>							
Arsenic	60	12,000	1920	5000	35	470	5.2
Cadmium	10.4	0.3	1.1	1.9	0.6	0.5	1.08
Chromium	9	7	7	1530	1370	400	0.13
Copper	79	29	18	90	15	37	1.46
Lead	32	8	6	95	87	50	0.12
Mercury	0.3	0.38	0.60	3.4	5.8	0.98	<.01
Nickel	15	6	<3	82	147	112	0.75
Zinc	30	20	<20	400	40	40	0.41

T = Value is greater than limit of detection but less than limit of quantification.

** = Overall loading to Hylebos negative.

+ = Present; also present in controls.

* = Value is greater than or equal to limit of quantification but unconfirmed by GC/MS.